FIREWORKS

The Art Science and Technique

by

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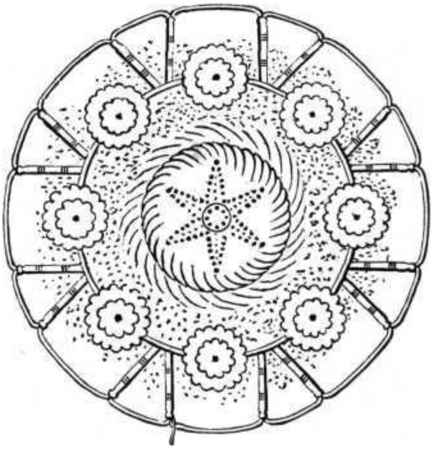

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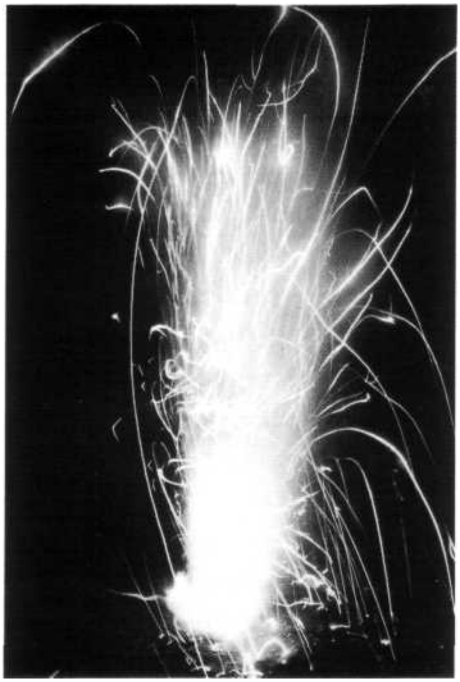
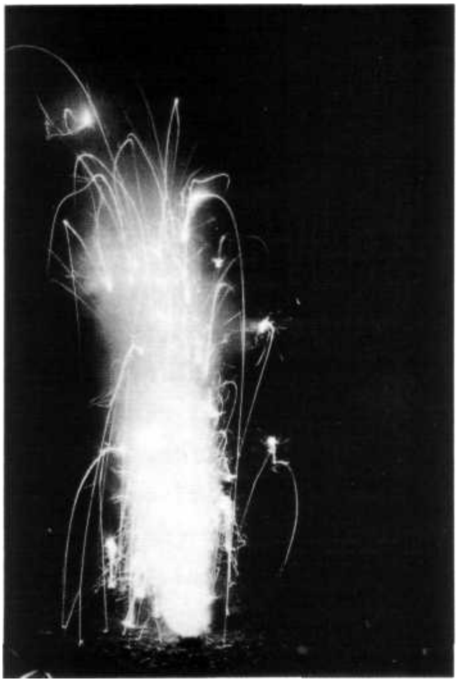
1. Titanium sparks



2. Aluminium sparks
(from flake aluminium)



3. Magnalium sparks

(See pages 127 and 220.)

PREFACE

My first work on "Hana-bi", which means fireworks in Japanese, was published in 1957 but it went out of print several years later mainly because of the publishing company. I began the second work ten years ago to meet the demand of many people and have at last completed the script.

The purpose of this work is to help beginners who are professionally engaged in manufacture or planning fireworks in factories. I have laid emphasis on three points, the creation of beauty, the nature of materials and safety control. Part 1 contains a brief history of fireworks in Japan mainly according to researches of Y.Sakenobe and Dr.H.Nambo. Part 2 describes firework art, for this art is the soul of fireworks. My hope is that readers might study the subject more deeply so that fireworks might be more attractive. Part 3 concerns the science of fireworks. This is not from an aesthetic standpoint but rather basic knowledge which is indispensable for producing fireworks. Part 4 concerns pyrotechnics; in this part I have assigned many pages for the description of firework materials following the requests of readers of my former work. But I am afraid that there may be some gaps due to lack of experience and knowledge. I have tried to modify firework compositions a little according to recent work by S.Lancaster. Part 5 is concerned with safety control based on our empirical laws.

This work is primary a practical one, and the description of theory has been kept as simple as possible. This is to meet the need of my former readers. Therefore I separated the theoretical part from this work and described it in my other book, "Feuerwerk vom physikalischem Standpunkt aus, Hower Verlag, Hamburg, 1976". I would be very much delighted if any reader has a special interest in it. I am very much indebted to E. Hübbe when he was in Nico Pyrotechnik in Hamburg for publishing the book.

Although this work is almost completely rewritten from the first book, it cannot cover all of the latter. Fortunately the main parts of the first work was put as one chapter in the book by R.Lancaster, "Fireworks, Principles and Practice, 1972", and I am grateful for this.

I would like to express grateful thanks to following people who have kindly assisted me in this work. M.Hosoya (director of Hosoya Firework Co.) taught me firstly in 1951 about the Machida school of firework manufacture and he has been always in close contact with me; I am deeply in his debt. Y.Nakahara (formaly Kinsei) and the late K.Takada (Hosoya Firework Co.) helped me as assistants in my work for many years. H.Murai (director of Daiichi Yakuhin Kogyo Co.) often presented me with important information. T.Nyumura (The Space Development Association) helped me formerly as an assistant in the Hosoya Firework Co. The late Dr.S.Yamamoto (professor of Tokyo University) introduced me into the world of fireworks in 1951 and stimulated my interest.

Concerning the art of fireworks, I have been very much indebted to T.Miki (founder of PL Order in Osaka), who allowed me to plan and practice the large displays of PL festival from 1964 to 1966. N.Koda (Echigo Firework Co.) gave practical help by testing my proposal in the firework art by firing shells for me. To these people I am most grateful.

I am very grateful also to friends in overseas countries for their assistance and encouragement. R.Lancaster M.A. has been a devoted cooperator in the preparation of this book. Professor A.A.Shidlofskii (Institute of Chemical Engineering in Moscow) often urged me to write this book and presented me with his work "Fundamental Pyrotechnics (Основы Пиротехники),1973", which is quite companionable and has been always at my side. Dr.H.Hartig (Konsumzündwarenwerk in Riesa, East Germany) also kindly presented his book, "Zündwaren, 1971", which is quite original and a most useful reference book. R.Hamberger (Hans Hamberger AG. in Oberried, Switzerland), W.Zink (Zink-Feuerwerk in Cleebronn, Germany), Dr.F.-W.Wasmann (Institut fur Chemie der Treib- und Explosivstoffe, Pfinztal-Berghausen, Germany), R.G.Cardwell (Pyrotechnica Publications, Austin in the USA) and other persons equally interested in fireworks have often encouraged me. Miss Sigrid Wied (Georg Richter Co. in Hamburg, Germany) showed great devotion in the correction of my work concerning firework art, "Die zweckmäßigste Auswahl fur den Abschuss von japanischen Feuerwerksbomben, 1968", which constitutes the background of Part 2 of this book.

April 1981

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CONTENTS

TABLES

Part 1. A brief history of Japanese fireworks

It is said that the word "Hanabi", the Japanese name for fireworks, was used for the first time in 1585. "Hana" means flowers and "Bi" is a softened sound of "Hi" which means fire, and"Flowers of fire" is the Japanese name which corresponds to the word "Fireworks". In 1613 an English man, a messenger of James I, king of England, came to Sumpu (now Shizuoka) in Japan to see Ieyasu Tokugawa, the founder of the Tokugawa government. Under the guidance of a Chinese merchant he brought fireworks and displayed them there. It is uncertain where the fireworks were made, either in England or possibly China. The fireworks might possibly have been fountains or volcanos at present. The commencement of firework production in Japan might possibly have been of the type made about 1620 or later. [Re.N.Sakenobe, Journal of the Industrial Explosives Society, Japan, Vol.28,321(1967)]. In 1659 Kagiya, the famous fireworker, began his work in Edo (now Tokyo). In 1733 the famous firework display at the River Ryogoku (also called Sumida) in Edo took place. The display originated from a Buddist memorial service for many people who died from cholera in 1732. [Re.H.Inagaki,Annual Report of the Japanese Firework Industrial Society, 3, 2 (July 1955)]. On this site the fireworks were fired or exhibited from ships and that display greatly influenced the development of Japanese fireworks. In 1810 another famous fireworker Tamaya branched out from Kagiya, but he had to leave Edo in 1843 by the order of Tokugawa government because of a fire accident. Under the Tokugawa government fireworks were developed also in many districts in Japan under the patronage of the feudal lords. The types of fireworks were probably round shells and set pieces. For a long period the colour of fireworks was dark red or amber which came from black powder until coloured flame compositions came into use in about 1880; this was caused by the introduction of potassium chlorate from Europe accompanied by safety matches. In 1926 Gisaku Aoki completed the double petalled chrysanthemum and in October 1928 at Inariyama in Nagano he displayed a double petalled chrysanthemum with pistil at the memorial firework display for the enthronement ceremony of the Emperor. The colour arrangement was very simple, i.e. the centre of the flower was red, the middle part was blue and the outer petals were amber. Afterwards this kind of multi-petalled chrysanthemum was widely developed in Japan to become the most representative firework in Japan. The River Ryogoku display was discontinued in 1961 but it was recovered in small scale in 1979. This firework festival which has such a long history (about two hundred years) may seem rather unusual in the rest of world.

Part 2. The art of fireworks

Fireworks are an aesthetic arrangement of various fire producing elements. People call these phenomena and often the articles which produce these phenomena "fireworks". The word "pyrotechnics" originated from Greek and is synonymous with "fireworks", but it has a wider scope than "fireworks", in that they are not only produced to be admired and enjoyed but they are also made for military and industrial use.

The fire reacts, trembles and flickers for itself and we talk of "Burning like fire!"; we feel indeed that fire has life. In this respect we can find in fire an essence of art in fireworks. This would be the reason why even simple lance-work is admired by many people today in spite of the sophisticated development of illuminations.

Firework art is concerned with space and time by creating a contrast from one moment to the next moment, or between a place and another. The background of firework display is nature which is quite changeable and often disturbs the artistic effect of fireworks. Firework art is different from the pictorial art, i.e. there is no framework, and it can be appreciated from all quarters. The reason why the spherical and crown shaped fireworks have been highly developed, lies in the fact that they lend themselves to such surroundings to produce an effectively artistic firework arrangement.

1. The constitution of firework art

1.1. Nature as the background

Background here means not only the "back cloth" of the firework display, but the whole environment. Nature means the natural order involving natural and artifical things such as sky, cloud, mountain, gorge, forest, lake, sea, ships, houses, palaces, temples, churches, shrines, lights, the moon, the sun, wilderness, desert etc.

In autumn and winter in Japan the sky clears up and gives the best colours to the fireworks, but in July and August when most of the firework displays are held, the sky is somewhat cloudy and we are obliged to manage with this unsatisfactory background. A brimming river or lake is one of the most desirable backgrounds because it harmonises well with fireworks, and gives calmness. A firework display on a plain is calm, but in a gorge is intense with its loud echoes.

Weather conditions particularly disturb the beauty of fireworks and a cloudy sky especially hides the flowers of fire. Strong wind is not desirable, but no wind is equally unhelpful because it causes a large volume of stagnant smoke which is produced by the fireworks; a breeze is most desirable. The humidity of the air needs to be low, because high humidity creates dense smoke at the display. A display of fireworks in a thunderstorm is a terrific sight, but there is a liability to get misfires and it is quite dangerous. The brightness of the background has a great influence on the effect of fireworks. The point has been made that a clear and bright sky gives the best effect for daylight fireworks and a dark sky in which many stars are twinkling gives the best results for night fireworks. The most difficult time for firework displays is shortly before sunset.

Nature cannot be controlled by man but it is possible to foresee the conditions to some extent. When we plan a firework display, we try to arrange it so that it harmonizes with these backgrounds as far as possible.

1.2. The elements of fireworks

Light, smoke, noise and floating matter(parachute, flag, paper bag shaped like a figure, bill etc.) are the four elements of fireworks. The first three are especially important. The difference between light and smoke lies in the fact that the former emits the light for itself and the latter reflects light from the sun, the moon or a flare; but in wider meaning both are a light. When we classify lights by their emitting mechanism, colour, emitting substance, brightness etc., we have 26 kinds, the number coinciding incidentally with that of the English alphabet (Table 1).

Table 1. Classification of firework light sources

Light Source			Brightness				
			Minimum W 2	Weak W 1	Normal S	Strong F 1	Maximum F 2
Emitted Light	Flame	White					a ♩✡
		Red			m ♩·		b ♩*
		Yellow			n ·♩		c *♩
		Green			o ·♩		d *♩
		Blue			p ♩.		e ♩*
		Violet			q ♩-		f ♩✱
	Twinkling Flame	Red				g ♩++	
		Yellow				h ++♩	
		Green				i ♩++	
	Sparks or Fire Dust Sparks	Reddish		s ♩-			
		Flickering		r ♩=			
		Golden				l ∘♩	
		Silver				k ♩°	
		Flash				j ♩✧	
Reflective Light	Smoke	White	t ♩°				
		Red	u ♩·				
		Yellow	v ♩				
		Green	w ♩				
		Blue	x ♩.				
		Violet	y ♩·				
		Black	z ♩×				

In the table, (g) and (q) are not yet as popular as others. The (r) called "Silver Wave" is in fact not silver, but looks as if it were mixed with fire particles of various colours; red, green, blue etc.

This classification may be somewhat rough, but it is adequate for ordinary planning mainly because firework flowers generally have a very short life time, and too fine a consideration about the classification is useless. But when we aim at a special artistic effect, we have to classify the lights more precisely than this. For example, the "red" has in fact many kinds; crimson, ordinary red, vermilion, pink etc, which are almost all available in fireworks. For the "green" we can produce grass green, ordinary green and blue green. For the "blue" light blue and violet blue.

The reddish sparks (s) are obtained from charcoal fire or steel filing fire. In Japan this light source is called "Hiki", which means an amber stream. We have more lonely red orange one, named "Yugen-biki", which means an amber stream of mystery.

Each symbol in the table, which is an imitation of a musical note, shows the kind of light source and is quite useful for planning artistic contrasts and programs of fireworks. The symbol *i* shows one shell. The position and the form of dots show the kinds of colour and brightness. In this book the symbol is called "firework note".

1.3. Rough drawing

Firework is an art of audio-visual imagery, which changes from moment to moment, and is difficult to express by photograph or picture. The moving picture is also unsatisfactory at present for the expression of fireworks. If an instrument could express the 26 kinds of light on a screen correctly, it would be a tremendous advantage in the progress of firework art.

However a picture is more effective than a photograph as an auxiliary method for expressing the image and is used quite frequently.

The illuminant in fireworks is called a "star". Perhaps the name came from the fact that the illuminating light resembles a real star in the sky. There are two configurations of the star; with tail (s, r, l, k) and with no tail (a~f, m~q, g~i, j). Smoke(t~z) always has a tail and is called a "smoke star". In pictures a star with a tail is expressed by a line, vith no tail by a point. The trajectory of a star with a tail is denoted by a straight line or curved line (Fig.1). a is an image of a fast star and b a slow star. The slow star is curved by the force of gravity. Artists

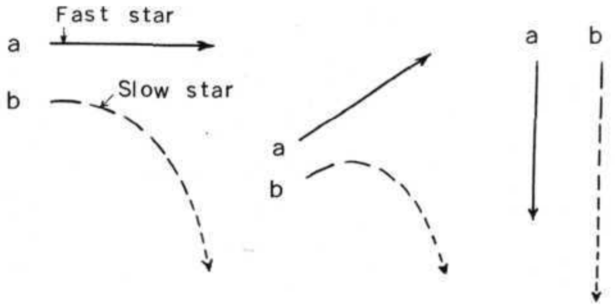


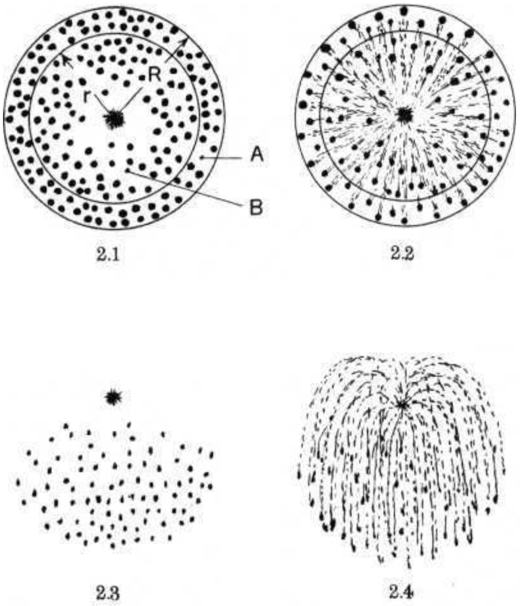
Fig.1. Rough drawing of stars with tail

dislike vague imagery; the line must be clearly straight *ov* curved. A line which curves slightly is said to be "dangling" and one which bends at the end is called "swimming". The manufacture of such fireworks is thought to be bad practice. The fast star has a period of *2~4* seconds and the slow star 7~8 seconds. A star time somewhere between these two is not generally used because of the above reason. There are cases when a star looks as if it flies like the line a, but appears on a photograph like b. This is really no problem because the image is more important than the physical reality in the case of fireworks.

When we draw these lines, we must consider the firework technique. The stars with a long burning time which can be drawn by the line b are Palm(l), Hiki(s) and smoke(t~z). But in the future with the development of technique it should become possible to produce (r) with long burning time.

Fireworks do not have frameworks like pictures. Accordingly the composition of fireworks must be specially considered. Fireworks are placed centrally in the space and all firework elements are concentrated towards the centre. Allternatively the elements are allowed to flow out of the centre. This is the rule in firework art, and is suitable for both cases; one flower and a group of several flowers.

A group of stars assemble as a flower. Each flower has a different name.

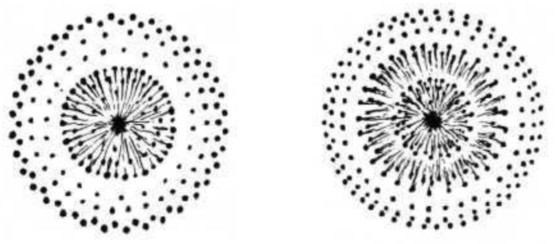


2.1 2.2

2.3 2.4

Fig.2. Representative firework flowers

The flower 2.1 and 2.2 consist of stars with a short burning time and 2.3 and 2.4 have a long burning time. The flower 2.1 and 2.3 consist of stars with no tail and 2.2 and 2.4 with a tail. 2.1 and 2.2 are round and the configuration is called "Bon" in Japanese, which means a round tray. Sraw a concentric circle of $\underline{r}=0.76\underline{R}$, where $\underline{R}$ is the radius of the Bon. We find that the number of stars in the outside area A and that in the inside area B are the same, and the ratio of the areas A:B is equal to 1:3. Thus the distribution of the stars in Bon is dense near the outside and thin at the centre. In the case of a peony it is particularly felt that something is wanting at the centre and so in high class flowers the centre is filled with a pistil (Fig.3).



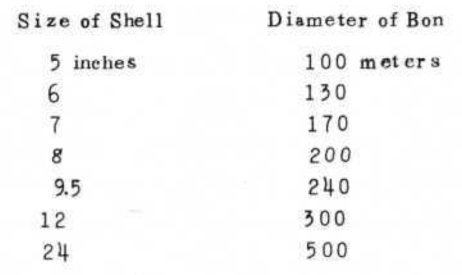
3.1. Flower with pistil

8.2. Double petalled flower with pistil

Fig.3. Flowers which have a pistil in the centre

The diameter of a round flower must be correct. If it is too large the density of the stars is low, and the flower feels lonely. If too small, it looks as if it has shrunk (Table 2).

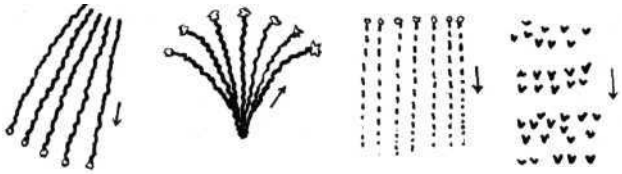
Table 2. Standard diameters of round flowers



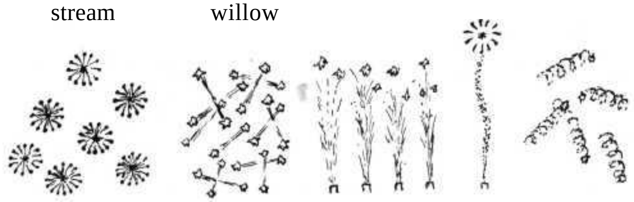
Size of Shell	Diameter of Bon
5 inches	100 meters
6	130
7	170
8	200
9.5	240
12	300
24	500

The willow is a modified form of a round flower. The only difference between the two is that the willow has a vertically symmetrical axis and appears most clearly in the configuration when we see it at right angles to the axis; the round flower however is symmetrical in all directions.

We have other varied irregular forms other than the round and willow but generally they have no artistic centre. Such a flower cannot be expected to give an artistic effect by itself, one tube of a Niagara Falls for example cannot be seen as the falls. Consequently we must aim at a group effect with these fireworks (Fig.4).



4.l.Willow stream 4.2. Fan-shaped willow 4.3. Falls 4.4. Ripple

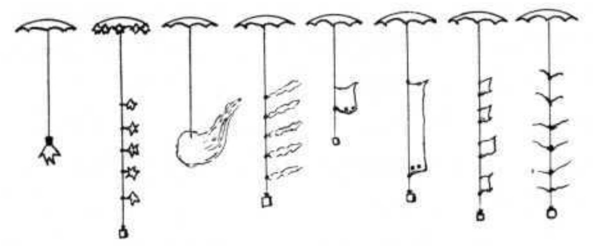


4.5. Snail flowers 4.6.Comets 4.7. Standing fire 4.8. Charcoal-ball 4.9. Bees

Fig.4. Flowers of irregular forms

The willow stream 4.1 is drawn by a group of lines. Large and short or long and thin lines are technically available. If the shell explodes ascending, the stars appear like 4.2. Falls 4.3 consists of a group of fire dust stream and resembles willows. Willows however have fire points each of which draw a stream-line moving at the end, but in the falls the fire points do not move. Ripples 4.4 consist of twinkling stars (g,h,i), which fall like rain 2.3, but they have a special beauty. The small flowers 4.5 consist of many small flowers which are thrown at random. They are given various names such as "thousand flowers", "a garden of hundred flowers" etc. Comets 4.6 also called "divided cannon" each piece displaying two stars which run in opposite directions to each other. Standing fires 4.7 are also called "tiger tails" where the stars ascend from the ground, streaming fire dust sparks. Some standing fires have no such tails, but ascend like fire balls. 4.8 is called "charcoal-ball" from the look of the shell. The bees 4.9 are a group of hummers,each streaming fire dust sparks as they fly spirally. They have another name "a mad lion". They are used not only in shells in the sky, but they are also fired directly from the ground.

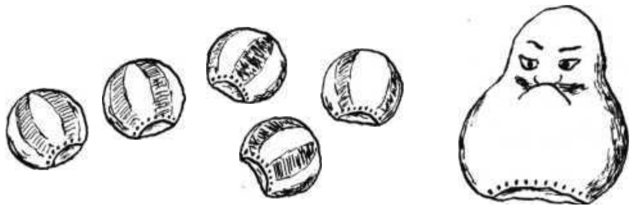
A group of many reports called "ten thousand thunders" create loud reports with strong flash lights.



5.1. Flare moon 5.2. Chain with ring 5.3. Dragon 5.4. Smoke chain 5.5. Short flag 5.6. Long flag 5.7. Multiflag 5.8. Thousand crows

Fig.5. Various parachutes

Parachute are used to extend display time (Fig.5). A single parachute is not so attractive, but a group of several presents a spectacular sight. Similarly there are other floating items such as lanterns, Dharma etc.(Fig.6).



6.1. Lantern 6.2. Dharma

Fig.6. Floating figures

1.4. The names of fireworks

The name is an important spiritual factor. Fireworks which have no name are like the Dharma which has no eyes, and there is a loss of artistic value.

When the display of each article is important, a name is given to each one, and when a group is important, it is given to the group. The most popular names are as follows:

(1) Round flowers.

Chrysanthemum; a round flower, which consists of stars with a tail (Fig.2.2).

Peony; a round flower, which consists of stars with no tail (Fig.2.1). But it is often confused with the chrysanthemum.

Full Stars; Another name for the peony.

Relieved Pistil; A pistil, which is relieved against petals.

Mixed; A flower with stars of mixed colours.

Mixed Pistils; Pistils of mixed colours.

Double petalled flower; A flower, which has two petals in concentric circles (Fig.3.2).

Choji Chrysanthemum; A chrysanthemum with a pistil which is larger in diameter than ordinary pistils. The "Choji" is a kind of chrysanthemum.

Nishiki; A chrysanthemum with gold petals; though the petals have a tail, it is called sometimes Nishiki-Peony. Originally "Nishiki" is the name for a noble cloth, Cloth of Gold.

Silver Wave: Stars which stream twinkling fire dust sparks. The sparks consist of not only silver, but also red, blue, yellow etc.

Flash(or Brilliance); A flash at the end of each petal.

Dahlia(or Cosmos); A flower of most brilliant stars(F2 in Table 1).

Tip Cracker: A flower which cracks at the end of each star.

Yellow Chrysanthemum: A daylight flower with yellow smoke petals, which are produced by realgar.

White Chrysanthemum; A daylight flower, with white smoke lines produced by a blackpowder-type composition.

(2) Small round flowers.

Flower Garden(or Thousand Flowers); A lot of small round flowers which appear at the same time (Fig.4.5).

(3) Willows.

Crown Willow(or Crown Chrysanthemua); A modified type of the chrysanthemum, the stars of which have a long burning time and fall with streams of fire dust sparks (Fig.2.4).

Willow; A group of stream-lines produced by light or smoke stars.

Rain; A group of stars without stream (Fig.2.3).

(4) Comets.

Branching Cannon: Another name for the comets.

Branching Stars; Another name for the comets also.

Spider Web; A lot of comets which cross each other.

(5) Parachutes.

Moon: A large illuminating flare with a parachute.

Dragon: A star with a rather large tail.

Smoke Dragon: A smoke star with a parachute.

Chain: Stars which are arranged on an invisible line hanging from a parachute, to look like a chain.

Flower Parasol with Chain: Stars are arranged along the edge of a parachute which suspends a chain (Fig.5.2).

(6) Noise .

Signal Gun: A loud report. The name comes from its use as a mid-day signal in earlier times.

Thunder: A report.

Flash Thunder: A report accompanied by a strong flash.

Five Step Thunder: Five reports which sound one after another at regular intervals.

Ten Thousand Thunder: A large number of simultaneous reports.

Bees: A lot of hummers which fly round like bees.

Flute: A whistle.

(7) Water fireworks.

Gold Fish : A lot of streamers which run up and down in the water.

Drift Flares: Flares which drift in the water.

(8) Change of phenomena and miscellaneous names.

Kyoku: It might come from feat, which is called "Kyoku-Gei" in Japanese. In our fireworks Kyoku means momentary change of phenomena by the use of some mechanism, or sometimes it is a piece which functions with such a mechanism. Accordingly in widest sense all fireworks belong to Kyoku but the word is used only in a narrow meaning for example:

"Bunsei no Kyoku" ("Bun" means to divide, "sei" means stars, "no" means of): Comets appear at intervals.

"Kyoku-do" (Do means a trajectory): When a shell displays noise or smoke on its ascent we call the phenomenon or the noise or smoke "Kyoku-do".

Residue: The appearance of the second phenomenon after the first one has gone out.

Relieved Pattern: A pattern which is relieved clearly against petals of a chrysanthemum or willow as the background.

By combining the above names we can express the phenomena which are created by a shell and fireworkers can understand to some extent the construction of the shell from the name. For example:

Twice Changing Chrysanthemum with a Moon Residue and with Kyokudo; A shell ascends displaying some small effects; thunders, small flowers, smoke etc. one after another on the trajectory. When the shell reaches the maximum height, it displays a round chrysanthemum flower; the colour of the flower changes from one effect to another. When the flower goes out, a flare of bright light remains.

Amber Chrysanthemum with Small Flowers in Relief and with Kyokudo of Ascending Small Flowers: The shell ascends displaying small flowers on the trajectory and at the maximum height explodes into a large amber chrysanthemum and then small flowers are displayed in relief against the background of petals.

However these names are not artistic for they are too much of an invention and we prefer more imaginable names to the above. For example:

Salute: Another name for thunder. It best expresses the mood of the sound "bang! bang! bang!" immediately after the appearance of round white smoke puffs high in the blue sky at a festival.

Willow in the Moon: Willows which hang down in the still moon light. In reality, firework phenomena move, but we feel a profound calm in the movement.

Flower of Winter: This is the name of a flower which has petals of amber to flash, inner petals of blue and a pistil of twinkling green (Fig.16).

Yashi(Palm): Golden willow stars (due to sparks from titanium).

2. The arrangement of firework phenomena

We can roughly arrange the elemental phenomena into a complete firework flower design. However we must further pay attention to the following.

2.1. Simplicity and clearness

In fireworks very complicated arrangements are so easily available that people are apt to select colour changes which are too complicated. The colour change should be as simple as possible, i.e. twice or at the maximum three changes. The petals should be, at the maximum, double. The colours should not be mixed in petals or pistils in ordinary cases. Mixing red and yellow stars sometimes succeeds, but red and green looks dirty. During the simultaneous display of a large amount of firework pieces, it is important to create a spectacular sight or a large volume. In such cases only a simple arrangement of colour, change, shape, kind of phenomena etc. will succeed.

The artistic object must be clear for a half-hearted and featureless display is most disappointing. Clarity can be produced by good contrasts.

2.2. Harmony and contrast

It has already been pointed out that firework art has no framework with the result that fireworks often lose their stability and are apt to give people unpleasant feelings. We must avoid this possibility by selecting the types of fireworks.

The round tense firework flower always fits very well with any background because it has a centre to the flower. The flower is varied in size, but gives a feeling of stability. However a lengthy display of the round flowers causes people to lose interest as time goes on, i.e. they become bored in spite of the differences of colour or changes among the flowers. Clearly the stability of the round flower is too good to keep the artistic effect psychologically at a high level for a long period, even if the shells are elaborately manufactured. Accordingly it is better to divide the displays with fireworks which break the harmonization (s.2.3)^

Fireworks have artistic directions which may be schematically shown as in Fig.7.

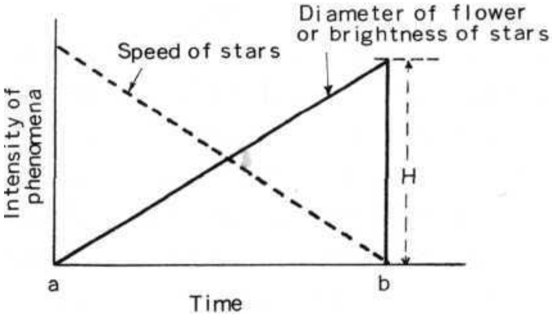


Fig.7. The change of firework phenomena

The flower increases from small to large, the stars increases their brightness from a weak to a strong level, there is a change in colour from a cold to a warm chroma and a decrease in speed from quick movement to stillness as the time passes. These phenomena begin from the starting point a, reach the end point b and suddenly vanish with a sharp finish. A change in the opposite direction is unstable and gives us unpleasant feelings. In the same way, for example, when a chrysanthemum has a pistil the pistil must vanish before the petals because the direction of the change must be from the small to the large.

Fireworks consist of contrasts in light. There are two kinds of contrast; space contrast and time contrast, in colour and brilliancy. Accordingly we have four relationships in these contrasts:

(1) Colour-Space (Spatial arrangement of colours),
(2) Colour-Time (Time arrangement of colours),
(3) Brilliancy-Space (Spatial arrangement of brilliancy),
(4) Brilliancy-Time (Time arrangement of brilliancy).

Here we are going to consider the contrast taking the chrysanthemum as a representative example.

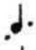
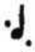
Time contrast. In this case the brilliancy change contrast (4) overpowers the colour change contrast (2). In Table 1 (page 4) brilliancy is classified in five columns. Generally we succeed in display in the time change of brilliancies among the ranks without considering the particular colours. For example, the change Wl-->S, amber to red (s-->m) and amber to green (s-->o) are both effective for building up a good flower. In the same rank it is the normal rule to change the colour from the cold (blue or green) to the warm (red or yellow) effects. The change from green to red (o-->m) is successful, but the opposite (m-->o) does not give a good effect. These principles are comprehensible also by the rule of artistic movement shown in Fig.7.

Space contrast. Colour contrast is more important than brilliancy. This rule comes from the requirement to make each colour clearly visible without being disturbed by the dazzle. For example, when a weak blue light is placed near a strong red light, we cannot easily recognize the blue as it is overshadowed by the dazzle from the red which is more brilliant. Accordingly it is the best to select colours in the same class in Table 1. Namely, if we use the blue in the S class as the petals, we should use the red in the same class S as pistils, i.e. p and m are used. This is to use the "same visibility effect".

But there are some fireworks, which are based on the opposite idea. This aims at the "relief effect" using lights of different brilliancy. For example, when we use stars of class S as pistils and that of class W1 as petals, we can always obtain a good flower in spite of the colour of the stars. In general the stars of lower class brilliancy plays a background role against those of the higher class. (But the opposite seldom exists; a typical case would be Nishiki, which has golden petals(l) against blue pistils(p).) Don't forget the dazzle in this case also. For example, a flower which has petals of reddish s in Wl and pistils of brilliant red b in F2 does not succeed because we cannot recognize the petals because of the dazzling effect of the pistils. The dazzle is minimized by keeping the stars of high brilliancy compact and spreading those of lower brilliancy.

What is chosen, the same visibility effect or the relief effect, depends upon the artistic purpose when planning the space contrast. In ordinary cases, we make an effort so that both effects are consistent with each other; thus we use a cold colour (green or blue) as the background (petals) against a warm colour (red or yellow) as the objects (pistils), even when we use the stars in the same class of brilliancy, to get a good relief effect.

But there are some fireworks which aim at only the relief effect. One of the extremes is the "Willow in the Moon", where an intensive flare illuminates the background which consists of many streamlines of smoke. The light of the flare is rather pale and the smoke lines are yellow, but we don't sense the colours, merely the contrast between the brilliancies rather like a black and white drawing. Another of the extremes may be the "Flower in the Sunset", which is a smoke flower with red stars of high brilliancy as the pistils. In this case only the red of the pistils makes a deep impression, and any coloured smoke; red, yellow, green, blue or violet; can serve as petals because it has only an auxiliary effect against the pistils.

To show contrasts the firework note is very convenient. The time contrast is the strongest, when the dots are arranged diagonally opposite, e.g.  or  , and gentle, when the dots are on the one side, e.g.  ,  ,  or  . In each symbol the time change of the colour or lights proceeds usually from a cold to a warm colour or from weak to intensive light according to the rule described in 2.2. For example, the symbol  shows the change from  (green) to (red). When the direction is not clear, it is shown by figures like  , which means the change from (gold) to (yellow). The space contrasts are arranged in the order of intensity as follows:A , B , C , D , E , where the first symbol  in each denotes the petals and the second  the pistils, and the one couple of the symbol  denotes one flower. A,B,C and D use a warm colour as the pistils against a cold colour as the petals, and aim the relief effect of the pistils on the petals. On the contrary, at E blue pistils sink in yellow petals. Such a reversal contrast is seldom used, because it does not always succeed.

2.3. Breaking harmony

Our traditional firework flowers today are also under the influence of the avant-garde movement which breaks the harmony. However look at history!

The firework flower was originally created in an effort to bring the capricious fire phenomena, which are almost always inharmonic, into harmony, and as a result it has reached the perfectly round chrysanthemum pattern.

However such a completeness produces deadlock,with the result that we get the idea to break the harmony. But breaking the harmony should never be opposite to the principles described above. An unpleasant firework flower is always displeasing and it is pointless to break the harmony. Changes must not disturb, but rather help the harmony of the flower.

First,the breaking harmony should be "nil"; pause, monotony, noncentre etc. belong in this area. The pause between displays is quite important to complete each display. The monotonous display before or after a high contrast display may help the latter in harmony. A single petal flower which has no central stars may help the effect of the chrysanthemum with pistils. Thunder, which has no colour and shape, may be one of the most powerful harmony breakers. A great many thunder reports with a lot of flashes presents a spectacular sight and a sharp time contrast against the calm round chrysanthemums.

Secondly, an inverse harmony break may be proposed. All the artistic movements may be divided in three; being(+), nil(o) and inverse(-). The above belong to the "nil" or the "being". The "inverse" has negative artistic movement which is obtained by writing a figure oppositely against Fig.7 as far as possible (Fig.8).

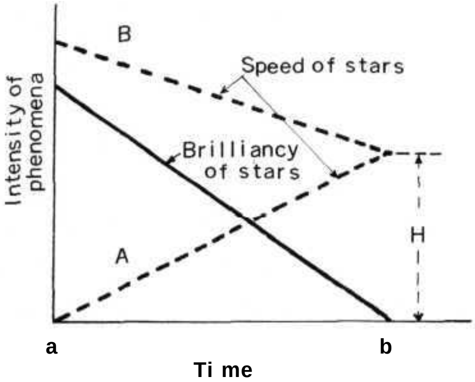


Fig.8. The change of firework phenomena which aim inverse harmony

The movement of stars is generally very rapid at first, but soon they become slower and slower with a growth in brilliancy. This is the right harmony. The inverse harmony goes to the contrary, i.e. the brilliancy of the stars diminishes lower and lower. In this case the speed of stars cannot follow the line A, according to the physical law they follow B. Such a display has a kind of force which arouses us to hope for the recovery of the right harmony which has been lost.

2.4. Strain and relaxation

9.1. 9.2. 9.3. 9.4.

Fig.9. Various shapes of flower

A firework flower like 9.1 which stretches its petals straightly and uniformly gives us a feeling of tension. On the contrary, the flower like 9.2 or 9.3 which has a round shoulder or like 9.4 which is elliptical in shape gives us a feeling of relaxation. The flower which has strong flashes at the end of the petals gives us another feeling of tension. It must be remembered that the flower like 9.3 which leaves the ragged fire dust gives us relaxation. If we hear the noise of explosion just at the moment of the full development of the flower, we feel tension, and the beauty of the flower is extremely enhanced. A distant flower, from which we cannot hear the noise, is seen somewhat relaxedly.

2.5. Rhythm and firework music

Fireworks are an art of time and space and it may be thought that it is possible to introduce music rhythms into firework displays, music being the most representative art of the time. In practice however the creation of correct rhythms is difficult in fireworks at present.

Music exists surely in a room, but in the open air it is a different matter. Place a piano, flute and violin on a vast ground so that they are 300 meter apart from each other. How could we conduct the concert? The three sounds reach the conductor or an audience at different times, but the baton of the conductor is recognized by the three positions at the same time. The low speed of the sound, about 330 meters per second, causes confusion and it also very much disturbs the musical combination of light and sound.

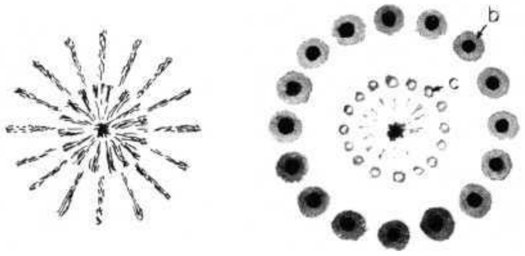
To avoid the confusion the musical firework display must be limited in as small a place as possible. Therefore the firing site must be correspondingly narrow also, and the diameter of the area should be, for example, less than 50 meters. The audience must be well away from the firing site. When we display 6 inch shells, which ascend to a height of about 250 meters, the distance ought to be about 600 meters because each of the flowers develops fully in about two seconds, and people hear the explosion sound at the moment of the fulness of the flowers.

We have five kinds of sounds; shooting and explosive sound, thunder report, whistle and humming. When we arrange these sounds at proper time intervals, e.g. of 2 or 4 seconds in the case of 6 inch shells, we can make the sounds into a rhythm to create firework music. In this case, the first three sounds play the role of percussion instruments. But to bring the five sounds into music, the time of ignition, delay, explosion and the period of the whistles and hummers must be accurately controlled.(See 4).

3. Various beauties of firework flowers

In this section specific examples of the beauties of the firework flowers are described, and the principles of this beauty are set out.

Elegance. "Akizakura" means autumn cherry blossom. The name Cosmos is also suggested by the author. At the first stage it appears with petals and pistils of the same weak reddish charcoal stream, and then it suddenly changes to a brilliant flower, where the petals are red(b) and the pistils are yellow(c) in class F2 (Fig.10).



First Second

Fig.10. Akizakura (Cosmos)

Low space contrast and high time contrast are the special feature of this flower.

Mystery. "Yugen-biki" which means mystery of willow (by M.Hosoya) is suggested as another example. The flower consists of stars with weak thin amber coloured streams (s) which are specially manufactured and which create a deep still feeling (Fig.11).

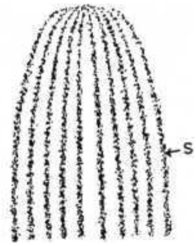


Fig.11. Mystery of willow

Splendour. This aims at the beauty of colours and their changes. The multi petalled flower with pistil which was completed by G.Aoki belongs to this type. Generally, to obtain the same visibility effect the high class brilliancy F2 is avoided, and to obtain the relief effect the petals are of cold colour, weak stream(s,r) or flash(j) and the pistils are of a warm colour.

Fig.12 shows an example of development of single petalled flower with a pistil.

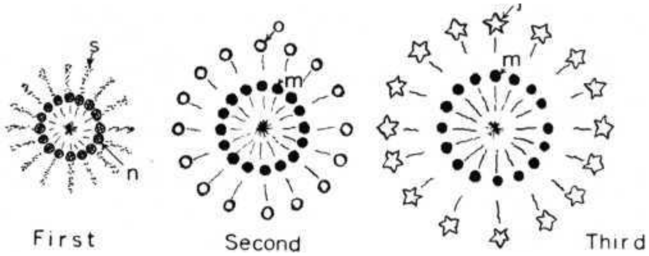
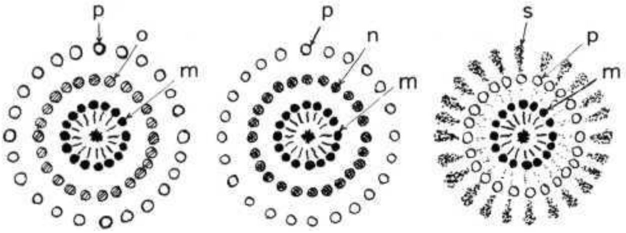


Fig.12. Development of a single petalled chrysanthemum with pistil

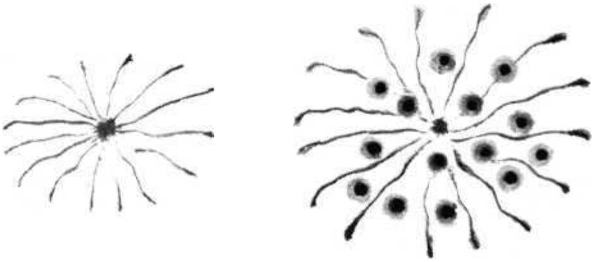
Fig.13 shows examples of full round double petalled flower. In this case the second petal asists the first (13.1), the pistil (13.2) or lies between the two (13.3) in space contrast.



18.1. 13.2. 13.3.

Fig.13. Full rounds of double petalled chrysanthemum with pistil

Fig.14 shows a daylight flower by the author called "Smoke chrysanthemum". This is one of the avant-garde flowers. At the first stage big smoke streams appear radially, and at the second stage brilliant red pistils appear suddenly in relief against the smoke streams. The lights of the class F2 appear quite clearly even in broad daylight, and especially the red F2 creates a beauty of high splendour in combination with smoke streams as a daylight flower. This comes from strong space and time contrasts of colours and brilliancies.



First Second

Fig.14. Smoke chrysanthemum with red pistils

Solemnity. This kind of flower may be called "Peony of Gold"; it has been most skillfully manufactured by Y.Iketani etc. The petals are gold (1) which is so called "Nishiki" and the pistils are blue(p). This flower may be associated with the Imperial crest of the chrysanthemum of Japan. (Fig.15).

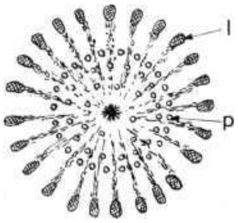


Fig.15. Peony of gold

Loneliness. "Flower of winter" by M.Hosoya may be presented as an example. This is a double petalled flower with pistils. Stars of low brilliancy are used under weak contrast, and they produce loneliness in sight. (Fig.16).

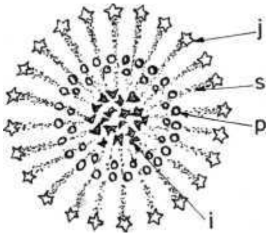


Fig.16. Flower of winter

Magnificent. A wide display area and a high density of stars give us a magnificent feeling. For example, 12 inch shells, 24 inch shells, 1000 meter waterfalls, 1000 meter stand fire etc. In this case the volume of flowers is considered more seriously than fine contrast.

Moderation. A flower of warm colour and a weak contrast gives us a moderate feeling. For example, a yellow petalled flower with red pistil, a flower of mixed colours (yellow and red) etc.

4. Examples of display

When displaying fireworks we are apt to shoot shells randomly. This is not good and must be avoided by elaborate display planning. Firework phenomena have an expence of space and time, which must be controlled under the direction of artistic movement (s.2.2).

To note the programme of a display, it is quite useful to use tables of music notes. Here the author proposes the so called "firework note", which was practically and conveniently used in the past (Fig.17).

F1-W1 No.12 Banqet of celebrated flowers (Osaka, 1965)

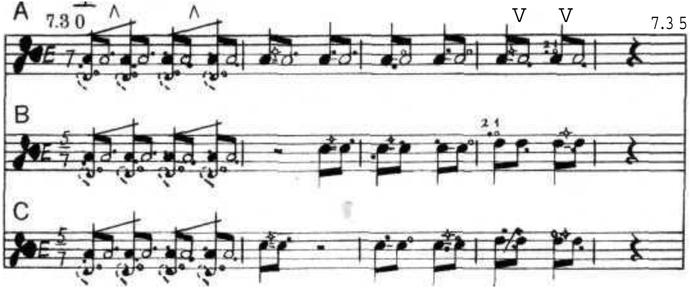



Fig.17. An example of firework note

The symbol on the left top of the note, F1-W1, denotes the maximum and minimum brilliancies (s.Table 1) in this display. It is called "the contrast of three degrees", to which another symbol $\underline{\cdot|\cdot}$ is added ($\underline{\cdot}$, $\underline{\cdot\,\cdot}$, $\underline{\cdot|\cdot}$, $\underline{\cdot||\cdot}$, $\underline{\cdot|||\cdot}$ meaning one, two, three, four, five degrees respectively). In this case the phenomena change within the range of the three classes of brilliancies (F1, S and W1). Accordingly we can know roughly by the symbols how highly the display impresses people.

The next five lines are drawn as in music, and on the left of each group the firing section is written as A, B and C. The group of five lines is combined with vertical lines at the left and right end, which means that the display is a combination of the three firing sections. Fireworkers in each section know their own tasks which are set for them after a glance of this note. The five lines have eleven positions including the upper and lower places, to each of which a size of shells is assigned (Fig.18). Unless otherwise provided, the middle line denotes 6 inch shells.

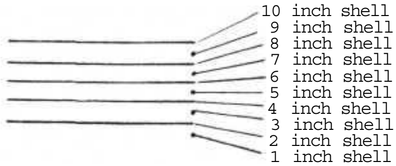


Fig.18. Positions of five lines for shell sizes

The symbol  denotes a night display and is called the "petal symbol". For a daylight display  is used.) In ordinary cases the centre of the petal symbol is placed on the middle line, but when we slide the sizes of shells against the five lines, the centre comes to the line which denotes 6 inch shells. (For set fireworks we use another symbol  in place of above for night and  for daylight.) The figures on the left and right end of the first five lines, 7.30 and 7.35, mean the beginning and end of this display, which is called a "unit display", i.e. it continues for five minutes. The letter E at the beginning of each five lines shows that the unit display consists of five steps of the same time intervals, i.e. one minute. (A, B, C, D, E, ... mean one, two, three, four, five ... steps respectively.) Each step is bounded by vertical short lines. The figure 17 at the right of E shows that seven shells of the same kind should be fired one by one by quick firing for each symbol on the five lines.

7 shows that the shells which are larger than the size denoted by the horizontal dot (-) belong to five shells quick firing and others to seven shells quick firing. The shells on the dot (-) belong to the downward, i.e. here to the seven shells quick firing. ∧ means " Fire more quickly than the normal speed", ∨ " Fire more slowly than the normal". The normal speed is such a speed that a man may load (or drop) the next shell into the mortar as soon as he recognizes the full development of the prior shell,  means a Kyokudo of silver stream,  pistils of irregular shape. An inclined line which combines two flower symbols at the top shows that two quick firings take place simultaneously at one firing section.  leans a short pause,  one step pause,  (or ) a symbol of separation which shows that the pistils diminish perfectly when the petals proceed to the last change.

The "banquet of celebrated flower" (Fig.17) is displayed as follows: At the first step green and blue flowers with red pistils of 5 inch shell appear and then yellow flowers with blue pistils at all firing sections, A,B and C. And silver streams are drawn from the ground to the sky. The second step begins with flowers of silver wave to flash with red pistils of 5 inch shell at A and of 7 inch shell at C, and ends with flowers of amber to red with red pistils of 5 inch shell at A and silver wave to flash with red pistils at B. The third step is filled with various flowers, which continue to the fourth step. The fifth step is all in pause. The programme is arranged so that the display develops from weak to strong excitation according to the ordinary rule.

The next note named "the music of fire" is an example which is constructed with only firework sounds.

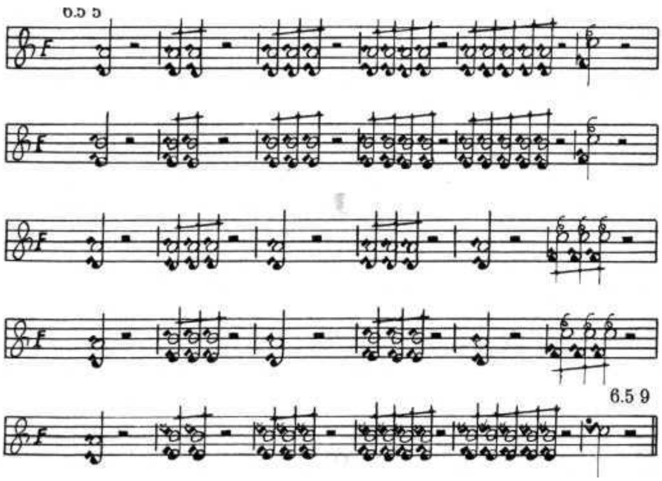
The music of fire (Osaka,1965)

One step : 8 seconds

Fig.19. A display of firework music

The symbol  means a shell which contains a few whistles of middle size; five or six pieces according to the size of the shell;  a Kyokudo which consists of one big whistle,  a thunder report shell which contains many reports; 20 to 30 according to the size of the shell;  a thunder report shell which contains one large report,  a shell which contains many hummers. The firing sounds and shell explosions are also taken into account.

The single whistle continues for four seconds. Each shell is manufactured so that it explodes just four seconds after the shot. The short pause  is filled with whistles or humming, and there is practically no pause in this period. The display begins from the left upper side of the note and progresses along the first, second , third, fourth and fifth five lines to the end.

At first only five inch shells are used and the number of shells at one shot gradually increases. It is ended with a large ? inch hummer. At the second stage it proceeds with only 6 inch shells in the same way as before and is ended with a 7 inch hummer also. At the third and fourth stages low and high tones are alternately repeated by changing the number of shells at one shot. At the fifth stage the tone is raised step by step with thunder reports increasing the number of shells, and at last it ends with a 7 inch single large report.

Thus the construction of the note is quite simple and complexity cannot succeed. The accuracy of period timing is most important for the success of such a musical display; this is a problem not only for the display, but also of the manufacturing technique. The firing area should be limited to less than 50m x 50m so that the sounds are produced from a narrow space as far as possible. A large field which creates no echo would be most suitable for this kind of display.

Part 3. The science of fireworks

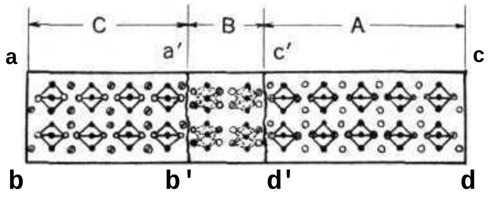
5. Thermit and the principles of combustion

It is well known that when we mix together 3 parts by weight of iron oxide with 1 part by weight of aluminium powder and ignite it, we obtain melted iron at about 2400 °C and aluminium oxide,the reaction being somewhat hazardous. This mixture was named "thermit" by the inventor. The reaction is considered as follows:

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe + 200\ \text{kcal.}$$

Fill a slender paper tube with the thermit to form a small cartridge, and ignite the one end, exposing the composition. We cannot ignite it with a flame of match, but a stronger heat source, e.g. the flame of a firework will succeed. Thus we know that it is necessary to give a quantity of energy for ignition which is larger than the minimum required for ignition. This energy is called "activation energy" and we use the symbol Ea for it.

Thus , once the thermit is ignited, the reaction is maintained by itself and it proceeds along the cartridge to the other end. Fig.20 shows the phenomenon schematically.



•:O.o.Fe,•:Al

Fig,20. Schematic expression of combustion reaction

In the figure it is assumed that the initial shape of the cartridge is kept unchangeable during the reaction. A is the part which does not yet react, B the reacting zone and C the part which has reacted already. The difference between A and C lies in the combination of atoms, which change through the zone B. At C the composition reacts, generating an amount of heat called the "heat of combustion", which is equivalent to the difference between the heats of formation of materials A and B. The heat of combustion raises the temperature of £ and diminishes gradually by radiation, conduction etc. In addition a part of the heat is turned back to A, and raises its temperature at the boundary c'd' to exite the next reaction continuously. In this book we call the heat the "turn back energy" with its symbol Ev.

The reaction zone B appears to run along the cartridge like a mechanical wave, and often we call it the "combustion wave".

The reaction of thermit is approximately solid to solid (or to liquid), and almost all the combustion heat is used to raise the temperature of the created material C, i.e. the heat concentrates in a narrow space, and therefore we obtain a very high temperature like 2400 C. The burning reaction of firework compositions is the same as thermit in principle, but more complex than the latter.

Generally the firework composition consists of solid materials which involve at least a substance which produces oxygen and another substance which absorbs oxygen in the burning reaction. The former is an "oxidizer" and the latter a "fuel" or "combustion agent". Other materials are involved in the composition as components according to the purpose. The products of combustion are in solid, liquid and gas state. The gas expands absorbing a part of combustion heat and accordingly the temperature of the reacted zone is generally lower than that of thermit. Generally a flame is produced when gases react with each other at high temperature. The reaction of the flame is promoted not only by the oxygen which remains in the flame, but also by the oxygen in the air.

6. Ignition and activation energy

6.1. Activation energy

The temperature at which a firework composition is ignited is called the "ignition point". It looks very simple, but as we see in the following description, the temperature is not strictly defined.

Keep a firework composition at rather high and constant temperature until it ignites. Measure the temperature T and the waiting time t (the period from the beginning of the heating to the ignition). Repeat the experiment at various temperatures and plot the results as a graph, e.g. see Fig.21. The curve I and II show the T~t relations for two different compositions respectively. In practice we use the temperature, with a waiting time of 4 or 5 seconds, as the ignition point.

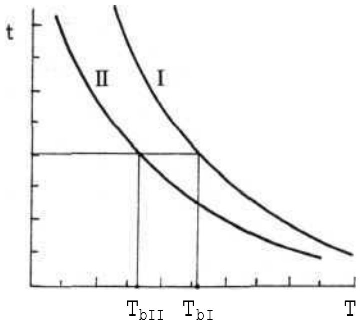


Fig.21. $\underline{T}$~$\underline{t}$, relations at ignition

The activation energy needed to cause the combustion reaction of the composition is expressed as follows:

$$\underline{Ea} = \underline{C}(\underline{Tb} - \underline{T}),$$

where Ea is the practical activation energy per unit weight of the composition at the initial temperature $\underline{T}$, $\underline{C}$ the average specific heat and $\underline{Tt}$ the ignition point. (Compositions are not generally in a uniformly solid state, and we cannot use the expression for the activation energy derived from Maxwell's distribution law as in the gaseous state.)

Ignition on the surface of a composition takes place, firstly by creating hot spots on the surface, and secondly by magnifying these spots. For this purpose we must give to the surface a quantity of energy which is at least more than the amount of activation energy. There are several ways to give the energy; to raise the temperature of the surface with other heat sources by radiation and conduction (indirect method), by mechanical action such as rubbing or striking (direct method) or by some chemical reaction. Generally ignition occurs by a combination of these actions, but they have been described separately to clarify the ignition mechanism as far as possible.

6.2. Ignition by heat radiation

If we focus the sun's beams on a surface of a composition with a convex lens, the surface will be heated gradually and catch fire. We can test the ignition sensitivity of the composition by finding the waiting time.

First we know that black compositions are far more easily ignited than white ones. This is naturally what we would expect. Adding *2%* charcoal or lampblack shows the effect. The finer the carbon particles are, the larger the effect is ; lampblack is more effective than the charcoal.

The addition of a small amount of a combustion catalyst as in solid rocket fuel for example gives a different effect according to the kind of oxidizer in the composition. For example, *2%* of potassium bichromate is quite effective for ammonium perchlorate or potassium nitrate, but almost ineffective with potassium chlorate or perchlorate.

The type of oxidizer has a large influence upon the ignition. Potassium chlorate and ammonium perchlorate are the best ignition promoters, and give different effects according to the kind of fuel, e.g. with shellac or BL-rosin (a kind of high melting point rosin) potassium chlorate is more effective than ammonium perchlorate, but with colophony it is the opposite, i.e. ammonium perchlorate is more effective than potassium chlorate. Potassium perchlorate is not as effective as potassium chlorate or ammonium perchlorate. Roughly speaking however, the ignition sensitivity of a potassium perchlorate composition which is made black with charcoal etc. is almost the same as that of a white potassium chlorate or ammonium perchlorate composition. The ignition sensitivity of potassium nitrate composition is the lowest. It must be noted that black powder and other compositions of the same type have a lower ignition sensitivity against radiation than might be expected, in spite of the black colour. For example, black powder which contains potassium nitrate, charcoal and sulphur in weight ratio 75:15:10 has almost the same sensitivity as potassium perchlorate composition, which is lower than that of potassium chlorate or ammonium perchlorate composition. If the amount of charcoal is further increased, the sensitivity of such a composition against radiation decreases further. The author cannot as yet determine the cause, but surely the amount of charcoal or other carbon particles should not be so great as to increase the sensitivity against radiation. In ordinary compositions the amount should be limited to less than *2%.* Red thermit which consists of 80% minium and 20% ferro-silicon is almost the same as potassium perchlorate composition in ignition sensitivity by radiation.

6.3. Ignition by heat conduction

In many cases special ignition compositions are pasted or pressed on the surface of a composition in order to firstly ignite the ignition composition and secondly the main composition. We call the former the "first composition" and the latter the "second composition". The ignition of the second composition takes place mainly by the heat of conduction from the first composition.

We must first clear up the character of the first composition. Paste the first composition on the outside of a small tin, which is filled with water. Ignite it. The water absorbs the heat of combustion of the first composition through the tin wall. The conductivity of the composition is not good usually, and the heat comes only from the last thin layer of the composition which is in contact with the tin wall. The heat which is conducted into the water per unit area of the tin wall is called the "force of ignition".

The force of ignition is at its largest with potassium perchlorate compositions. (About 16 cal/cm^2). In this case, the force of the black coloured composition is larger than that of the white. The force of potassium chlorate or ammonium perchlorate compositions is about a half of the potassium perchlorate composition and the colour of the composition has little influence upon the force.

Black powder, which is very often used as the first composition, has a force of only one half of the white potassium perchlorate composition. It must be specially noted that the red thermit has extremely great ignition force; it is three or four times that of the white potassium perchlorate composition and indeed eight times that of the black powder. (Red thermit is sensitive to friction, and the pasted surface must be protected with a cover in practical use.)

The next problem is how to ignite the second composition. For the first composition the author used black powder, which after experimentation has been found to have the smallest force of ignition, and red thermit the largest.

(1) Using black powder as the first composition.

Potassium chlorate composition is always quite easily ignited almost without reference to the kind of fuel. A small amount of carbon particles contained in the composition assures the ignition moreover. Potassium perchlorate composition is not so easily ignited as the potassium chlorate composition. In particular the white potassium perchlorate composition is considerably difficult to ignite. Lampblack however gives the perchlorate composition a good effect and is better than pine charcoal. The property of the perchlorate composition is very much improved by the addition of a small amount of potassium bichromate. This is the great difference in the case of radiation where potassium bichromate is not so effective. Ammonium perchlorate composition is always unsuccessful because a thin layer of hygroscopic ammonium nitrate forms between the black powder and the ammonium perchlorate composition and this disturbs the ignition. In this case, therefore, another kind of mixture must be used for the first composition.

The influence of the kind of fuel upon the ignition is quite large. BL-rosin almost always gives a good ignition, even with potassium nitrate composition. Pine root pitch is more effective than BL-rosin. Shellac or colophony gives a good ignition with potassium chlorate composition, but it is not good with perchlorate composition and gives no ignition at all in potassium nitrate composition.

(2) Using red thermit as the first composition.

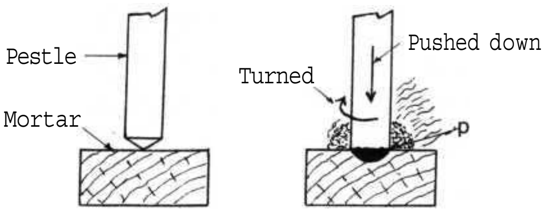
Potassium chlorate or ammonium perchlorate composition has very good ignition. Potassium perchlorate composition also has good ignition, exept a composition which contains shellac. A potassium nitrate composition is very difficult to ignite.

The above results (1) and (2) are based on systematical experiment with about 140 kinds of varied fundamental compositions. Generally, firework compositions in practice consist of more complex components, and the result might be sometimes different from what has been described above. We can only generalize from the above results.

For a composition which is difficult to ignite, e.g. a mixture of aluminium and potassium nitrate or barium nitrate, another means of ignition is proposed later (7.2).

6.4. Ignition by mechanical action

The mechanical actions consist of friction, striking and the sudden compression of the air. Humans have used these methods to obtain fire from ancient times, and they remain in the form of matches, lighters and in the ignition of some internal combustion engines. These principles of creating fire are quite important in pyrotechnics and are described here in some detail.



2 2.1 Being ready   2 2.2 In operation

Fig.22. Operation of making fire by friction

Fig.22 shows an experiment of creating fire by friction using wooden objects. The mortar and pestle are made of well dried wood, the mortar is of Japanese cypress and the pestle of red lauan which is harder than cypress. One end of the pestle is pressed on the mortar and turned by some device at high speed. The mortar gradually becomes concave at the contact point, generating smoke and producing carbonized wood powder around the pestle. Continue the rotation longer and press the pestle stronger against the mortar, and smoke is more extensively generated. Remove the pestle suddenly from the mortar, and a small hot spot may be observed at the edge of the mortar (point p). If the hot spot is breathed upon, the carbonized wood powder catches the fire. The fire is covered with the powder (charcoal), and preserved well.

The author tried the experiment about twenty times and succeeded only once, but more simple methods were used by our ancestors and have been handed down by some shrine today. The difficulties may come from the following: (1) The friction surface is too wide to collect the heat of the friction in one spot. (2) The heat which is necessary to carbonize the wood powder is taken away from the generated heat by the friction. (3) The heat of the friction diffuses by conduction through the mortar and pestle. (4) The resinoid and tar which come from the carbonization of the wood powder serve as a lubricant, and the heat of friction diminishes. (5) The ignition point of the carbonized wood powder is thought to be 300~400°C from other experiments. This is considerably high.

On the other hand, we know the conditions for creating hot spots and they may be listed as follows: (1) The collection of the heat of friction in a point. (2) The rejection of those reactions which absorb heat. (3) The conservation of generated heat. (4) The intensifying of the friction and the reduction of the lubricating action. (5) The lowering of the ignition temperature. The condition (1) is concerned mainly with the method and (2),(3),(4) and (5) with the device.

The magnification of the hot spot is done by breathing upon the hot spot in Oder to ignite the carbonized wood powder nearby. Namely, the principles of magnifying a hot spot may be as follows: (1) The substance which catches fire from the hot spot must be contact with it. (2) Oxygen must be provided from outside or the substance must contain oxygen. (3) The substance must be easily ignited at a relatively low temperature. (4) The place in which the hot spot is magnified must be protected from vibration, shock, heat diffusion and endothermic chemical reactions etc.

The conditions or principles described above can be applied not only to the above, but also to other ways of making fire. For example, the match of to-day has been improved through these principles.

Making the hot spot by striking may be a more advanced method than by using friction. This produces sparks by striking flint and metal together; these sparks are indeed the hot spots. The advantages are as follows: (1) It is easy to concentrate the heat in a very narrow space because the area of the striking surface can be kept as narrow as possible. (2) The hot spot consists of sparks which separate rapidly from the instrument without being disturbed by heat conduction. (3) The nature of the hot spots is a group of very small particles which come in quite close contact with oxygen in the air. Accordingly the hot spots have an extremely high intensity.

In this method hot spots are obtained by the surface oxidation of the substance, and it will not apply in a vacuum or in inert gases.

The instrument consists of two parts; one is hard and tough, the other is hard and brittle so that it can become small particles when struck and these have a relatively low ignition point. In uncivilized countries flint and pyrite or flint and steel are used. The flint is a kind of quartz which has a fine crystalline structure, it is also hard and tough. It gives its partner a quantity of energy and smashes a small part into particles by the striking action. The partner, pyrite or steel, is smashed and the particles are heated to the ignition point to become sparks. Generally the latter is sharpened. Pyrophoric alloy which consists of metallic cerium and some other metals is a more improved material than pyrite or steel. The ignition point of metallic cerium is 160 C, which is quite low. However simple cerium is too soft to use and it is easily oxidized in the air. Therefore it is mixed with iron to form an alloy. This alloy of cerium and iron in weight ratio 65:35 is called Auer's metal. Nickel and cobalt etc. can also be used instead of iron. Other kinds of alloys consisting of aluminium, magnesium and silicon are also used.

At present a method of creating hot spots by compressing gas is used by natives in Burma and Borneo and the history is very long. The method is to compress air quickly to a high temperature with a piston and cylinder in which an easily ignitable substance is placed. If we compress the air and prevent the escape of the heat, the relation of the temperature and volume ratio (or pressure ratio) is as shown in Fig.23. The temperature rise is very high. For this method a cylinder and piston are necessary and the instrument is complex and heavy.

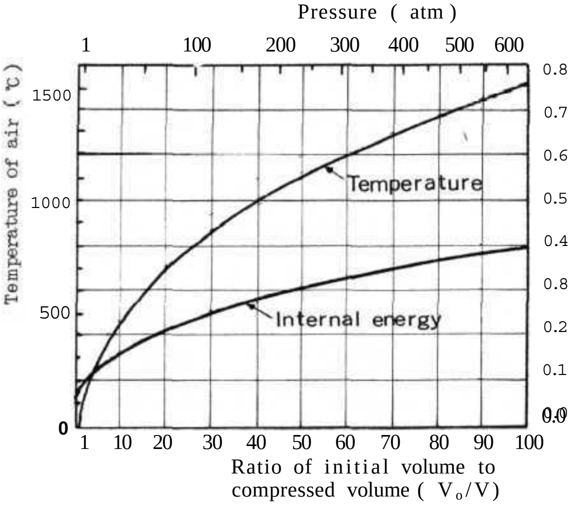


Fig.23. Temperature and internal energy of air at adiabatic compression

We may obtain the same result when we strike a piece of a self combustible substance which contains small air cells or is in contact with small enclosed air space (Fig.24 and 25). In this case the activation energy of the substance for ignition must be small, because the internal energy of the single air cell, or of the air space, is so small that the amount of heat given to the substance is not much even in a compressed state (Fig.23).

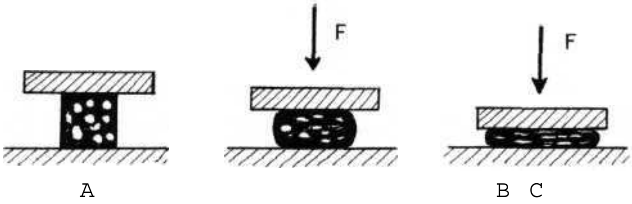


Fig.24. Striking a substance which contains air cells

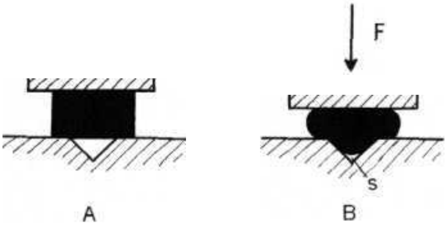


Fig.25. Striking a substance which is in contact with a closed air space.

7. Combustion and explosion

7.1. The progress of combustion

When a composition has a wide free surface and it is ignited at a point in the middle of the surface, the burning surface grows with the creation of a crater. The flame is produced at right angles to the surface. When a long piece of the composition is ignited at one end, the combustion proceeds along the piece to the other end. In this case, if the side of the piece is covered with some incombustible material, the burning surface is kept parallel with the time;this is called "parallel burning". Of course we assume that the composition is uniformly manufactured and the environmental conditions are kept constant during the burning.

Other types of burning are shown in Fig.26. A shows the burning of a single piece where the side is not protected from the fire. The shape of the burning surface becomes like a gimlet. We find two kinds of burning velocity; one is the velocity along the surface (surface velocity) and the other is the velocity perpendicular to the burning surface (inner direction velocity). B shows the burning of two long rectangular pieces placed together in parallel at a distance, so that they react to each other. The surface velocity is more together increased at the confronted surfaces than A. If the pieces are placed together more closely, the fire runs between the pieces instantaneously. This phenomenon occurs also with an unexpected crack or at a gap where two compositions are jointed. C is the burning which takes place in a hole and is regarded as a special case of B. On ignition the fire runs through the hole with a terribly high surface velocity, D shows the burning of quick match which is covered by

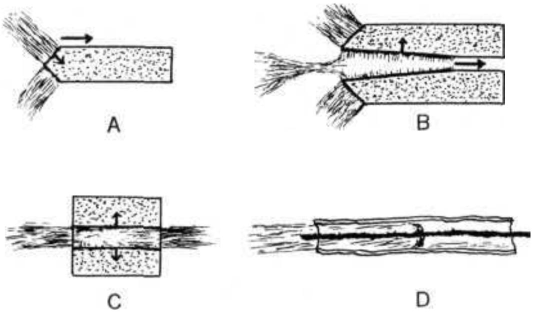


Fig.26. Various burning types

a loose kraft paper tube. The values of surface velocity are, for example, as follows:

Composition	Surface burning velocity
Black powder	5~17 m/sec
Potassium chlorate and hemp coal (77:23 in weight ratio)	12~46 "
Potassium perchlorate and hemp coal (77:23 in weight ratio)	10~19 "

Generally the quick match burns with a crunching sound because pressure increase by the combustion gas causes the paper tube to burst. The stronger the tube is, the larger the surface velocity becomes. If a metal tube is used in place of the paper one the surface velocity becomes tremendously high.

when a single grain of a composition is ignited at a point on the surface, it catches fire slowly around the surface, but when a group of many grains are ignited at some point, all the surfaces are instantaneously ignited, because the surface velocity is very much increased by the clearances among the grains. Accordingly the burning time of the group of grains is almost the same to that of a single grain if the grains are identical with one another in configuration and dimension. However in the case of a powder instead of the grains, the surface burning velocity diminishes on the contrary because the clearances among the particles of the powder are quite small. Therefore, it is known that there are certain levels of clearance which give the maximum surface velocity. This is the reason why we shoot firework shells with gunpowder in grains rather than the powdered state; the former drives the shells higher than the latter.

The inner direction velocity varies mainly according to following factors: (1) *Composition*. With regard to the oxidizers, potassium chlorate gives the highest velocity. Ammonium perchlorate is the next, and potassium perchlorate is the third. Potassium nitrate gives a low velocity except in the case of a black powder-type composition, which consists of potassium nitrate, charcoal and sulphur. With organic fuels, as far as the auther has examined them, pine root pitch gives the maximum, Accroides resin (Yacca) the next, BL rosin the third and shellac the fourth. Metallic fuel like magnesium or aluminium powder increases the velocity owing to the high temperature of the burning reaction. A small amount e.g. 2% of hemp coal, lampblack, potassium bichromate etc. are effective to increase the velocity. Potassium bichromate seems to give the most, but it spoils the colour of the flame. (2) *Specific gravity*. The smaller the value is, the larger the velocity. Accordingly the velocity is the largest in the powdered state and the smallest in the consolidated state. When a composition which contains water or solvent is dried quickly, the specific gravity decreases and it burns with a higher velocity than that which is slowly dried. A composition which is consolidated by the polymerization of polyester is quite hard and has a specific gravity of about 2.0 g/cc. Such a composition burns with a very small velocity. (Ordinary consolidated firework compositions generally have a specific gravity of 1.3~1.7.) (3) *Burning surface area*. The smaller the surface, the smaller the velocity. This phenomenon comes from the dispersion of the burning heat. (4) *Initial temperature*. The higher the temperature, the larger the velocity. (5) *Pressure*. The influence on the velocity is generally expressed by the following equation:

$$V = k(P/P_0)^{\alpha} ,$$

where V is the inner direction burning velocity, k a constant and a function mainly of the initial temperature, P the pressure at the burning, P_0 the normal pressure and α the pressure exponent. k and α depend on the kind of composition. For example, k = 3.2 mm/sec and α = 0.33 for an illuminant, k = 2.2 mm/sec and α = 3.1 for a colour flame composition and k = 0.4 mm/sec and α = 0.45 for a smoke composition, where the values of k are obtained at 15°C.

7.2. The stability of combustion

It is very difficult to continuously burn a single piece of wood, but if a group of several pieces of wood catch fire, the burning soon becomes stable and is not easily put out. In firework compositions it is the same as above. Firework compositions are generally used as single pieces, and here is a description of the burning stability of a single piece, in detail.

As described in 5. the combustion proceeds automatically by repeating the process; the layer of the composition at the burning surface absorbs an amount of the turn back heat from the flame or the reacting zone, which raises the temperature of the layer from the initial, to the ignition point, for burning to proceed.

The fine constructions of representative burning surfaces are shown in Fig.27. *A* creates oxygen bubbles caused by the dissociation of the oxidizer; potassium chlorate, potassium perchlorate, potassium nitrate etc. On the contrary, *B* creates no bubbles; this is where ammonium perchlorate is the oxidizer. Generally an organic fuel makes small craters caused by the dissociation of the fuel, because the temperature of the dissociation of the organic fuel is always lower than that of the oxidizer. The gas from the dissociated fuel is generated at the craters and comes out through the layer of the bubbles. If the fuel is carbonized at the dissociation, it remains as particles of carbon at the bottom of each of the craters, which are heated into hot spots. The fuel which is perfectly vaporized and not carbonized, e.g. colophony, cannot produce hot spots. The hot spots absorb the turn back heat well, and they increase the

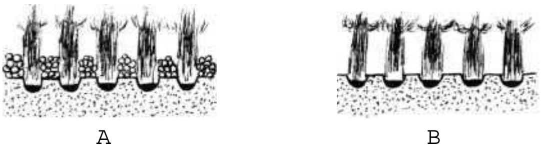


Fig.27. A representative fine structure of burning surfaces

stability of the burning; i.e. the fire is not easily put out by wind or water. If a small amount of carbon is added to the composition it is very effective to produce hot spots.

When a metal powder of aluminium or magnesium is used as the fuel, the craters would be formed at the position of the particles of the oxidizer, because the melting and boiling points of the metal are higher than that of the oxidizer. But in this case the hot spots are not so important, because the temperature of the flame is so high that the amount of the turn back heat is always large enough to keep stable burning.

It is difficult to keep parallel burning for a long time at a wide burning surface, even when the composition is elaborately manufactured, especially in a case of small inner direction velocity.

In the firework field, there are many cases where we must shoot burning pieces at a high speed, like the stars of a chrysanthemum or of Kyokudo. Accordingly it is important to know how the burning of such pieces bear the wind. In this book the maximum velocity of the wind, in which the pieces can continue the burning, is called "critical wind velocity". But this is limited to the compositions which burn and produce a flame.

The critical wind velocity is most influenced by the fine structure of the burning surface. The type A in Fig.27 is easily covered with foam when there are no hot spots. The foam prevents the burning surface from absorbing the turn back heat, and consequently the stability of the burning decreases; the critical wind velocity is low. When many hot spots are produced, the critical wind velocity becomes very high. To create the hot spots pine root pitch or BL-rosin are recommended. As described above, the substance which is easily vaporized without any carbon remaining is not effective. When we add carbon perticles to the composition to produce the hot spots, rather coarse grain like hemp coal is more effective than the fine particles like lampblack. The type B in Fig.27 has no foam, and the critical wind velocity has no relation to the hot spots. The burning surface absorbs the turn back heat by radiation and conduction from the flame very well, and generally the value of the critical wind velocity is high.

The above discussion is confirmed by an experiment (Table 3)« Potassium nitrate composition shows a very different character from others; the combustion is quite unstable, and we cannot pick up general rules from these data. We have no experimental data here concerning black powder type compositions (mixture of potassium nitrate, charcoal and sulphur) and metal powder compositions, but the burning of such compositions is quite stable and their critical wind velocities seem to be very high.

Table 3. Experimental values of critical wind velocity m/sec)

Kind of oxidizer		$KClO_3$		$KClO_4$		NH_4ClO_4		KNO_3	
Composition	Oxidizer(%)	83	83	81	81	85	85	83	83
	Fuel (%)	11	11	13	13	9	9	11	11
	Hemp coal(%)	-	2	-	2	-	2	-	2
	Glutinous rice starch(%)	6	6	6	6	6	6	6	6
Critical velocity at 1 at.	Fuel								
	Colophony	24	27	11	21	39	39	-	-
	Shellac	42	39	14	11	39	27	9	-
	BL-rosin	39	52	27	52	39	94	17	9
	Pine root pitch	73	>150	39	60	73	94	9	17
Fine structure of burning surface		A		A		B		A	

Note: (l)The content of the hemp coal shows an additional percent.
(2)The line under figures shows the composition which continues burning even under 10 mm of water.

The decrease of the atmospheric pressure decreases the stability of combustion; on the contrary, the increase of the pressure increases the stability. Therefore firework pieces must be constructed so that the burning pressure increases as far as possible. This is especially important in the case of ignition. For example, in Fig.28 A is more ignitable than B, when they are moving in high speed.

With regard to the shape of firework pieces, burning is more stable at the concave surface of a composition rather than a convex one, because if the fire is partially put out for some reason, the burning is recovered instantaneously from the fire of the neighbouring parts on the same surface. Stability is especially high in a hole (Fig.26,C). On the contrary, spherical pieces like the stars of a chrysanthemum give the lowest stability. It is a most interesting and important problem for us to be able to conquer this difficulty, which is described later (Fig.29 and 30).

There are some compositions which burn without flame, e.g. smoke compositions. In this case the burning is generally quite stable because the burning surface is covered by generated ash, and the combustion proceeds independently of environmental conditions. Even when an amount of water is poured on the burning composition, the water cannot reach the burning surface. Accordingly, to put out the fire, the ash must be removed from the surface before the water is placed on it.

The burning surface is sometimes destroyed by a mechanical action, e.g. shock or vibration, which strips off the burning layer from the composition to stop the combustion. Such an accident often occurs in the case of shooting stars; the burning surface is dug off by the propellant gas. To protect the surface from the mechanical action, we use a punched metal

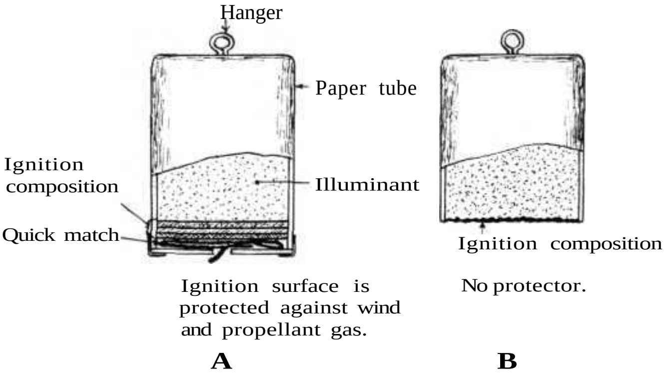


Fig.28. Hanging stars

plate or cardboard disc which is placed on the surface (Fig.28-A); a buffer of felt is also added to relieve the mechanical actions of shock and vibration.

The principle of delivering fire from a composition A, to another B, without failure is to allow the composition to change from A to B not suddenly, but gradually (Fig.29).

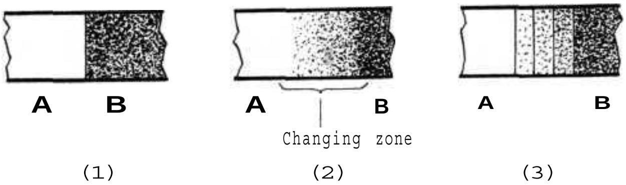


Fig.29. Schematic expressions of the combination of two compositions

(1) shows a combination with a sudden change from A to B; this is used, only when the ignitability of A is equal to that of B or the latter is larger than the former. (2) shows a combination with the most gradual change; even if B is quite unignitable like a mixture of aluminium and barium nitrate, the fire proceeds from A to B without fail, if B is only combustible. The longer the changing zone, the less failures occur. But this method is too ideal to apply to manufacture. (3) shows a combination in several steps which avoids difficulties in the manufacturing process. Fig.30 shows an example of spherical star in which the above principle is applied.

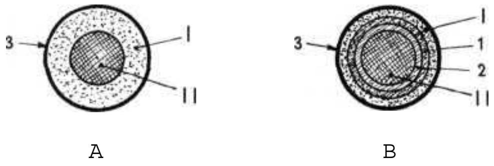


Fig.30. Examples of the combination of two compositions in spherical stars

The compositions are as follows:

	I	II
Potassium perchlorate	81%	36%
BL-rosin	13	-
Aluminium (fine flakes)	-	55
Soluble glutinous rice starch	6	9

The composition I contains no aluminium, and is easily ignited. Composition II contains a large amount of aluminium and is quite difficult to ignite, especially when it is consolidated, but it burns fiercely with a strong light and sparks. A shows the sudden change of the composition from I to II and it never succeeds. B shows the step change. Two middle layers, *1* and *2,* are placed between I and II, i.e. the composition changes from I to II in two steps. 1 consists of I and II in weight ratio 8:2 and 2 in 5:5. If one more layer in 2:8 were inserted, it would be more rational. The ignitability was tested by shooting these stars, which were about 15 mm in diameter, with a steel tube of 22 mm inside diameter and 4 grams of black powder as the lifting charge. In the case of the step change type, there was no ignition failure when it was tested 25 times.

7.3. Explosion

The concept of explosion is based on common sense rather than on science. The word means a sudden change of a state and its sudden development. When a phenomenon occurs suddenly, we don't call it "explosion", if it goes without this enlargement.

At present the concept of explosion is divided in two kinds of phenomena; combustion and detonation. The combustion means here a very rapid burning under high pressure, which is characterized by the burning equation on page 37. The burning velocity may be less than about 300 m/sec. Detonation is quite different from combustion in character and thought in that the phenomenon is a kind of shock wave followed by a chemical reaction. We call the wave the "detonation wave". The velocity of the detonation wave i.e. the detonation velocity in ordinary cases exceeds 1000 m/sec.

The structure of the detonation wave is schematically shown in Fig.31

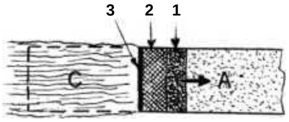


Fig.31. Schematic expression of detonation wave

L is the physical shock wave, in which the chemical reaction has not yet occurred, 2 is the reaction zone in which chemical reaction is taking place and 3 the surface on which the chemical reaction ceases. It is thought that the reaction zone is under the highest pressure. For example, in the case of industrial explosives, it is said that hexogen produces 330,000 atm and TNT 190,000 atm.

When detonation occurs even in the free atmosphere, the neighbouring things are broken into pieces or deformed. Combustion cannot produce such reactions in the free atmosphere. Accordingly we can know from the behaviour, whether it is a kind of detonation or not.

Generally firework compositions which contain potassium chlorate, perchlorate or ammonium perchlorate as oxidizer will detonate from a strong mechanical initiation, especially when the composition are in the powdered state. Potassium chlorate or other chlorate, red phosphorus, realgar, sulphur, antimony trisulfide etc. promote the inclination. On the contrary, potassium nitrate or other nitrates decrease it. Black powder is not likely to detonate.

Compositions which contain only a small amount of oxidizer, e.g. the smoke compositions, do not detonate.

It must be observed that a large pile of composition will detonate when it is ignited, even if a small amount does not detonate.

Table 4 shows examples of detonation velocity, which are measured by a revolving camera, on report compositions. The detonation velocities differ according to the method of initiation; by the primer or by the igniter.

Table 4. Detonation velocities of report compositions

Composition	Potassium perchlorate	(%)	70	64	72
	Aluminium (fine flakes)	(%)	27	23	28
	Sulphur	(%)	3	13	-
Loading density		(g/cc)	0,62	0,63	0,63
Detonation velocity	by No. 8 Detonator	(m/sec)	1418	1427	1223
	by electric ignitor	(m/sec)	867	-	-

7.4. Force of explosives

"Force of explosives" is a characteristic value which expresses the projection effect of a composition denoted by a symbol "f". The value concerns the explosion temperature (or combustion temperature) and mols of the gas generated per 1 kg of the composition, and it is denoted as follows:

$$f = NRT_b$$

where N is the number of mols of the gas, R the gas constant (8.48 kg.dm or 1.99 cal), T_b the combustion temperature. The unit of f is denoted by kg.dm/kg or simply by dm. The value of f is obtained by calculation or experimentally by a closed vessel test.

To make the meaning of the force of explosives clear, see the difference between the value and the value of heat of explosion, which is formulated as follows:

$$(Q + \Delta Q) = f \left(\frac{1}{n-1} + \frac{N'}{N} \cdot \frac{Cv'}{R} \right),$$

where Q is the heat of explosion per unit weight, which is measured or calculated at normal temperature, ΔQ the heat which is necessary to raise the temperature of the explosion product from 0°K to the normal temperature per unit weight, n a value equal to $1 + R/Cv$, where Cv is the average molar heat capacity at constant volume of the gas produced, N' the number of mols of solid (or liquid) material produced per unit weight, Cv' the average molar heat capacity of the solid material. According to the equation, at a definite value of heat of explosion, Q, the larger the number of mols of the solid meterial, N', becomes, the smaller the value of f becomes.

Generally speaking, the composition which produces a large amount of solid (or liquid) material and little amount of gas, e.g. a thermit, has almost no capacity for projection. On the contrary, a composition like smokeless powder, which generates almost no solid material, but almost only gas, has a large value of f, and shows a large projection effect. The force of black powder is about one third of smokeless powder, because it produces a large amount of solid material, i.e. about *70%* of the weight.

8. Eyesight

8.1. Human eyesight

Man has two kinds of optic nerve cells in his eyes; pyramids and bars. The former respond to the brightness and colour of a light, but the latter have no colour sense, and only sense black and white like a monochrome photograph. Almost in the middle of the retina there is a narrow place where only the pyramids concentrate and no bars are found; here the sense is sharpest. The greater the distance from this place, the more the density of the pyramids decreases and that of the bars increases.

A light stimulus against the human eye is different according to the wave length of the light and the kinds of optic nerve cells. Fig.32 shows this relation.

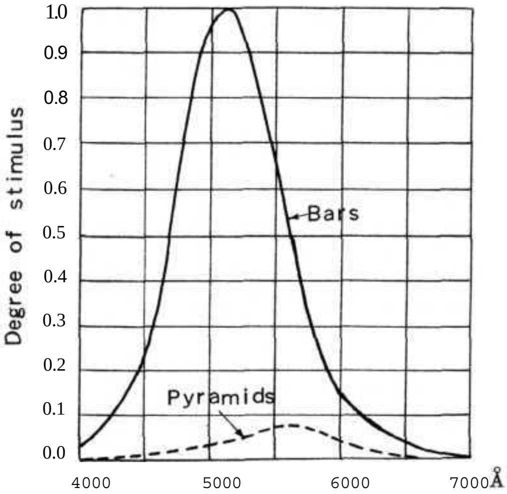


Fig.32. The degree of human eye stimulus

The degree of stimulus for the bars is the maximum at 5070 A(green), and for the pyramids at 5550 A (yellow green). Thus the sensitivity of the bars and the pyramids is quite different. Accordingly the brightness contrast is more impressive than that of colour in fireworks. The black and white stimulus is about ten times larger than that of colours.

The light source of fireworks are mostly illuminating, and more or less have a brightness. In such cases both the pyramids and bars respond to them well. However the reflective light sources like smoke are quite weak in brightness and the pyramids do not respond so well especially at night. The colour of the smoke is only seen most clearly under direct sunshine in a cloudless sky. The colour of smoke can only be admired at night by illuminating it with flare, but it will not succeed unlesa use is made of a light of tremendously high candle power.

How does the visibility increase, when the intensity of a light increases? For the relationship, we have a rule called Fechner's law. For example, when the brightness of the light increases in the ratio 1, 10, 100, 1000, 10000 cd/m², the light is visible as an intensity of 1, 2,3,4,5 times. The classification of the brightness in Table 1, i.e. from W2 to F2, is arranged nearly according to such a relation of visibility. The lowest brightness which is visible for human being is 1/10,000,000 of the brightness of the things which are directly exposed in the sun.

When we go suddenly into a dark place from a light place, nothing is visible, but after a little while the surroundings become gradually visible. This is called the "adaptation of the eyes". Therefore the eyes don't catch a short time light of lower brilliancy after or between lights of higher brilliancy. This principle is applied to the colour changing stars of the chrysanthemum. Generally we change the brilliancy of stars from lower to higher levels. Alternatively we often use a layer of lower brightness between two layers of higher brightness so that the flower of the chrysanthemum looks as if the stars change colour all at the same time, in spite of little manufacturing deviations. We call such a layer the "colour changing relay".

Colour blindness only affects a few people in general, but it is said that some kind of the blindness occurs for everyone if the visual angle of the target is very small; i.e. not more than 15'. This is the situation when we see an object 4.4 meters wide at a distance of 1000 meters. In this case the eyes respond only to red and green and to black and white; not to yellow and blue. This is called the "third blindness". We are always under the influence of the third blindness, when we see light stars in the far distance. A star which is seen as very poor light green nearby is visible as a deep green at a long distance. A white electric lamp looks yellow or reddish yellow from a far distance; only the red and green responses of the eye combine and may cause such a yellow colour. For this reason, the colours of fireworks must be inspected by looking at them from a distant place.

8.2. Brightness and colour

We have two kinds of colour producing light sources, the emitter (flames or sparks) and the reflector (smoke or parachute, flags, etc.). Here the former is described since it is the most important.

The emitter is characterized by three concepts; brilliancy, hue and purity. Hue means the kind of colour, i.e. red, yellow, green, blue, violet etc. Purity means the degree of whiteness of a colour.

The brilliancy of an emitter, which is visible as if it were a flat emitting surface, is denoted by the candle powder per unit area of the surface:

Brilliancy(average) = Illuminous intensity of light(cd)/
Area of emitter which is rectanglar
to the direction of the observer(m^2)

More precisely the brilliancy differs according to the part of the emitter and the direction of the observer.

The luminous intensity of light used in above equation is the illumination on the unit surface which is placed at a right angle to the direction of the emitter at a distance of 1 meter. To obtain the value, measure the illumination at some distance from the emitter using a photometer (the photoelectric cell type or photocell type is popular), and calculated from the following equation:

Illuminous intensity of light(cd) = Measured intensity of
illumination(lux) X Square of the distance
from the emitter to the photometer.

The units of light intensity are so numerous that we often become confused. But we have only one which we can measure, it is the luminosity, which is the same as the above luminous intensity of light. Other units are derived from the luminosity. The new unit of luminosity is the candela and 1 candle power equals 1.018 candelas. 1 candela means

1/60 of the light intensity per 1 cm of the black body at the solidifying point of platinum(1773 C) . 1 lux is the illumination at the surface which is 1 meter distant from the light source of 1 candela. 1 lumen is the amount of light beams from a light source of 1 candela per unit area at the distance of 1 meter. The spot light source of 1 candela emits light beams of 4π lumen in the sum of all directions.

The measurement described above is only applied to a relatively large light source, and not to sparks or fire dust, because the photometer cannot respond to such a weak light. In such a case we use a comparison method for it. Eyes cannot measure the brilliancy of an emitter directly, but can judge if two emitters, which are placed side by side, are equal or not in brilliancy. Therefore, to measure the brilliancy of sparks or fire dust, it is convenient to use a tungsten lamp as the standard. The relation of the brilliancy and voltage must be previously known. The voltage is adjusted untill the filament looks the same as the object in brilliancy at the measurement. The distance from the observer to the object has no influence upon the measurement theoretically. (The brightness of the image of the light source on the retina has no connection with the distance from the observer to the object, but is proportional to the brilliancy of the light source and the area of the pupil. At night generally the pupil opens to the maximum area against a weak light. In such a case the brightness of the image is proportional only to the brilliancy of the object.) Accordingly at the same time we can compare the brightnesses of two light sources which are placed at different distances.

Regarding the measurement of lights, we must be careful about the following: (1) Avoid the reflected light beams from generated smoke or from other obstacles by using a shading tube as far as possible. The flame in the test should be projected upwards, because the candle power of a downward flame is very much affected by the smoke and will appear about 1.6 times the same upward flame. (2) The relative response of aphotometer for each wavelength of light is generally different from that of the eye. Therefore we must use a filter to allow the former to coincide with the latter.

The relation between the hue and the purity of colours is shown by the chromaticity diagram (Fig.33).

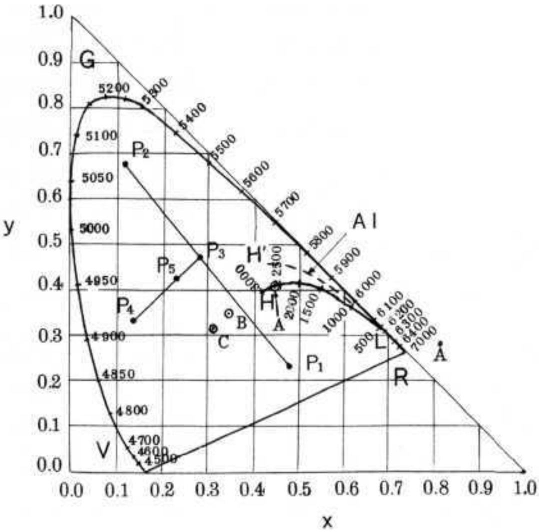


Fig.33. Chromaticity diagram

It is thought that man has three kinds of colour sense organs (pyramids); red, green and blue sense organs. Each of them respectively is sensitive to a particular range of light wave length. The red sense organ has the maximum sensitivity at 6000 A, the green at 5550 A and the blue at 4450 A. A light stimulates the three organs at the same time. The degree of the stimulation to the red sense organ is denoted by $\underline{X}$, to the green by $\underline{Y}$ and to the blue by $\underline{Z}$. We call the values "tristimulus values". The value of $\underline{Y}$ is also used to denote the brilliancy of the light, because the relative luminosity curve of the pyramids coincides with the stimulus curve of the green sense organ relatively. The values $\underline{x}=\underline{X}/\underline{S}$, $\underline{y}=\underline{Y}/\underline{S}$ and $\underline{z}=\underline{Z}/\underline{S}$, where $\underline{S}=\underline{X}+\underline{Y}+\underline{Z}$, are called trichromatic coefficients and have the following relation:

$$x + y + z = 1 .$$

If the two values, $\underline{x}$ and $\underline{y}$, are known other one, $\underline{z}$, is settled. Fig.33 is drawn on the base of this theory, and has two axises related to the values of x and y respectively. In the diagram colours are enclosed by a curve, RVG, and a straight line, RV. The colour of a light source is denoted by a point in this closed area. (See also Fig.47).

The diagram is quite convenient for designing colour flame compositions. For example, when a red colour represented by P_1 is mixed with a green P_2 , the new colour moves along the straight line P_1 -P_2like P_3. The coordinates have the following relations:

$$x_3 = \frac{x_1 S_1 + x_2 S_2}{S_1 + S_2}, \quad y_3 = \frac{y_1 S_1 + y_2 S_2}{S_1 + S_2},$$

where the suffixes, 1,2 and 3, show the points, P_1 ,P_2, and P_3, respectively. In the same way the colour at P_4 is also mixed with the colour at P_3, creating a new colour as P_5. According to the principle we can create a yellow flame by mixing strontium and barium salts in a proper ratio in a composition or a violet flame by mixing strontium and copper salts.

Solid or liquid material at a high temperature like sparks or fire dust has a special distribution of intensity of continuous spectra, which varies with the kind of the material and especially with the temperature.(In the case of a flame, it does not vary so much with the temperature.)

Considering the analogical inference, we can consider here the black body, which is perfectly black at normal temperature. (Soot has almost the same nature with the black body, and has an absorption ratio of *95%.)* The intensity of the radiation from the black body increases only with the temperature, and it changes the colour from black to red, orange, white as the temperature increases. The colour is determined by the temperature only, and is shown by the LH curve on the chromaticity diagram(Fig.33). For example, the orange is obtained at 1250°C and the white(silver) at 2250°C. The brilliancy of the black body is not shown in the chromaticity diagram, but in another graph, Fig.34, where the abscissa denotes the

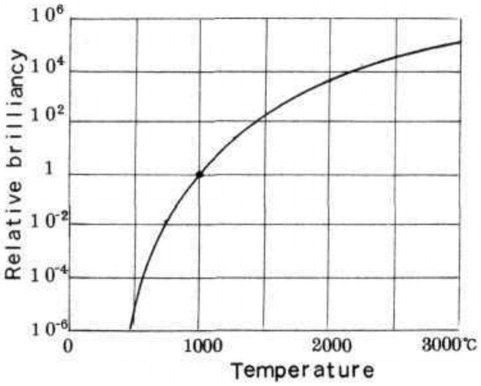


Fig.34. Brilliancy of the black body

temperature and the ordinate the ratio of the brilliancy, taking the brilliancy at 1000°C as 1. According to Fechner's law, the value 10 means a double increase of the eye sense, 10 a treble increase and so on. Therefore, for example, the black body at 2000 C is seen with about 4.5 times the eye sense at 1000°C.

We often measure the temperature of solid or liquid substances at high temperature by comparing them with the brilliancy or colour of the black body. This value does not show the true temperature of the substance, but this method is quite favourably used because we have no other simple method like this. The temperature which is measured by the comparison with the brilliancy of the black body is called black body temperature or brightness temperature, and with the colour of the black body colour temperature. The former means the temperature of the black body which has the same brilliancy with the substance. Practically the brilliancy of the substance varies with the wave length of the emitted light from the substance, and the wave length must be limited at the measurement. For this purpose a glass which transmits only red light corresponding to a mono wave length of 6500 A is used. The latter means the temperature of the black body which has the same colour as the substance. In this case the chromaticity of the light emitting substance must resemble that of the black body. There is no meaning of the colour temperature, if the chromaticity of the substance does not lie near the line, LH, in Fig.33. Generally a substance which emits light of the same chromaticity as that on the line, LH, is called the grey body.

Further let us consider an empty spherical shell with a thin wall which has a small hole(Fig.35). This hole looks black at the normal temperature, because the light beams entering the sphere through the hole are reflected many times and are absorbed by the inside of the wall almost perfectly. Accordingly the hole is regarded as the true black body. When the sphere is heated, the temperature of the outside of the wall may be the same as the temperature in the sphere because the wall is very thin. In this case,

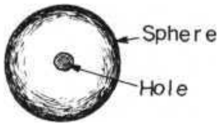


Fig.35. Sphere with a small hole

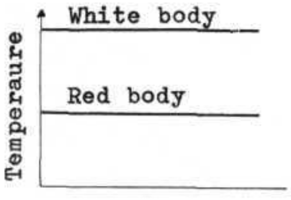


Fig.36. The principle of colour temperatures

the hole must be the same as the black body in colour and brightness, which are related to the true temperature of the sphere. Namely we can know the true temperature of the sphere by the brilliancy or by the colour of the hole. The outside surface of the sphere and the hole look somewhat different. The brilliancy of the former is lower than that of the latter. Therefore the brightness temperature of the sphere(the substance) is smaller than the true temperature. The colour of the outside surface is generally, especially in the case of metals, whiter than that of the hole. Therefore the colour temperature of the sphere(the substance) is higher than the true temperature for many kinds of substances. However carbon shows an opposite nature. Generally speaking, the colour temperature is nearer to the true temperature than the brightness temperature, and the true temperature lies between the colour and brightness temperature(Fig.36).

It must be noted that the concept of the colour temperature does not always show the temperature. It is concerned with the colour which is estimated only by the scale on the chromaticity line, LH, rather than the temperature. Therefore we can reduce a light source of low temperature to a high temperature scale using a filter. The standard lights are made according to this principle. The standard light A(an electric lamp, the colour temperature of which is 2581°C) is changed to the standard B(4597°C) and C(6467°C) only by using liquid filters. A shows the ordinary electric light at night, B the average light of the sun at noon and C the average day light.

The fire dust or sparks which are produced by iron or carbon create the colour which resembles that of the black body. The colour of the sparks of "Senko-Hanabi" which is caused not only by carbon but also other materials, also resembles the colour of the black body. We feel that the colour of the aluminium fire dust is a little different from the black body. The colour changes from red-orange to yellow, white yellow and silver as the temperature increases, and the locus may be written as the LH' line (Fig.33). Anyhow we can produce various colours of the fire dust or sparks except blue and green by adjusting the temperature and selecting substances which make up the component material in firework compositions according to the principle of the colour temperature.

9. Flames

The flame of an alcohol lamp looks almost colourless. When a length of platinum wire which is dipped into a metal salt solution is put into the flame, the flame is coloured in the upper part by the wire. The colour is peculiar to the kind of the metal; strontium colours the flame red, sodium yellow, barium pale green and copper blue. This is applied to the qualitative analysis of metal ions as the colour flame test. The emission of the coloured light is caused by atomic metal gas or a gas consisting of molecules of metal compound, and the process may be set out as follows:

> Solid metal salt --> Vaporization --> Chemical reaction -->
> Creation of emitters (molecules or atoms) --> Excitation -->
> Emitting.

The principle of firework coloured flame is the same as that of the above, but the mechanism for producing colour is more complex. Although the colour of a flame is said to be peculiar to the kind of metal, the colour of the firework flame is considerably different from that in the laboratory. For example, copper gives a violet blue to the firework flame, but blue green in the laboratory. Barium gives bright green to the former with some conditions, but only pale green in the latter case.

As described above, the radiation of the light beams is caused by molecules or atoms, which are once excited to a high energy level at a high temperature and then fall down to a lower one, discharging the energy, which corresponds to the difference between the two levels, as the light. Accordingly, it is necessary first to obtain a high temperature in the flame to produce good colour, but some emitters of molecules dissociate, if the temperature rises too high,copper compounds for example.

Firework flames of such a high temperature are obtained by burning compositions which contain an oxidizer and a fuel. An organic fuel, such as shellac or rosin, gives a temperature of about 2200°C to the flame, which is called the "low temperature class flame". Magnesium as the fuel gives 2500~3000°C to the flame, and is called the "high temperature class flame".

9.1. Low temperature flames

The temperature of the flames produced by the compositions which consist of shellac and various kinds of oxidizers are shown in Fig.37~40,

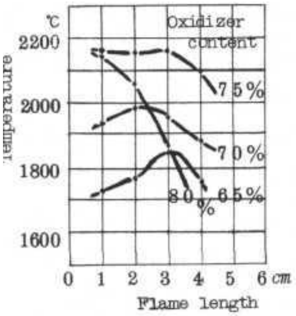


Fig.37. Flame temperature from potassium chlorate and shellac

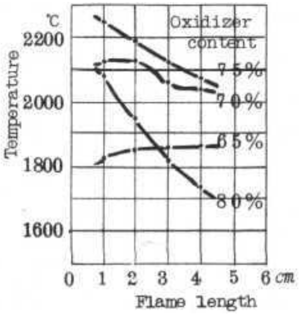


Fig.38. Flame temperature from potassium perchlorate and shellac

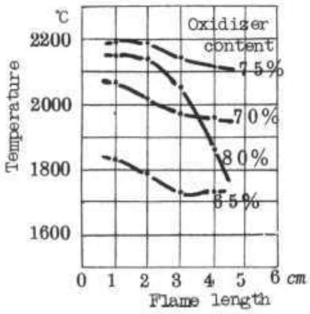


Fig.39. Flame temperature from ammonium perchlorate and shellac

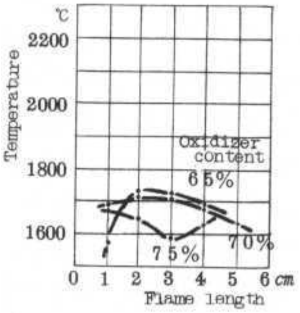


Fig.40. Flame temperature from potassium nitrate and shellac

where the compositions are denoted as follows:

Oxidizer	x %
Shellac	y %
Sodium oxalate	10 %
	100 %

The temperature were measured by means of the so called line reversal method, where the sodium oxalate was necessary to produce the Na-D lines.

Three oxidizers, potassium chlorate, potassium perchlorate and ammonium perchlorate, give a quite similar distribution of temperature in combination with shellac along the length of the flame. The maximum temperature is obtained at 75 weight % of the oxidizer without reference to its type, where the ratio F/0, which means the weight ratio of the fuel to the oxidizer, amounts to 17:83 or 20:100.The maximum temperature amounts to more than 2250°C for potassium perchlorate, 2200°C for ammonium perchlorate and 2180°C for potassium chlorate, and these values are not very different from each other. The temperature effect of the three oxidizers is enough to excite emitters so that good coloured flames can be obtained.

On the other hand, potassium nitrate gives quite a different distribution of the temperature. The maximum temperature amounts only to about 1700°C. Such a low temperature cannot excite the emitters. Therefore potassium nitrate is not used for low temperature class compositions.

The flame temperature depends upon the kind of fuel also. The following table shows the examples.

Table 5. Observed flame temperature for representative fuels

(By line reversal method, 10 mm distant from the burning surface, F/O- 20/100.)

	Potassium perchlorate	Ammonium perchlorate
Pine root pitch	2455 ℃	2238 ℃
Shellac	2245	2198
Rosin	2322	2092
Wood meal	2057	2025

To obtain a coloured flame, we use a colour producing material, which is mixed into the composition. The colour depends upon the cation, metal atoms, in the material, and hardly at all upon the anion, e.g. $-NO_3$, $-CO_3$, -Cl or $-C_3O_4$. The latter however has an influence upon the temperature of the flame. Generally the anion which produces oxygen in the flame, such as-NO_3, increaes the temperature while others decrease it. Therefore the content of the latter must be limited as much as possible. In practice we use 10~20% of the total, and a large content is not always successful in colour production. In general the materials are selected considering not only the temperature and colour effect, but also the burning rate, hygroscopic nature and the reaction tendency with other components etc.

9.2. High temperature flames

The temperatures of flames produced by the following compositions are shown in Fig.41.

Oxidizer	x%		x%
Magnesium powder	y%	or	y%
Shellac or PVC	10%		-
	100%		100%

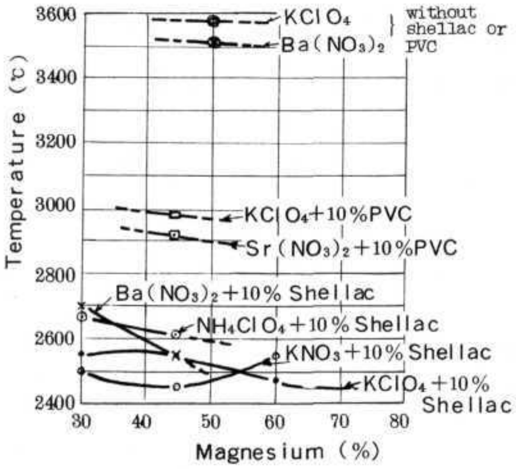


Fig.41. Temperatures of high temperature class flames

The compositions contain no sodium salt for the temperature measurement, because at such a high temperature the Na-D lines caused by impurity in oxidizers appear quite clearly. The position where the temperature was measured, was 10 mm apart from the burning surface along the centre line of the flame.

The data are not so accurate as those of the low temperature class flames, but we can assess the general tendencies.

The compositions, which have only two components, an oxidizer and magnesium powder, give 3400~3500°C. Even when a small amount of organic substance is added to the composition, the temperature decreases remarkably.

We have no data here about the distribution of temperature in the flame, but we get some idea from the following fact. In a mixture with 30~40% magnesium the brilliancy of the flame is highest at the base of the flame and decreases along the flame length.

9.3. Reaction in the flame

The important emitters of firework flames are molecules with the exception of Na atoms. The molecules are produced in quite different forms from the original colour producing materials mixed into the composition. The chemical combination of the emitters are relatively simple and in general are outside the ordinary valency law. For example, they are written as SrCl, BaCl, CuCl etc. and not $SrCl_2$, $BaCl_2$, $CuCl_2$ etc.

Important reactions in the flame are as follows:

(1) SrOH(orange red) + Cl or HCl --> SrCl(deep red)
(2) BaO(white) + " --> BaCl(deep green)
(3) CaOH(orange) + " --> CaCl(orange)
(4) CuOH(pale green) + " --> CuCl(violet blue)
(5) MgO(s. p.65) + " --> MgCl(invisible).

The left side molecules are produced in a flame which is lacking chlorine or hydrogen chloride; on the contrary the right side molecules are rich in the gas. Each of the molecules produce the colour in brackets. From (1) to (4) are the reactions which deepen the colour. The substances which produce chlorine gas in the flame are potassium chlorate(quite poor), potassium perchlorate(quite poor), hexachlorethane(rich) etc. and those which produce hydrogen chloride are polyvinyl chloride(rich), BHC(rich), ammonium perchlorate(quite rich) etc. In particular ammonium perchlorate is the most effective for deepening the colour.Care must be taken not to allow the flame temperature to drop by the addition of too much of these substances to the composition. Therefore the content of the chlorine or the HCl donor(except those which also play the role of oxidizer or fuel) in a composition should be limited to a small amount of 2 or 3% in the low temperature class flame compositions, and 10~15% in the high temperature class. Reactions(1)~(4) are gas to gas reactions. But (5) is a solid to gas reaction, and it is effective to reduce the continuous spectrum from the solid or liquid particles of magnesium oxide which change to magnesium chloride gas.

The reducing reaction of carbon particles: If carbon particles are produced in the flame, magnesium oxide is reduced as follows (J.H.McLain, Pyrotechnics,The Franklin Institute Press(1979), p.85):

(6) $MgO(\text{solid or liquid}) + \text{heat} \rightarrow MgO(\text{gas})$

(7) $MgO(\text{gas}) + C + \text{heat} \rightarrow Mg(\text{gas}) + CO(\text{gas})$.

This reaction proceeds at a very high temperature(at low temperature it turns back). When we superfluously add shellac or another organic substance to a composition, this reaction takes place, and the generation of the magnesium oxide particles in the flame is reduced to decrease the continuous spectrum. This is clearly observed on a spectroscopic photograph. At the end of the flame the reaction reverses, and MgO appears as white smoke and C is oxidized to CO or CO_2 by the oxygen in the air. Too much organic material produces soot; therefore the practical limit of the content may be of 15~20%.

The technique to obtain a good flame colour is to determine the composition so that the desired emitter atoms or molecules increase in number and other useless items decrease, by using the principles described above.

9.4. The flame spectra of firework compositions

There are two kinds of flame spectra; high temperature gas produces atomic and molecular spectra and high temperature solid or liquid particles produce continuous spectra. Important spectra are as follows:

(1) Strontium spectra(Fig.42)

An atomic spectral line 4607A(violet) always intensively appears in the flame, but it hardly disturbs the red colour action of the flame. A molecular spectrum band SrOH appears in the flame which contains little or no chlorine or hydrogen chloride gas. Such a flame is obtained, for example, by a composition of 60% strontium nitrate, 30% magnesium and

10% shellac. The colour of the flame is a pretty orange-red like the morning sun. Another molecular spectrum band SrCl appears in the flame, which is rich in chlorine or hydrogen chloride gas, and gives deep red. The band occurs, for example, at a composition of *75%* ammonium perchlorate, 15% shellac and 10% strontium carbonate.

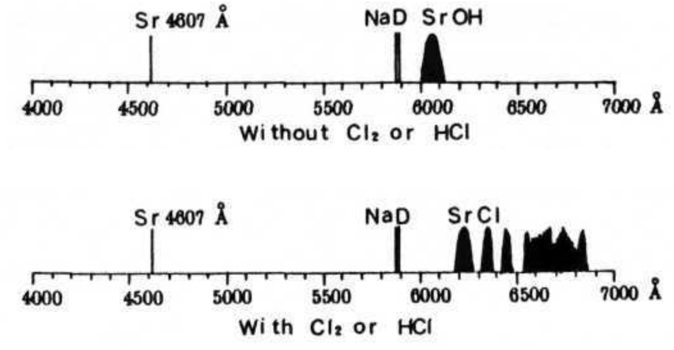


Fig.42. Strontium spectra

(2) Barium spectra(Fig.43)

An atomic spectrum line 5536 A(yellow green) always appears clearly, but is not intensive enough to disturb the flame colour. A molecular spectrum band BaO appears in the flame which contains little or no chlorine or hydrogen chloride gas. On the contrary another molecular spectrum band BaCl appears with chlorine or hydrogen chloride gas.

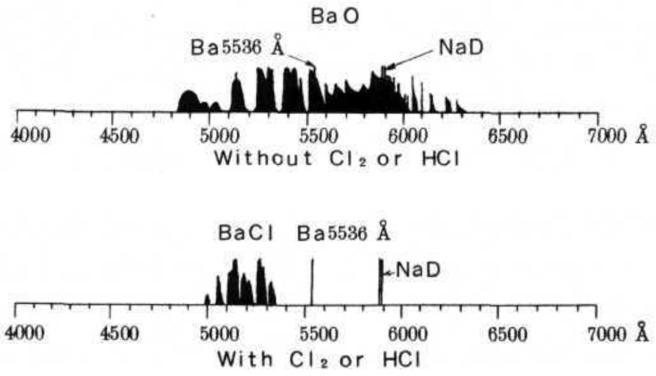


Fig.43. Barium spectra

The band BaO is obtained, for example, by a composition of 60% barium nitrate and 40% magnesium. It gives a high brilliancy to the flame, which looks white, and is useful as an important light source for illuminants. The band BaCl is produced, for example, by a composition of 50% barium nitrate, 35% magnesium and 15% PVC. It gives a brilliant deep green, which is an important green light source for fireworks.

(3) Calcium spectra(Fig.44)

Where the flame contains neither chlorine nor hydrogen chloride a molecular spectrum band CaOH appears, and the colour of the flame becomes orange. In the presence of chlorine or hydrogen chloride gas another spectrum band CaCl appears in the flame. In this case the colour of the flame is an intensive reddish-orange which is not as good as red, but it is sometimes used for cheap toy fireworks.

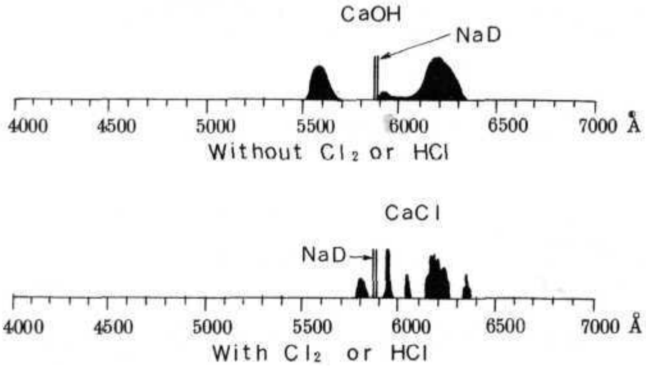


Fig.44. Calcium spectra

The band CaOH is obtained, for example, by a composition of 40% magnesium, 50% potassium nitrate and 10% calcium carbonate, and the band CaCl by 75% ammonium perchlorate, 15% shellac and 10% calcium carbonate.

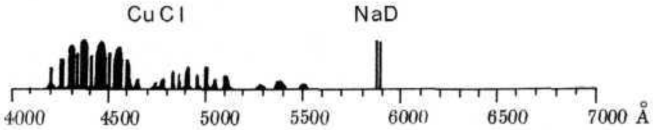
(4) Copper spectra(Fig.45)

The band CuCl appears in a flame which is rich in chlorine or hydrogen chloride gas, and gives the flame a pretty violet blue colour. For example, a composition of 75% ammonium perchlorate, 15% shellac and 10% Paris green produces such a coloured flame. The band CuCl seems to decompose at high temperatures, and it is difficult to produce blue with this band in the high temperature class flames, unless the magnesium content is decreased to about 10%.

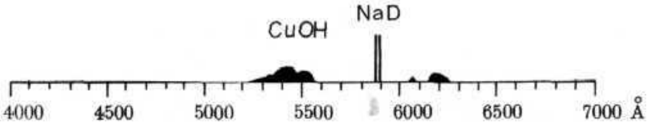
The band CuOH appears in a flame which contains no chlorine or hydrogen chloride gas, or even in the case of small dissociation of a chlorine compound in the flame. The colour caused by this band is light green, and it greatly disturbs the blue which we want. For example, a composition of 75% potassium perchlorate, 15% shellac and 10% Paris green produces both CuCl and CuOH bands. This is caused by the fact that KC1 gas, which is produced in the flame, does not dissociate sufficiently to create the CuCl band alone. In this case the colour of the flame is light blue and not so good.

The CuO band(red) occurs, when the flame has an excessive amount of oxygen. It appears at the top of the blue flame of a composition which contains copper or copper salts. However it is very weak and does not disturb the blue colour.

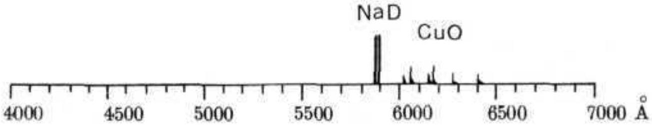
The Cu_2 band is not available for firework flames, but it can be observed as quite brilliant green sparks at an electric discharge between copper wires, as we see often at the bow contact of a tramcar.



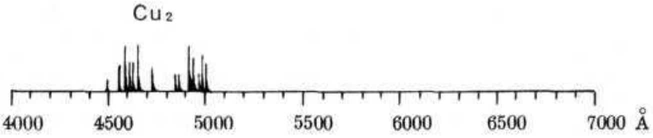
With CUor HCl



Without Cl_2 or HCl



With excessive amount of O_2



From an electric discharge
between copper wires

Fig.45. Copper spectra

(5) Sodium spectra (Fig.46)

The most important atomic spectra of sodium are Na-D lines; 5896A and 5890A. The lines are observed clearly in a flame of relatively low temperature and in a composition which has a small amount of a sodium salt. On the contrary, in a high temperature and a relatively large amount of the sodium salt a strong continuous spectrum appears at both sides of the D lines where the D lines change into dark absorbtion spectra. This continuous spectrum is quite intensive and is used for illumination. Such a flame spectrum is obtained, for example, by a composition of 60% sodium nitrate and 40% magnesium. In the case of a low temperature class flame, which is produced by a composition of potassium perchlorate and other organic fuel, the continuous spectrum is also observed because of the relatively high temperature of the flame; with ammonium perchlorate it cannot be observed because the temperature is relatively low. Various reactions in the flame have no direct influence on the sodium spectra.

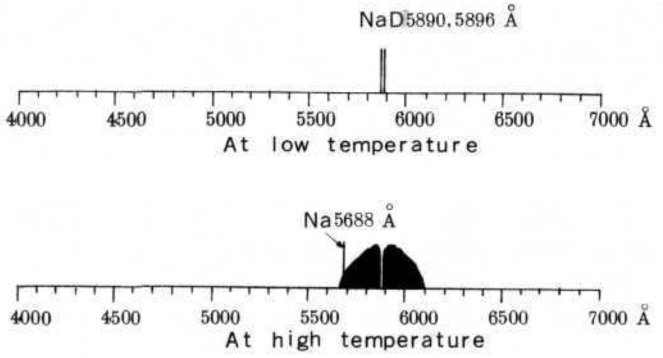


Fig.46. Sodium spectra

(6) BO_2 spectrum (green)

The BO_2 spectrum for a green flame might be suggested using boric acid as a colour producing agent, but it is too weak to use practically in firework compositions.

9.5. The adjustment of the colour of flames

To adjust the colour of flames first we must know how to use the chromaticity diagram. This was desctribed already in 8.2. Fig.47 shows the same chromaticity diagram as that in Fig.33, but the colours and corresponding spectra are written into it. The names of colours are presented by K.L.Kelly as follows[J.O.S.A. 33(1943) 627]:

1 = red,
2 = reddish orange,
3 = orange,
4 = yellowish orange,
5 = yellow,
6 = greenish yellow,
7 = yellow green,
8 = yellowish green,
9 = green,
10 = bluish green,
11 = blue green,
12 = greenish blue,
13 = blue,
14 = purplish blue,
15 = bluish purple,
16 = purple,
17 = reddish purple,
18 = red purple,
19 = purplish red,
20 = purplish pink,
21 = pink,
22 = orange pink,
A = CIE illuminant A,
B = CIE illuminant B,
C = CIE illuminant C.

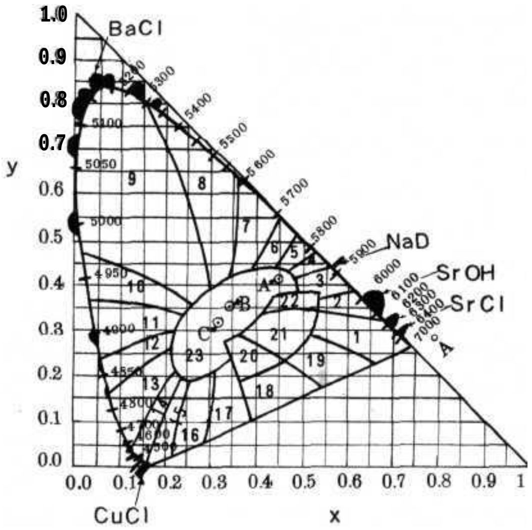


Fig.47. Chromaticity diagram with colour names and spectra

The most important spectra are arranged along the edge of the diagram; SrOH, SrCl(red), Na(yellow), BaCl(green) and CuCl(blue). Fortunately, the red, green and blue spectra stand at the three corners respectively, therefore it is possible to obtain an intermediate colour by mixing these spectra, i.e. by mixing the colour producing agents for the spectra in the composition. For example, a violet flame is obtained by mixing strontium and copper salts as in the violet star composition(p.216).

9.6. Undesirable spectra and their rejection

Various spectra which occur in a firework flame, except the useful spectra described above, generally decrease the purity of the flame colour and make the flame become whitish. According to the chromaticity diagram, the flame colour has an inclination to move from the edge to the centre. We must therefore reject the occurrence of such spectra as far as possible.

The spectra which disturb the colour of flames are as follows:

(1) The spectra which occur from oxidizers and other inorganic substances

Potassium chlorate, potassium perchlorate etc, which contain potassium atoms create undesirable spectra; continuous spectrum caused by the atoms and atomic line spectra. The former appears in almost all the visible zone and is the most intensive at about 4500A(blue). This spectrum makes the flame white, and sometimes it is used to produce a white flame. This spectrum cannot be rejected unless the potassium salts are precluded from the composition. If good colouring is desired, ammonium perchlorate must be used in place of above oxidizers. In the latter, the atomic line spectra are very weak and do not much disturb the colour.

Strontium compounds, such as strontium nitrate, carbonate etc.,produce an intensive Sr line 4607A(blue), which cannot be avoided whenever we use these substances. The intensity of the line is smaller than that of the useful bands, SrOH and SrCl, but it rather pulls the red towards the violet.

Generally impurities in the oxidizers or other inorganic materials disturb the flame colour. Strontium salts usually contain some barium salt as an impurity which produces the undesirable spectrum BaCl or BaOH band and disturbs the colour of the flame. Accordingly it is necessary to use strontium salts of high purity to obtain a good red flame. Strontium and barium belong to the same group of elements, and it is difficult to separate barium and strontium salts industrially, but in a laboratory strontium salts can be purified until they have a barium content of less than 0.0002%[Ж. Прик. Хим. 44(10),2157~2126(1971)]. The atomic spectra Na-D lines appear in almost all cases because every inorganic substance in firework composition contains sodium compounds as an impurity. The Na-D lines disturb any flame colour except a yellow flame. It may be difficult to obtain perfectly Na-free ingredients, but we must endeavour to get materials with a minimum sodium content.

(2) The spectra which come from fuels

When magnesium burns, molecular bands due to MgO occur. They appear with a sequence of head at 5192A(green) and 5O07A(blue green), being degraded to violet. The intensity of these bands is smaller than that of SrCl or SrOH, but they disturb red and yellow. This is unavoidable, when we use magnesium as a fuel. With aluminium, A10 bands occur with sequence heads at 4648A(blue), 4842A(green blue) and 5O79A(green); they disturb red and yellow, but not so intensively. This is also unavoidable.

Moreover, magnesium and aluminium produce an intensive continuous spectrum due to solid or liquid particles of oxide, MgO or Al_2O_3, which covers all the visible range and disturbs the colouring of the flame quite intensively. MgO is vaporized(by sublimation) at 2770°C, and Al_2O_3 melts at 2030°C and is likely to dissociate into A10 gas at 3500°C[Ellern, Pyrotechnics,p.267(1968)]. According to a spectroscopic study made with high temperature class flames, the magnesium oxide is partially vaporized and partially in solid particle state. Aluminium oxide is similar to magnesium oxide in nature. To decrease the continuous spectrum, it is quite effective to add some substance which produces hydrogen chloride gas to the flame, e.g. ammonium perchlorate, polyvinyl chloride etc. is added to the composition. These substances change the oxide particles in the flame to the chloride, which may be easily vapourized to decrease the intensity of the continuous spectrum. For example, the magnesium chloride thus produced should have a melting point at 714°C and a boiling point at 1418°C and the aluminium chloride is sublimed at 180°C. Another effective method is to reduce the metal oxide particles to metal vapour by adding some organic material, e.g. shellac, rosin etc., to the composition. This is not so successful for a metal which has a high boiling point like aluminium (2327°C), but quite effective for one, which has a low boiling point like magnesium(1120°C).

Too much organic fuel in a composition produces a continuous spectrum in the flame which is caused by the emission of carbon particles at high temperature. In the case of the low temperature class compositions this spectrum spreads from red slightly towards the violet zone, more or less to 5200A(green), and the flame looks red orange. To decrease this spectrum the ratio of the content of fuel to that of the oxidizer, F/O, must be properly selected. In general as far as our ordinary fuels are used, the value of F/O is about 2:10. With red flames the ratio can be increased a little more than this value because we can use the red part of the continuous spectrum because of the carbon particles.

10. Sparks

Sparks are liquid or solid particles which are created at the burning surface of a composition and which pass through the flame. The difference between the sparks and the ash or smoke, is that spark particles retain their ability to emit light at high temperature after they are discharged into the air.

Sparks in the broad sense are classified further by words such as "fire dust" and "sparks". Fire dust means a group of particles at high temperature which do not branch during their life, like the sparks of aluminium. The word "sparks" refers to those particles which branch like iron sparks.

10.1. The structure of a fire dust particle

When we collect fire dust on the surface of water in a vessel, it is suddenly cooled and we can find the construction of a particle as shown in Fig.48.

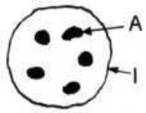


Fig.48. A fire dust particle

A: Active substance

I: Inactive substance

A single particle consists of an active and an inactive substance. The active substance is oxidized by the oxygen in the air to keep the particle at a high temperature. When all the active substance in a particle is oxidized, the particle is cooled and no visible light is emitted. The inactive substance adjusts the exposure of the active substance to the air and controls it to avoid a violent reaction. If there is no inactive substance in the particle, the particle burns out in the flame to produce no fire dust. For example, there is no fire dust in a composition which consists of ammonium perchlorate and charcoal.

Aluminium fire dust consists of melted aluminium as the active substance and melted Al_2O_3 as the inactive substance in a particle; in the fire dust of black powder(a composition of potassium nitrate, sulphur and charcoal) charcoal is the active material along with the burning product K_2S_x . K_2SO_4, K_2CO_3 etc. is the inactive part.

10.2. The colour of fire dust

As described in 8.2, the colour of fire dust depends upon the temperature and the kind of material. Aluminium can produce orange, yellow or gold, white-yellow, silver. Black powder-type compositions produce dark red to a kind of bright orange. These colours are adjusted practically by the selection of the types of oxidizers and fuels and the regulation of F/O (s.15).

The colour of flames described earlier is very clear and gives us a somewhat sharp feeling, but the colour of fire dust is gentle and elegant.

10.3. The division of fire dust particles

A single particle of the fire dust is a mixture of liquid and solid substances and has cohesion. When a strong wind blows against the particle, it is divided into many smaller particles by the occurrence of a spray-like phenomenon. This is called "fire division".

Fine fire division produces quite beautiful fire dust, but its life is shortened. On the contrary, rough fire division decreases the beauty, but lengthen the life. In view of this, it is necessary to plan the composition or the manufacturing process of the composition to obtain proper fire division according to the intention.

The fire division occurs most easily when the cohesion of the particle is weakest. With the fire dust of black powder-type compositions the point may be a content of about *7%* sulphur. If the sulphur content is larger than that, the potassium sulfide, K_2S_x. content,in a particle increases to produce strong cohesion, which makes the fire division more difficult. If the content is less than that, unburned charcoal aggregates and in this case the fire division is also difficult.

The manufacturing process of black powder type composition has a large influence on this division. The three components, potassium nitrate, charcoal and sulphur, must be intimately mixed if we hope to get good effect. For example for a composition of 58% potassium nitrate, *7%* sulphur and 35% charcoal, the average life time of the fire dust from this composition which is mixed by a ball mill, is about half this value when it is mixed by hand. With aluminium fire dust compositions, for example, a composition of potassium perchlorate and aluminium in weight ratio 5:5 gives good fire division, but many of the fire dust particles burn out before escaping from the flame, and the life is shortened. As the content of the aluminium is increased to the ratios; 4.5:5.5, 4.0:6.0 etc., the life becomes longer and longer(the colour of the dust changes from white to yellow) and at last, at the ratio 3.5:6.5, the fire division becomes difficult and cannot be used practically. These were tested with 200 mesh flake aluminium. The grain size and configuration also have a great influence on the division.

Moreover the fire division depends upon the wind velocity, i.e. for a flying star it depends on the velocity of the star. The most representative example is the "Chrysanthemum of Mystery"(see 15.2). When we ignite this star on the ground no fire division occurs, but when we fire it through the air we see a lonely kind of fire dust which is caused by the movement of the star. Another good example is the star "silver wave"(see also 15.2). This star burns on the ground producing only a small number of poor sparks and remains as a melted cinder. However when it is shot, a good fire division occurs with a beautiful effect.

It will be seen that the fire division can be tested only when the burning star is moving through the air.

10.4. The phenomenon of Senko-Hanabi(Japanese sparklers)

It is important to study the phenomenon of the Senko-Hanabi in order to acquire knowledge about the phenomena of the fire dust and sparks, and further about the prevention of accidents.

Senko-Hanabi is an old firework in Japan. In 1927 Dr.Nakaya first presented the results of his physical study on this item[Nakaya and Sekiguchi:Riken Report ,6,p.1083(1927)]. In 1957 the author made an effort to clarify the mechanism of sparks from the chemical point of view [T. Shimizu:Studies in fireworks on the Japanese Senko-Hanabi, Journal of the Industrial Explosive Society,Japan,18,p.359(1957)]. A.Maeda and his pupils at Shinjuku High School in Tokyo made experiments on the problem in detail[Shinjuku-Koko(High School), Studies on the old Japanese firework Senko-Hanabi(1962)]. Here is a summary of the important results in precis.

The phenomenon of Senko-hanabi occurs after a black powder-type composition burns out; at the cinder stage it coheres into a fire ball and emits many pine needle-like sparks from its surface as it reacts with oxygen in the air. In this case the remaining charcoal and potassium sulphide which is generated by the burning reaction in the cinder play an important role. The potassium sulphide remains red and hot as a fire ball and the oxygen in the air reacts slowly upon it. Particles of the charcoal in the fire ball are projected at frequent intervals from the surface of the ball owing to the explosion of the carbon; the particle which is projected explodes successively into a pine needle-like sparks. The reason why the carbon explodes is not clear at present.

The pine needle-like sparks resemble the sparks of iron which are obtained by grinding iron. In the latter case, the melted substance is iron and the sparks are caused by the explosion of the carbon in the iron. Accordingly we can get some idea of the carbon content of the iron by observing the sparks [Kawai: Metal materials,p.91(1960)]. At 0.2% carbon content there are few sparks, but as the carbon increases more sparks are produced, and at 0.7~0.8% carbon content we get most sparks. The difference between Senko-Hanabi and iron sparks lies in the fact that in the former the carbon is not in a dissolved state, but in the latter it is dissolved.

Using compositions which consist of carbon powder(paulownia charcoal, pine charcoal or pine soot), sulphur and potassium nitrate, we obtain the zones in which the pine-needle-like sparks occur(Fig.49).

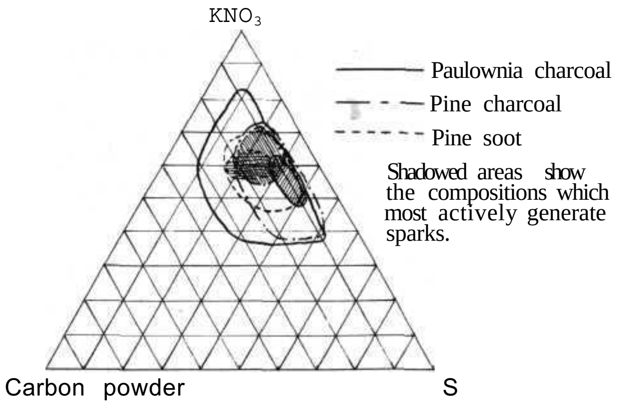


Fig.49. Effective zones of Senko-Hanabi composition of KNO_3-S-C system

As we see in the diagram, the zone depends a little upon the kinds of charcoal or soot.

When the carbon content in the composition is too much and that of the sulphur is too little, the fire ball is not created. On the contrary, when the former is too little and the latter too much, the composition burns with a violent reaction and blows off the fire ball substance because the cohesion is too low to create the fire ball. Too much potassium nitrate also results in a violent reaction and the fire ball is not produced. Accordingly the best composition may be 60% potassium nitrate, 10~20% charcoal or soot and 20~30% sulphur.

When realgar is used in place of sulphur we can obtain larger and more beautiful sparks than with sulphur. In this case the sparks are accompanied by long smoke lines. The cinder may contain arsenate and this item must not be used indoors (Fig.50).

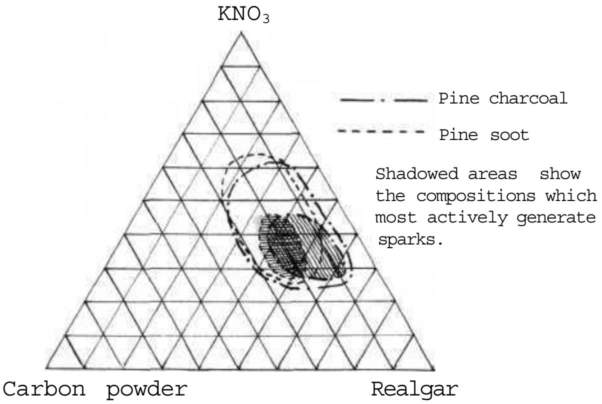


Fig.50. Effective zones of Senko-Hanabi composition of KNO_3-Realgar-C system

The best sparkling zone of this item lies at 35% potassium nitrate, 45% realgar and 20% charcoal or soot.

There has been a problem with the kind of carbon powder from the earliest times. Pine soot generally gives the largest pine needle-like sparks; but sometimes we have a kind of soot which gives only small sparks. The reason is not clear at present. I.Yamamoto, one of manufacturers of Senko-Hanabi, said that the sparks appear with considerable difference depending on the place where the soot condenses during production. Paulownia charcoal also gives big sparks, especially big willow-like sparks at the end. Pine charcoal gives rather small sparks, but produces them quite frequently. The sparks from hemp coal are not as good as those from pine charcoal. Household charcoal causes a violent reaction at first and blows away the fire ball substance, and even if the fire ball is formed, it produces no pine needle-like sparks, but only willow-like ones. It is not yet clear what property of the carbon causes these differences. Anyhow it is true that very fine particles of carbon of vegetable origin give the best effect.

There are two ways to hold the composition of Senko-Hanabi; one is a dry process twisting a piece of Japanese paper tape 23 mm wide and 200 mm long containing about 0.09 £ of the composition at one end; the other is a wet process where sticks made of rush or straw are dipped into a liquid mixture to a desired depth, withdrawn and dried in the sun. The liquid mixture is made by adding glutinous rice starch and water to the composition.

In the dry process it is said that the order of mixing the ingredients is very important to obtain good sparks. At first potassium nitrate and pine charcoal are mixed intimately, then pine soot is added to the mixture, kneading it together, and at last sulphur is added to this.

According to Maeda's classification, the life of a Senko-Hanabi is divided into five periods as follows: (1) Birth (11 to 15 seconds). Hold a piece keeping the composition end down and ignite it at the end. It burns violently, leaving a wire-like cinder. (2) Infancy (3 to 4 seconds). The cinder shrinks gradually to a fire ball, which increases in brilliancy. In the fire ball, substances move like boiling water. The temperature of the ball is about 860°C. (3) Youth(8 to 11 seconds). Large intensive pine needle-like sparks are projected from the fire ball. (4) Middle age(9 to 10 seconds). From the fire ball somewhat small sparks are very frequently projected. The temperature becomes 940°C. (5) Old age(18 to 20 seconds). The sparks lose vivacity and change to a willow-like form. The temperature falls down to 850°C. The substances which are contained in the fire ball at each period are shown in Fig.51 according to the analysis by Maeda. In this case no realgar is used.

We see in the figure that the weight of the ball decreases gradually. This is caused by the projection of a part of the fire ball material as sparks and by the decrease in sulphur as sulphur dioxide produced by the reaction with oxygen in the air. In the fire ball we find carbon, K_2CO_3, $K_2S_2O_3$, K_2SO_4 and potassium sulphide K_2S_x. When we use realgar in the composition in place of the sulphur, we find no K_2SO_4. Of these substances the active ones are the carbon particles and K_2S_x; the former causes pine needle-like sparks and the latter keep the fire ball in a red hot molten state by the heat generated from the reaction with oxygen in the air, and the latter envelopes the carbon particles to reduce violent reaction with the air. The other inactive substances participate in the reaction, not

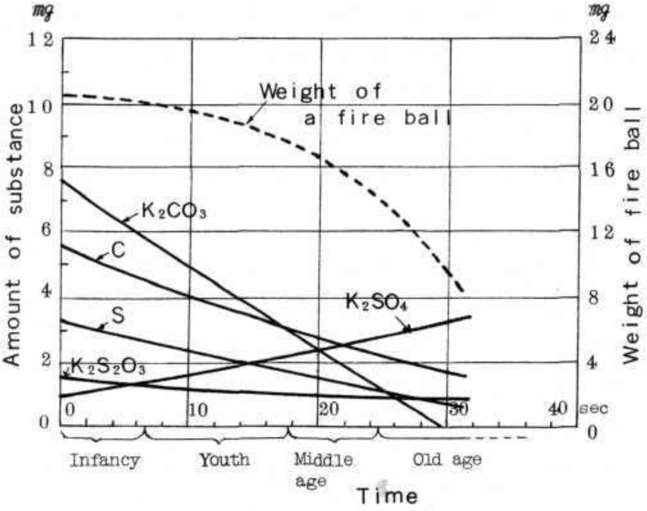


Fig.51. The amounts of substances in a fire ball in milligram(by A. Maeda)

directly, but indirectly to reduce the reaction rate.

From the above study it is clear that we might make such Senko-Hanabi-like sparks with only the two materials, carbon particles and potassium sulphide. The author succeeded in this.

Potassium carbonate	3.5	grams
Sulphur	1.8	"
Pine charcoal	0.8	"

Take the potassium carbonate in a porcelain crucible and heat it. Add the sulphur to it and mix together, stirring, until a molten substance is obtained after some reaction has occured. The representative reaction equation may be as follows:

$$2K_2CO_3 + (2x + 1)S \dashrightarrow 2K_2S_X + 2CO_2\uparrow + SO_2\uparrow$$

Then add the pine charcoal to it and mix well, stirring, and we obtain a black granular product.

Pick up the product on some nichrome wire at its spiral end. Put it quickly into the oxidizing flame of an alcohol lamp. The substance begins to react, bubbling, and is gradually heated to a red and somewhat transparent fire ball. It then begins to project pine needle-like sparks quite actively. The maximum flying range of the sparks is about 18 cm. The sparks are far bigger than those obtained from ordinary Senko-Hanabi. This reaction does not cease even when the lamp is removed.

With the next composition we obtain the same result.

Potassium hydroxide	5.6	grams
Sulphur	3.6	"
Pine charcoal	1.6	"

Place the potassium hydroxide in a porcelain crucible and heat it until it melts. Add the mixture of the sulphur and charcoal, which is previously prepared, to this. The potassium hydroxide reacts with the sulphur to produce a black substance in a plastic state. Stir well and knead it. The reaction may be as follows:

$$2KOH + (2 + x)S \dashrightarrow K_2S_x + \overset{\uparrow}{SO_2} + \overset{\uparrow}{H_2S}$$

At last we obtain a black, dough-like mass, which smells of hydrogen sulphide.

When we replace the potassium hydroxide with sodium hydroxide, we obtain strange sparks of another shape rather like many pieces of string thrown into the air:

Sodium hydroxide	4.8	grams
Sulphur	3.6	"
Pine charcoal	1.6	"

The fire ball substances, which are obtained by suddenly cooling the fire ball at the beginning of the Senko-Hanabi display or the above methods, have a life of less than 4~5 hours. After this time the substances lose their ability to spark. Perhaps it may be caused by the degeneration of the potassium sulphide.

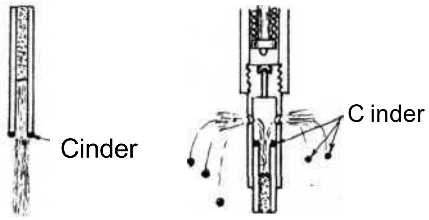
100.5. Various relationships with the phenomenon of Senko-Hanabi

Black powder-type compositions have been used from ancient times, and even at present firework pieces cannot be produced without such compositions, One of the most important characteristics of these compositions is that the cinder, after the burning or explosion, remains in an active state in the air. This fact exerts a remarkable influence upon fireworks both in agreeable and disagreeable ways.

On the good side, we can mention the production of fire dust or pine needle-like sparks. The Senko-Hanabi is the most popular one. The "Silver Wave"(see 15.2) also belong to this type. In this case the realgar content considerably helps the Senko-Hanabi phenomenon. The sparks looks like red, green and yellow twinkling stars.

The compositions by R.Lancaster(R.Lancaster: Fireworks, principles and practice,p.89(1972)) contain gunpowder(black powder), sulphur, potassium nitrate, charcoal etc., and the twinkling or glittering effect might be caused by the Senko-Hanabi reaction of the cinder.

On the bad side here is an example. When the gas, which is produced by the burning of black powder, streams out of a narrow orifice, it accumulates the potassium sulphide particles it contains, at the outlet in drops. This causes the Senko-Hanabi phenomenon.



5 2.1 A fuse burning 5 2.2 An ignition device

Fig.52. Some Senko-Hanabi phenomena

Fig.52.1 shows the burning fuse of a shell. Some years ago such a fuse fell on a straw-thatched house and caused a fire. Fig.52.2 shows an ignition device for a smoke in which a fuse is burning. The cinder accumulates at the outlet of the fuse, and is intermittently blown out through small holes as small drops which can drop on the composition to cause an unexpected ignition. To avoid these phenomena we must improve the composition so that it will not produce the fire ball material. For this purpose the sulphur content should be decreased, as we see in Fig.49. It is also better not to use realgar as the component, because it helps the production of the fire ball material.

Sometimes we see the sparkling of a fire ball caused by burnt quick match. When shells are fired one by one in the same mortar, sometimes an unexpected explosion occurs when a lifting charge is loaded into the mortar. This may be caused by the remaining fire in the mortar which is activated a little while by the Senko-Hanabi reaction. Accordingly, we must scrub the inside of the mortar and check it before loading to see if the fire spot remains in it or not.

The black powder cinder, as described above, consists mainly of potassium sulphide and is strongly alkaline and hygroscopic. It does not dissolve in oil but is water soluble. Steel mortars therefore when used with a black powder charge should be washed with water to clean off the dross, well dried and then smeared with oil.

We often have sore eyes from particles of dross of sparks from black powder. When this happens wash the eyes in running water.

10.6. Metal sparks

Iron sparks are produced by molten iron in which carbon dissolves. The sparks look like pine needles as in the case of Senko-Hanabi. They are produced by branching explosively from one particle, one after another. When the iron has no carbon content, it does not produce these sparks.

Magnalium which consists of 50% magnesium and 50% aluminium also generates branching sparks, but are not so large as those of iron pyrophoric metal, for example, an alloy of aluminium, magnesium and silicon, creates large sparks. R.Lancaster recomends titanium turnings to obtain silver sparks[R.Lancaster: Fireworks, principles and practice, p.51(1972)]. (See photos on the front page.)

11. Smoke

11.1. The principle of generating smoke

Smoke is a cloud of very small solid or liquid particles floating in the air; they are produced by various substances in a vaporized state. The smoke is obtained from vapour. Solid or liquid materials are difficult to make into smoke even when they are divided into tremendously small particles. The mechanism of generating smoke is quite different from that of sparks which are produced from a solid or liquid substance directly at a burning surface.

We have two methods to obtain smoke. One is to cool a vaporized substance in order to obtain fine particles of the same substance i.e. the original material; this is a "physical smoke". The other method is to obtain fine particles, which are different from the original nature of the material, by some chemical reaction, e.g. burning etc; this is "chemical smoke".

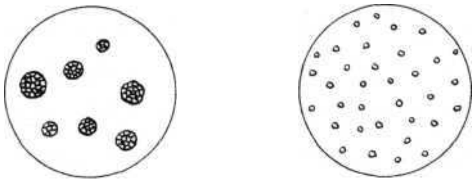
To produce the physical smoke, prepare a mixture of substances A and B in the vaporized state. A must have a higher boiling point than that of B. Cool the mixture, and at first A appears in liquid or solid state and B prevents A from cohesion by dispersion between the particles of A. Accordingly, A appears as very fine particles which hang in the air. This is the principle of creating physical smoke. For example, fog is a physical smoke. When the air(B), which contains a small amount of water vapour(A), is cooled, the vapour(A) becomes mist. This is fog. The smoke of dry ice is also physical smoke. Water vapour(A) and carbon dioxide gas(B) are mixed at their boundary and then cooled to create a white smoke, water mist.

To obtain the chemical smoke, produce substance A and B simultaneously by chemical reaction(burning), A becomes the smoke particles and B, which is in a gaseous state, prevents the particles of A from cohesion. In any case, the original burning materials must be in a gaseous state before the burning reaction.

11.2. Physical smoke

First we mention dye smoke, which is obtained by burning a mixture of some volatile dye and pyrogen. In this case the gas of the dye corresponds to the substance A and the gas which is produced by the pyrogen to B. The pyrogen must produce not only the heat necessary for vaporizing the dye, but also the gas which prevents the cohesion of the dye particles.

When we heat the dye alone in a crucible, the vapour does not look like smoke but only like thin vapour. This vapour is observed through a microscope as in Fig.53.1.



5 3.1 Particles from vapour

5 3.2 Particles from smoke

Fig.53. Sketches of dye particles

In this case one of the particles consists of many fine particles which cohere together. This is caused by a lack of the B-substance and it is not good as a smoke particle.

On the other hand, when we ignite a mixture of some pyrogen(e.g. milk sugar: potassium chlorate = 3:6) and the same dye contained in a canister with a small hole, we have a good smoke with quite a pretty colour which jets out of the hole. The particles are sketched through the microscope as Fig.53.2. In this case the burning gas of the pyrogen plays the role of the B-substance and completely prevents the cohesion of the dye particles.

The dye, A-substance, must be stable against heat and have a small heat of vaporization. Moreover, it must have a rather high condensation point, not less than 100°C, and it must condense before water vapour condenses because in many cases B-substances generally contain a high percentage of water vapour. If the water vapour condenses earlier than the dye vapour, the effect of the B-substance may be very much decreased. However too high a condensation point is not good for the vaporization.

The dyes which are ueed for firework materials are described in 13.4. The volume of the dye gas has a connection with the volume ratio of A to B, which may be the best at 5:5. Whether the dye is easily vaporized or not, is known by the temperature at which vaporization begins and its boiling point.

Concerning the nature of the pyrogen there are three main requirements: firstly the quantity of the heat generated must be large as far as possible, secondly it must be ignited at a relatively low temperature and also be able to continue burning at a relatively low temperature. Lastly it must produce as large a volume of gas as the B-substance.

The first condition is necessary to obtain a large volume of dense smoke from a small generator. Namely with a large quantity of heat we can increase the weight ratio of the dye to the pyrogen. For example, in a mixture with potassium chlorate and carbohydrate as the pyrogen, producing a quantity of heat of about 900 calories per gram, the dye content in the smoke composition can be increased to about 60%, but if we use celluloid, which produces only about 400 calories per gram in place of above mixture, the dye content is limited to about 30%.

The second condition corresponds with the fact that we must select a pyrogen which has a low ignition point as far as possible. A high ignition point damages the dye, but a very low ignition point is not good for storage because of the risk of spontaneous ignition caused by a rise in temperature in the atmosphere(Table 6).

Table 6. Characteristic values of representative pyrogens

	Ignition point (℃)	Produced gas		Heat evolved (cal /g)
		Water vapour (ℓ/kg)	Other gas (ℓ/kg)	
$KClO_3$(70%) + Milk sugar (30%)	223	225*	-	780
〃 + Sugar (30%)	205	216*	223	870
〃 + Dextrine (30%)	249	208*	-	770
〃 + Wheat flour (30%)	273	-	-	810
〃 + Potato starch (30%)	268	208*	-	720
Celluloid	248~268	?	357	400
Nitrocellulose	228	?	145	500

Note: (l)The values marked with (*) are calculated, the others are observed.
(2)The mark (-) denotes that no value is available.

Sugar gives the lowest ignition point and the starch the highest. In general it is said that sugar or milk sugar gives the most beautiful smoke colour. The reason may be due to their low ignition point. But practically the difference between the effects of above carbohydrate are not particularly marked.

With reference to the third condition, the volume of the gases generated by pyrogens are shown in Table 6. (For the volume of dye gases see 13.4). We have no accurate values for the volumes with celluloid and nitrocellulose, but the gases are likely to be CO, CO_2, NO_X, H_2O.

Another kind of physical smoke would be the smoke from sulphur(white) or from realgar(yellow), which is obtained by burning a mixture of one of these materials and potassium nitrate. In this case the sulphur or realgar belongs to the A-substance and the B-substance is mainly sulphur dioxide gas. The mechanism of the smoke generation is that a part of the sulphur or realgar in the composition burns, and another part is vaporized by the combustion heat to make a uniform mixture of gases, A + B. The gas jets out of the outlet of the canister, and is suddenly cooled to create fine particles of sulphur or realgar. (Realgar may produce arsenic trioxide, As_2O_3, which is poisonous, and is forbidden for indoor use.)

11.3. Chemical smoke

Black smoke. A carbon rich material produces this smoke when it burns in an oxygen negative state.

Potassium perchlorate($KClO_4$)	57%
Sulphur(S)	13"
Anthracene ($C_{14}H_{10}$)	30"

The composition is charged into a canister and closed with a lid which has an outlet hole. When it is ignited, a small red flame jets out of the hole and produces black smoke from the top. The chemical reaction may take place as follows:

$$5\ KClO_4 + 5\ S + 2\ C_{14}H_{10} \longrightarrow 5\ KCl + 5\ SO_2 + 10\ H_2O + 28C$$

The left changes to the right certainly in the following order:

(1) $\frac{5}{2}\ KClO_4 + 5\ S \rightarrow \frac{5}{2}\ KCl + 5\ SO_2 + 335\ kcal$,
(2) $2\ C_{14}H_{10}(solid) + 43\ kcal \rightarrow 2\ C_{14}H_{10}(vapour)$,
(3) $\frac{5}{2}\ KClO_4 + 20\ kcal \rightarrow \frac{5}{2}\ KCl(vapour) + 5\ O_2$,
(4) $2\ C_{14}H_{10}(vapour) + 5\ O_2 \rightarrow 10\ H_2O(vapour) + 28\ C(solid\ particles)$.

In the reaction (4) the gas already produced by the reactions (1),(2) and (3), i.e. SO_2, KCl etc., prevents the carbon particles(A-substance) from cohesion by intervention among the particles, acting as the B-substance. If the content of the anthracene in the composition is increased too much, the carbon particles cohere into long chain-like forms.

White smoke. The following composition is most popularly used:

Hexachloroethane(C_2Cl_6)	52%
Zinc dust(Zn)	21"
Zinc oxide(ZnO)	27"

This is charged into a container in the same way as the black smoke and ignited by the help of thermit; a small flame vigorously jets out of the hole, generating white smoke at the top of the flame. The reaction may be as follows:

$$3\ Zn + 3\ ZnO + 2\ C_2Cl_6 \longrightarrow 6\ ZnCl_2 + 3\ CO + C + ca.300\ kcal.$$

The reaction may occur in the following order:

(1) $2\ C_2Cl_6$(solid) + 30 kcal --> $2\ C_2Cl_6$ (vapour),
(2) $3\ ZnO$(solid) + $2\ C_2Cl_6$ (vapour) --> C(solid ash) + $3\ CO$ +
$3\ ZnCl_2$(vapour) + $3\ Cl_2$+ 47.7 kcal,
(3) $3\ Zn$(solid) + $3\ Cl_2$ --> $3\ ZnCl_2$ (vapour) + 189 kcal.

In practice a large part of the carbon produced by the reaction (2) remains in the container. A part of the metallic zinc is vaporized at 907°C and the reaction (3) occurs with a small flame. The vapours of the zinc chloride and carbon monoxide mix together uniformly and jet out into the air through the hole where they are cooled. In this case the zinc chloride condenses as A-substance and the carbon monoxide prevents the zinc chloride particles from cohesion acting as the B-substance. The zinc oxide particles are not so visible, but they easily absorb the moisture in the air and become small liquid particles which are visible as a dense white smoke.

Phosphorus or metalic sodium burn in the air generating dense white smoke. The principle of smoke production is the same as the above. The reaction may occur as follows:

$4\ P + 5\ O_2$ --> $2\ P_2O_5$ + ca.700 kcal,
$4\ Na + O_2$ --> $2\ Na_2O$ + ca. 200 kcal.

Bonfire smoke is produced under the same principle described for black and white smoke. But the difference is that in the case of the bonfire the particles of smoke only absorb the moisture little and do not always grow to a visible size. The smoke therefore sometimes looks almost violet in the distance. The moisture in the air has a great influence upon the growth of the particles of the A-substance when it is hygroscopic. For example, in dry weather a zinc chloride smoke looks thin. A composition which contain ammonium perchlorate, e.g. a colour flame composition or a rocket propellant, has smoke which is almost invisible in dry weather, but it looks quite dense in wet weather. This is due to HCl in the burning gas. A particle of water mist dissolves 400 times its volume of HCl gas at normal temperature. If there is some water mist in the air, the HCl gas dissolves in it to cause a sudden partial decrease in atmospheric pressure and the partial temperature may fall to some extent. This causes the condensation of water vapour in the saturated state to form another mist which absorbs the HCl gas again. This phenomenon spreads wider and wider in the damp air and creates a large volume of dense smoke. It is observed that the smoke is not created at the flame, but at a distance from the flame where the burnt gas and the air mix well together.

11.4. Colour changes in smoke

In the majority of coloured smokes, even with some physical smokes, colour change generally occurs during the generation of the smoke. A clear beautiful colour changes gradually to a whitish or yellowish one, or suddenly a flame appears and burns out the smoke particles to make them invisible.

The colour change in the smoke is caused by the following phenomena:

(1) Condensation of the A-substance. The A-substance in a vaporized state in the smoke composition container is cooled to a liquid or a solid state and remains in the container, and almost only the B-substance, water vapour, cabon oxide etc., jets out of the outlet. In this case the smoke looks white. This occurs, when the dye has a high boiling point, e.g. like phthalocyanine blue. To prevent this phenomenon, we must keep the space in the container at a high temperature so that condensation cannot take place. For this purpose a lagging material such as a paper tube is generally used inside the container.

(2) Filtration of the A-substance.The A-substance in the vapourized state is cooled to particles and filtered by the layer of cinder which is produced by the burning reaction, almost as if the smoke were filtered by filter paper. In this case the substance which comes out of the outlet is mainly water vapour, and the colour of the smoke is white. This occurs in smokes with a long burning time which accumulate a large quantity of ash in the container. To avoid this, a composition which produces a porous or shrinkable cinder is used to allow the smoke particles to pass through the layer of the cinder without being filtered. For example we use a mixture of celluloid and guanidine nitrate as the pyrogen similar to a technique used in insecticidal smokes. (But this type of pyrogen cannot be used for high boiling point dyes, because it does not generate enough heat.) We generally leave a space for the path of the smoke particles in the container (see R.Lancaster: Fireworks, principles and practice,p.187 (1972)J. In this case the container must be also well insulated against cooling in order to decrease the condensation of the generated vapour of the dye as far as possible.

(3) Decomposition of the A-substance.Too much pyrogen causes the decomposition of the A-substance through over-heating. Similarly when the vapour of the A-substance passes through red hot cinder, which sometimes occurs with certain kinds of composition, the A-substance decomposes. In

this case the smoke is cream coloured, and it is easy to separate this reaction from the others. This tends to occur with a dye which has poor heat resistance like para red. Oxidizers other than potassium chlorate provide another example, e.g. potassium nitrate, potassium perchlorate, ammonium perchlorate etc. In this case the A-substance is decomposed by the high ignition temperature, which also means a high burning temperature, Further more, the decomposition occurs also when the container is too large so that it easily accumulates a large amount of heat to raise the temperature of the inner space. In order to protect the dye from the heat and avoid decomposition, the heat generation of the pyrogen must be adjusted to a moderate value. In a composition which consists of three components, dye, carbohydrate and potassium chlorate, generation of heat is controlled by the potassium chlorate content: The carbohydrate has little affect and the quantity can be 15~35%, but too much produces an excess of water vapour which gives a whitish colour to the smoke. Using small smoke generators, each containing about 10 grams of composition and a fairly low combustion heat, the permitted maximum and minimum limits of the potassium chlorate content for various dyes is set out in Table 7.

Table 7. Limits of the potassium chlorate content in dye smoke compositions

	Maximum limit	Minimum limit	Effective range
Rhodamine B	32%	20%	12%
Oil red	36	33	3
Para red	20	13	7
Oil orange	30	20	10
Auramine	33	24	9
Phthalocyanine blue	35	30	5
Indigo pure	36	30	6

Note: The compositions consist of dye, potassium chlorate and milk sugar. The quantity of the milk sugar is 20%.

The maximum limit is the limit which causes decomposition of the A-substance and the minimum, the limit where smoke generation stops.

These limits will decrease to lower values than those if larger generators are used and in circumstances where the heat accumulation varies.

Flame production by the A-substance. When the A-substance is inflammable such as dyes, sulphur, realgar or carbon particles, the smoke sometimes disappears; it is burnt off near the outlet of the container by a flame which is generated by the action of the air. It generally happens because the gas jet has too high a temperature. This occurs especially when the gas stagnates near the outlet alongside some obstacle; attention must be paid to the fact that the smoke generator often produces a flame when it is laid on its side in a grass field. To avoid the flame the gas jet is cooled by sudden expansion at the outlet. For this purpose it is better to use a specially made nozzle like a rocket motor, but generally we use one or two small holes made in the container because of the low cost and simplicity; of course it must be more carefully modified. Many have tried to add sodium hydrogen carbonate to the composition, but this is not very effective.

12. Sound or noise

Fireworks are generally accompanied by various kinds of noise. This increases the effect of the firework display and produces feelings of tension.

The types of firework noise are as follows: (1) The noise caused by firing, which is not so great at a distance, but quite loud at the firing site. Workers at the site sometimes stuff their ears with cotton-wool etc. (2) Noise due to the explosion of a shell in the sky. This is sometimes loud and sometimes soft according to the content of the bursting charge. A large shell with a large amount of bursting charge, e.g. 40 to 50% of the total weight of a shell like a chrysanthemum(Warimono) gives a tremendously loud noise. (3) Thunder, report or signal maroon. This was formerly used as a signal at mid-day. At present this is a characteristic firework display noise. The kind of sound produced varies according to the configuration of the ground and the weather. In a glen it is quite loud and has an echo. On the contrary in a vast field it sounds as if something were pounded. On the shore of a lake near the Alps in Switzerland it sounds like a great clap of thunder with a considerably long echo which lasts for several seconds. For the amusement of children small bangers are quite attractive and full of spirit. (4) Hummer or Bees. This sound produces humming. (5) Whistle. A sharp burning sound like a whistle. This is produced by a whistle composition and not by mechanical action. The frequency of the sound is about 2600 times per second, and it is difficult to alter it.

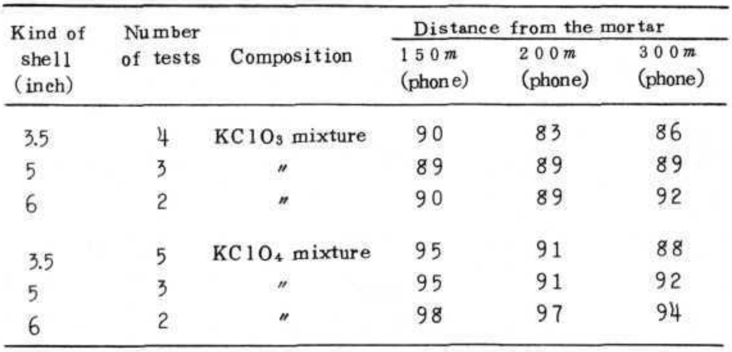
Table 8 shows data of the intensity of thunder reports placed on the ground and measured by an audiometer at a distance of 20 meters.

Table 8. Intensities of thunder reports on the ground

Kind of composition	Charge (gram)	Intensity (phon)	Kind of composition	Charge (gram)	Intensity (phone)
A	15	125	A	5	103
B	"	118	A	10	114
C	"	96	A	15	118
D	"	85	A	20	121
E	"	106	A	25	125
F	"	117	A	30	125
G	"	117			

A further group of data of reports in the air at Saitama-ken are set out below:

Table 9. Intensities of thunder reports in the sky



Kind of shell (inch)	Number of tests	Composition	Distance from the mortar		
			150m (phone)	200m (phone)	300m (phone)
3.5	4	$KClO_3$ mixture	90	83	86
5	3	〃	89	89	89
6	2	〃	90	89	92
3.5	5	$KClO_4$ mixture	95	91	88
5	3	〃	95	91	92
6	2	〃	98	97	94

When we compare the intensities of these reports with noise of others, we know that the noise from a jetpropelled aircraft 300 meter away from us has almost the same intensity. However the thunder reports have a much shorter duration than the noise of the aircraft which is more disturbing.

Part 4. Pyrotechnics

13. Materials

The materials which are used in this field may be classified from the standpoint of use and storage as follows:

- I. Material for compositions
  - Chemicals
    - Oxidizing agents
    - Colour producing agents
    - Chlor producing agents
    - Other chemicals
  - Fuels
  - Carbon powder(Charcoal, Soot etc.)
  - Metal powder
  - Black powder(Gunpowder)
  - Pyrotechnic pieces (Igniter, Fuse etc.)
  - Dye and Pigments for Smoke
- II. Material for construction
  - Binding agents
  - Paper or paper-made parts
  - Parts made of cotton, wool, hemp, silk etc.
  - Scobs, Cotton seeds etc.
  - Parts made of wood
  - Parts made of metal
  - Parts made of bamboo
- III. Material used as aids in production
  - Solvent, Lubricants etc.

The firework industry is quite small in scale, and generally it is necessary to use materials which are produced for other purpose or in some cases bi-products, which change according to the development of social conditions. Here is a description of the important materials, including the materials which are not always easy to obtain at present in Japan or in other contries, but which cannot be ignored. This is mainly for guidance in finding good substitute materials.

1.3.1. Oxidizing agents

(1) Potassium nitrate, KNO_3

Molecular weight: 101.11; colourless crystals of the rhombic system; specific gravity: 2.109(16°C); makes transition to trigonal system at 129°C;

melting point: 339°C; generates oxygen at 560°C and over, and a large amount of oxygen at about 600°C to remain as potassium nitrite:

$$2\ KNO_3 \rightarrow 2\ KNO_2 + O_2\ -58.5\ kcal.$$

It is not particularly soluble in cold water, but increases its solubility as the temperature increases, i.e. 13.3 grams at 0°C, 31.6 grams at 20°C, 169 grams at 80°C and 246 grams at 100°C, in 100 grams of water. The aqueous solution is almost neutral, a specimen on the market showed a pH of 6.2 (14°C) in a 10% aqueous solution. It is hardly hygroscopic, the fine grain potassium nitrate on the market absorbed only 0.03% of moisture at 10°C and 80% relative humidity over 50 days. Insoluble in alcohol.

Potassium nitrate powder tends to cake gradually. But recently we can have very fine powder made by a method using a surface activator, which prevents the powder grains from caking. In this form it is handly to use, but when we use it in solution or when it is consolidated in a composition by pressure only without a binding agent e.g. blackpowder for rocket propellants, it is better to use the former.

Potassium nitrate alone does not explode even with a strong impact. Potassium nitrate mixed with red phosphorus is sensitive to shock. This is explained thus: the impact of iron upon iron often causes it to ignite, but with iron and aluminium or iron and brass it is difficult to ignite. The mixture burns with a flame, but does not explode, when ignited.

Potassium nitrate is a strong oxidizer at high temperatures. But its mixture with an ordinary organic fuel, e.g. shellac or rosin, burns irregularly, producing potassium nitrite in a liquid state. In this case 1 gram of potassium nitrate produces about 0.158grams of effective oxygen. But when it is mixed with charcoal and sulphur or with magnesium it decomposes well and the amount of effective oxygen increases to the maximum value of 0.396 grams.

Potassium nitrate as the oxidizer in a composition cannot give a high temperature to produce a coloured flame, except in combination with magnesium. But it is used for making good sparks. Only with magnesium it can produce a high temperature flame of red, grass green or yellow.

A small amount of potassium nitrate mixed into the powder of some combustible substance, like carbon powder, can remain alight for hours. This principle is applied to the body-warmer stick.

Potassium nitrate in dust makes it quite inflammable and dangerous. The dust must be burnt up in small amounts or buried in the ground.

Potassium nitrate is not poisonous.

The history of potassium nitrate is as old as that of black powder. It is said to have been known since 660. In China it has been produced since ancient times. The old method of manufacturing was as follows: Mix scraps of vegetable and animal material with earth, and spread it on the ground in a hut to avoid exposure to the sun. Leave it for long time, pouring urine on it at times, and then white crystals of calcium nitrate will appear on it like frost. This is caused by the action of bacteria. Then extract it with water and add potassium carbonate(extract of wood ash) to form a precipitate of calcium carbonate, which is removed. Boil down the mother liquor, to obtain crystals of potassium nitrate. This process requires considerable time and space. It is also produced from the earth underground, when calcium nitate is created over a long period by the same principle.

It is thought that fireworks began with the history of potassium nitrate. It has been used for compositions which produce fire dust or sparks as well as a white smoke which has been called "Wabi"(Japanese fire). It could not produce coloured flames, but before the appearance of potassium chlorate, fireworkers made various efforts to create colour with it as far as possible.

<u>Manufacture</u>. Potassium chloride and sodium nitrate are dissolved in hot water and the solution is concentrated by heat until most of the sodium chloride crystallizes out of the mother liquor because of its low solubility:

$$\mathrm{KCl} + \mathrm{NaNO_3} \dashrightarrow \mathrm{KNO_3} + \overset{\uparrow}{\mathrm{NaCl}}.$$

When the crystals of the sodium chloride are removed we have potassium nitrate in the mother liquor which is left to precipitate foreign matter. The skimmed mother liquor is removed to a crystallizing vat and left for 10 to 15 hours to obtain crystals of crude potassium nitrate which are purified by recrystallization. The raw material, potassium chloride, is imported from France, West Germany, Spain, North America etc.

<u>Packing and volume for storage</u>. Kraft paper bag or corrugated cardboard case; 1.3 cubic meters per 1000 kg.

<u>Quality</u>. One analysis of the material on the market showed 0.01% moisture and 0.02% chloride(NaCl) as impurity.

<u>Types</u>. Two kinds are on the market ; one is in very fine particles which cake very little, and the other is rather coarse and it easily cakes.

<u>(2) Potassium chlorate, $KClO_3$</u>

Molecular weight: 122.55; colourless monoclinic crystals; specific gravity: 2.33; melting point: 368°C; dissociates at 400°C and over generating oxygen. This reaction proceeds as follows:

$$2\ KClO_3 \dashrightarrow 2\ KCl + 3\ O_2 + 21.3\ \text{kcal}.$$

The reaction proceeds violently over 500 C. Dr. Osada drew inferences from his experiments that this is caused by KC1 which is first produced and which promotes the reaction rate of the dissociation. It is said that the following reaction, producing chlorine gas, occurs over 600 C.

$$2\ KClO_3 \dashrightarrow K_2O + Cl_2 + \frac{5}{2}\ O_2 + 100.6\ \text{kcal}$$

This could be assumed from the appearance of a SrCl band in the spectrum of a red flame, but in practice we cannot smell the chlorine gas.

Potassium chlorate is not as soluble in water as potassium nitrate; i.e. 3.3 grams at 0°C, 7.3 grams at 20°C, 37.6 grams at 80°C and 56.3 grams at 100°C in 100 grams of water. The solution in water is almost neutral; a pH of 6.8(24°C) was obtained from a sample on the market. It absorbs moisture more than potassium nitrate; 0.07% moisture was measured after leaving it in 80% relative humidity at an average temperature of 10°C for 50 days. 0.83grams of potassium chlorate is soluble in 100 grams of alcohol. It is also soluble in alkali.

Potassium chlorate powder made by crushing the crystals, tend to cake more than potassium nitrate. But now we have a very fine powder which is made by using a surface activator as with potassium nitrate. This does not cake and is very useful, but in the match and other industries which use the chlorate in solution, the former is much preferred.

Potassium chlorate is a strong oxidizer at high temperatures. It burns in combination with fuels, shellac, rosin etc. producing a high temperature flame and white smoke of KCl-particles. The ratio F/O is generally 2:10 to give the highest flame temperature. In this case we smell no chlorine or hydrogen chloride gas. 1 gram of potassium chlorate produces 0.392 grams of oxygen. This amount is similar to that of potassium nitrate.

Potassium chlorate alone explodes with a strong impact but not when initiated by a No.6 detonator.

Potassium chlorate in composition gives a high temperature flame which is enough to excite molecules to emit coloured light. Moreover it contains chlorine atoms which are effective to deepen the colour of the flame; i.e. it can produce the colour creating molecules, SrCl, CuCl, BaCl etc. in the flame.

Potassium chlorate becomes quite sensitive in contact with red phosphorus and ignites very easily by friction. These properties are used in match. When it is mixed with sulphur or compounds of sulphur like realgar, antimony trisulphide etc., the sensitivity to shock or friction is highly increased. According to the late professor S.Yamamoto of Tokyo University, when a mixture of potassium chlorate and realgar was shaped into a small tablet in a hand press and left on a table, a little while later the tablet caused spontaneous ignition and burnt out. He tried the same tests several times and the results were the same. He concluded that it was caused by inner friction which occurs with the recovery of the stress produced by the press[s. Yamamoto: Studies in safety in firework manufacture I(1959)].

Potassium chlorate reacts with sulphuric acid to produce chlorine dioxide, ClO_2,, which is yellow heavy gas(about 2.3 times of the air. Its melting point is 10 C) and it is decomposed explosively by sunlight into chlorine and oxygen and ignites any combustible material in contact with it. Accordingly, when a drop of 60% or more cone, sulphuric acid is added to a mixture of potassium chlorate and sugar, it ignites instantaneously.

According to Dr. Osada, potassium chlorate reacts with hydrochloric acid to produce chlorine dioxide, ClO_2.,and chlorine, Cl_2, where the latter reduces the explosive tendency of the former. And in this case it is as dangerous as it is with sulphuric acid. Potassium chlorate does not react with nitric acid, but if there is potassium chloride in the potassium chlorate, it causes a violent reaction with the generation of chlorine dioxide. Accordingly, the amount of potassium chloride as an impurity is significant. Potassium chlorate reacts with phosphoric acid less violently than with hydrochloric acid, but it also generates chlorine dioxide. In view of this the red phosphorus which is used to toy pistol caps etc. must be thoroughly purified from phosphoric acid.

In a commercial sample of potassium chlorate Dr.Osada found 0.0002% of potassium chlorite and 0.0l6% potassium chloride with a gradual increase with exposure to sun light; in the sun during December the chlorite increased to 0.002% and in ultraviolet light after 500 hours the chloride increased to 0.16%. Potassium chlorite, $KClO_2$,, ignites or explodes in contact with sulphur or a sulphide and potassium chloride, KCl, as described above. Therefore the chlorite probably promotes the decomposition of $KClO_3$ when it is heated. Of course, the amount of potassium chlorite or chloride may be too small to cause a spontaneous explosion, but ultraviolet light does not improve the quality of potassium chlorate.

Potassium chlorate reacts with ammonium perchlorate and other ammonium salts in a wet state or in solution to produce ammonium chlorate, which forms colourless crystals and gradually decomposes even below 100°C [see (4)]. The late professor S.Yamamoto pointed out that some forms of asphalt contain ammonia, and such types of asphalt should be avoided for firework use. In view of this as asphalt or pitch is not recommended for use in combination with potassium chlorate [see R.Lancaster: Fireworks, principles and practice, p.30 and p.45(1972)].

Potassium chlorate begins to decompose at about 70°C by the catalytic action of metal oxides; manganese dioxide, copper oxides etc. produce oxygen. The reaction actively progresses over 100°C. $FeCl_3$, $CuCl_2$, Cr_2O_3 and $K_2Cr_2O_7$ also promote the reaction.

Potassium chlorate was found by Berthollet, a French chemist, in 1786. He tried to manufacture an explosive by replacing the potassium nitrate of black powder with potassium chlorate, mixing the materials in a water mill. He was witness to an explosion which caused the death of some people. Later potassium chlorate become an important material for matches. In 1827 John Walker invented a friction match which had a composition consisting of a mixture of potassium chlorate and antimony sulphide. It was ignited by rubbing it with a striker of glass powder paper. Since red phosphorus was discovered in 1844 a new method of friction ignition was developed by Pasch in Sweden and Bottger in Germany[H.Hartig: Zündwaren, p.43(1971)]. Potassium chlorate arrived in Japan perhaps about 10th year of Meiji(1877), with matches. When it was used for firework compositions, high temperature flames which gave epoch-making beautiful colours of fireworks, became easily obtainable. But it has been a matter of sincere regret that potassium chlorate has often caused explosive accidents. It would be ideal to reject this material from fireworks, but it is quite difficult even at present, because no other oxidizer can surpass potassium chlorate in burning speed, in ease of ignition or in noise making, using the smallest amount of composition. The match head composition cannot be made without it; it is also absolutely necessary for some dye smoke, small crackers and various kinds of toy caps. However these articles tend to become a source of explosion, and we must treat potassium chlorate compositions with respect and caution.

Manufacture. Potassium chlorate is manufactured at present by the three following processes.

(a) Electrolysis of potassium chloride. Potassium chloride solution in water containing a small amount of potassium bichromate is kept at pH = 6.5~6.8 by hydrochloric acid, electrolyzed by a graphite anode and a steel plate cathode and cooled. The potassium chlorate crystallizes out of the electrolyte. The reaction of the electrolysis is very complicated, but in a word one molecule of $KClO_3$ and three molecules of H_2 are produced from one molecule of KCl and three molecules of H_2O. The potassium bichromate protects medial products from reduction in order to help the creation of ClO_3^- ions.

(b) Milk of lime process. Quick or slaked lime is added to water to produce a suspension which is circulated in a chlorinating tower to absorb chlorine gas pumped through it. When the temperature rises to 6o~7O°c, the following reaction occurs to produce calcium chlorate:

$$3Ca(OH)_2 + 3Cl_2 \longrightarrow \frac{1}{2} Ca(ClO_3)_2 + \frac{5}{2} CaCl_2 + 3 H_2O$$

A small amount of calcium hypochlorite is produced but it is decomposed by adding sodium sulphide. The liquid, after the insoluble matter is removed, is heated to about 80°C adding cone, potassium chloride in 10% excess, and the following double decomposition occurs :

$$\frac{1}{2} Ca(ClO_3)_2 + KCl \longrightarrow KClO_3 + \frac{1}{2} CaCl_2$$

It is cooled to 20°C, and about 90% of potassium chlorate is obtained as crystals, which are recrystallized, dried in a revolving drier by hot air or by vacuum drier and crushed to powder[Handbook of potassium salt industry p.126(1958)].

(c) Electrolysis of sodium chloride. The electrolysis of sodium chloride solution in water produces sodium chlorate, which is made into potassium chlorate by adding potassium chloride:

$$NaClO_3 + KCl \longrightarrow KClO_3 + NaCl$$

The NaCl produced in the solution is collected and used again by re-cycling. Except for the preparation of the electrolyte in the beginning, the supplement of sodium chloride is almost unnecessary; only potassium chloride is required. The solution is electrolysed using graphite anodes and steel plate cathodes as in the case of (a) and adding a small amount of potassium bichromate. The pH value is adjusted to about 6.5~6.8, the bath voltage 3.1~3.5 and the temperature about 40~50°C. When potassium chloride is added to the electrolyte, the potassium chlorate crystallizes out. The crystals are recrystallized, dried, crushed to powder and sieved to requirements. This process has one more double decomposition step than (a), but needs less electric power than (a).

Packing and volume for storage. Wooden or cardboard cases. 1.3 m^3 per 1000 kg.

Quality. One analysis showed that a commercial sample contained 0.01%

moisture, 0.10% KCl. There are two kinds; one is crushed crystals which pass 150 mesh and the other is a fine powder which is treated by a surface activator to pass 200 mesh. As described above, the latter cakes little.

(3) Potassium perchlorate, $KClO_4$.

Molecular weight: 138.55, colourless rhombic crystals, specific gravity: 2.524 and this high value is worth noting. It makes a transition to the tetragonal system at about 300°C. The material on the market melts at about 570°C. At this temperature it decomposes generating oxygen:

$$KClO_4 \rightarrow KCl + 2\ O_4 + 0.68\ \text{kcal}$$

(In some books it is written as an endothermic reaction, but this is due to the difference of the heats of formation for $KClO_4$ and KCl used in the calculation; $KClO_4$ and KCl have almost the same heat of formation.) Potassium perchlorate is not very soluble in water, and the solubility does not differ too much with temperature; 1.01 grams at 0°C, 1.06 grams at 10°C, 1.68 grams at 20°C, 13.4 grams at 80°C, 22.3 grams at 100°C per 100 grams of water. This presents some trouble with the recrystallization of this material. A solution of the material on the market is almost neutral, e.g. a 1% solution in water showed a pH value of 7.3 at 23°C.

Potassium perchlorate is almost non-hygroscopic; but an experiment showed that it absorbed *6%* moisture in an atmosphere with 100% relative humidity at ordinary temperature during ten days. 0.008 grams of potassium perchlorate is soluble in 100 grams of ethanol, 0.105grams in 100 grams of methanol at ordinary temperature.

Crushed potassium perchlorate powder cakes gradually during storage, but it does not become as hard as potassium nitrate or chlorate.

Potassium perchlorate alone explodes with a strong impact, but on the detonator test no explosion occurs.

Potassium perchlorate is a strong oxidizer at high temperatures. It is the same as potassium chlorate in that it burns with a fuel such as rosin in a mixture of about 10:2 ratio, producing a high temperature flame and a white smoke of KCl-particles. With shellac it burns less easily. It is used for coloured flame compositions, but the burning rate is not so great as it is with potassium chlorate compositions. On burning it does not smell of chlorine gas. The available oxygen per 1 gram of potassium perchlorate amounts to 0.462 grams, which is 1.18 times more than that of potassium chlorate.

A spectral analysis showed, that the colour producing mechanism of flames due to potassium perchlorate is entirely the same as those of potassium chlorate. Therefore replacing chlorate by perchlorate in the composition causes no colour change in the flame.

Potassium perchlorate becomes sensitive in contact with red phosphorus; the mixture detonates with a loud noise by an impact between metal pieces of aluminium or bronze. When the mixture is ignited, it detonates instantaneously. However match or toy pistol caps cannot be made from compositions which contain potassium perchlorate in place of chlorate, because the ignition is uncertain. When potassium perchlorate is mixed with realgar, antimony trisulphide, sulphur etc. it also becomes sensitive; realgar particularly increases the sensitivity to friction. But the degree of sensitivity is not as large as it is with potassium chlorate.

When potassium perchlorate is added to hydrochloric acid or nitric acid, it causes no reaction. With cone, sulphuric acid it smells only slightly of ClO_2; this is caused by some impurity such as KCl. The mixture of potassium perchlorate and sulphide cannot be immediately ignited by adding conc. sulphuric acid; this is a principal difference from the potassium chlorate mixture[S.Yamamoto: Studies in safety in firework manufacture, I, p.24(1959)].

According to Dr.Oeada the substances ,KCl, $FeCl_3$, $CuCl_2$,, Cr_2O_3, $K_2Cr_2O_7$, LiCl etc., promote the decomposition of potassium perchlorate as in the case of chlorate. In particular Cr_2O_3 is very effective at 410°C, and LiCl at 430°C, but these temperatures are a little higher than they would be with chlorate[J. Industrial Exp. Society, Japan, p.479, vol.28, No.6(1967)].

Potassium perchlorate is far less likely to decompose in ultraviolet light than the chlorate, i.e. 1/10 the amount of the latter.

Potassium perchlorate was perhaps produced industrially at the time when carlit was invented by Dr.Carlson in Sweden. At first ammonium perchlorate was used for carlit as the oxidizer, but it caused trouble by producing HCl gas, which was generated during the explosion; the ammonium perchlorate has been replaced partially by potassium perchlorate which does not produce HCl gas.

Manufacture. At first sodium chlorate is prepared by the electrolysis of industrial salt or the milk of lime process described in (2). The sodium chlorate is further electrolyzed to produce sodium perchlorate, and when potassium chloride is added to cause double decomposition, crude potassium perchlorate is obtained. This is recrystallized and crushed to powder. It is impossible to obtain potassium perchlorate by the direct electrolysis of potassium chlorate, because of the low solubility of potassium perchlorate in water.

The electrolysis of sodium chlorate is an oxidizing reaction:

$$NaClO_3 + H_2O \dashrightarrow NaClO_4 + H_2$$

For the industrial process a platinum anode and steel plate cathode are used, and a small amount of potassium bichromate is added to the electrolyte, The electric current efficiency is good when the concentration of the sodium chlorate is high, but it suddenly decreases as the concentration falls. The double decomposition which produces potassium perchlorate is as follows:

$$NaClO_4 + KCl \longrightarrow KClO_4 + NaCl$$

In this case the potassium perchlorate crystallizes out as fine crystals because of its low solubility in water.

Packing and volume for storage. It is packed in a tin or corrugated cardboard case; 1.20 m^3 per 1000 kg of potassium perchlorate. The volume per unit weight is rather small because of the high specific gravity.

Quality. One analysis of a commercial sample showed 0.20% chloride and chlorate, 0.009% Pb, 0.009% Fe, 0.005% total nitrogen, 0.16% moisture, 99.30% pure content and very little other impurity. For firework use the amount of chloride and chlorate must be less than this.

Ammonium perchlorate, NH_4ClO_4

Molecular weight: 117.49, colourless rhombic crystals, specific gravity: 1.95 and it is the least used of all the oxidizers in the firework industry. It has a transition point to the tetragonal system at about 240°C. It is said that pure ammonium perchlorate sublimes without melting when it is slowly heated in the air, but when we heat the normal commercial material in a porcelain crucible with an electric heater, it decomposes violently at 26O~36O°C. A sample which was recrystallized four times decomposed at 386°C. From this fact we know that ammonium perchlorate decomposes easily due to the action of some impurities, Cr etc.

Ammonium perchlorate has been studied quite often in recent times because it is used for solid rocket fuel[H.Osada and E.Sakamoto: Thermal decomposition of ammonium perchlorate, J.Exp.Soc.,Japan,24 No.5, p.236 (1963); H.Osada and S.Kakinouchi: Initiation of the ignition of solid composite propellant, 26, No.4, p.200(1965)]. It is thought that there are two kinds of decomposition; the first occurs below 300°C, and the other over 300°C. The reactions seem to be different from each other. They are very complicated and the products are detected as N_2O, N_2, NO, NO_2, NH_3, $HClO_4$, HNO_3, HCl, HNO_2, O_2.

Ammonium perchlorate dissolves in water in large amounts even at room temperature; 29,4 grams at 0°C, 33.2 grams at 10°C, 37.2 grams at 20°C, 65.6 grams at 80°C, 77.3 grams at 100°C per 100 grams of water.

Commercial ammonium perchlorate is slightly yellowish. Its solution in water is almost neutral; the pH value was 6.8 at 24°C in a 10% solution. It absorbs moisture more than potassium nitrate and chlorate; 0.19% water was detected after a 50 day test at an average temperature of 10°C and about 80% relative humidity. It is slightly soluble in alcohol; 2 grams per 100 grams of ethanol; soluble in acetone and insoluble in ether.

Ammonium perchlorate powder tends to cake gradually, but it does not as quickly as potassium nitrate or chlorate.

Ammonium perchlorate is a strong oxidizer at high temperatures. It burns with shellac, rosin etc. in the ratio of about 10:2 producing a high temperature flame. The burning products are almost only gaseous substances which do not produce smoke in the dry air but they do smell of hydrogen chloride gas. However in wet air a white dense smoke appears due to the action of the hydrogen chloride gas. The available oxygen per 1 gram of ammonium perchlorate is 0.342 grams, which is 0.74 times as much as that of potassium perchlorate, being based on the reaction:

$$2\ NH_4ClO_4 \dashrightarrow N_2 + 3\ H_2O + 2\ HCl + 2.5\ O_2$$

Ammonium perchlorate alone explodes with a strong impact, but it showed no tendency to explode when initiated by a No.6 detonator.

As described above, compositions which contain ammonium perchlorate as the oxidizer produce a high temperature flame which is enough to excite colour producing molecules or atoms in order to give a good flame colour. Moreover the flame contains HCl gas which reduces the molecules to SrCl, BaCl, CuCl etc. to deepen the colour, or it reduces the solid metal oxide particles in the flame to the chloride, e.g. MgO(solid) to MgCl(gas), to increase the transparency of the flame and to give a bright colour.

Ammonium perchlorate reacts with magnesium in the presence of moisture or water to produce ammonia gas and magnesium perchlorate:

$$2\ NH_4ClO_4. + Mg \dashrightarrow 2\ NH_3 + Mg(ClO_4)_2$$

The reaction can be detected by the smell of ammonia. In this case a large amount of heat is generated, often enough to cause a fire due to the accumulation of heat. But under perfectly dry conditions this reaction does not occur. This reaction can be suppressed by $K_2Cr_2O_7$ even in the presence of moisture or water. Ammonium perchlorate reacts also with copper.

$$2\ NH_4ClO_4 + Cu \dashrightarrow 2\ NH_3 + Cu(ClO_4)_2$$

When ammonium perchlorate is mixed with red phosphorus it becomes very sensitive to shock, but not so much to friction. With realgar, sulphur, antimony trisulphide etc. it also becomes sensitive almost like the above. The degree of shock sensitivity of ammonium perchlorate due to such substances is almost the same as that of potassium chlorate, but higher than that of potassium perchlorate. The low friction sensitivity of ammonium perchlorate due to these substances is one of its attractive features in comparison with potassium chlorate and perchlorate [T.Shimizu: Sensitivity tests on firework compositions, J.Exp.Soc.Japan,24, No.6, p.343 (1963)].

Nitric acid and hydrochloric acid do not react with ammonium perchlorate, but when cone, sulphuric acid is added to it, it generates a white smoke which smells slightly of ClO_2.

Ammonium perchlorate causes double decomposition with potassium nitrate, but no double decomposition with sodium nitrate.

$$NH_4ClO_4, + KNO_3 \dashrightarrow KClO_4 + NH_4NO_3$$

The ammonium nitrate which is produced by above reaction is quite hygroscopic. Therefore if a composition which contains ammonium perchlorate comes in contact with another composition which contains potassium nitrate such as black powder, a wet layer of ammonium nitrate occurs between the two compositions and causes misfire. With barium nitrate this double decomposition does not occur, and a mixture of barium nitrate and ammonium perchlorate is allowed in the preparation of firework compositions.

Ammonium perchlorate and potassium chlorate cause a double decomposition to produce ammonium chlorate and potassium perchlorate when they are mixed in wet state:

$$NH_4ClO_4 + KClO_3 \dashrightarrow NH_4ClO_3 + \overset{\uparrow}{KClO_4}$$

Ammonium chlorate decomposes gradually at room temperature. Needless to say compositions which contain ammonium perchlorate and potassium chlorate must be avoided. An experiment for producing ammonium chlorate by above reaction can be carried out as follows: Add 35 grams of potassium chlorate, $KClO_3$, to 100 ml. of water and dissolve it with heat. Add 36 grams of ammonium perchlorate, NH_4ClO_4, to the solution and stir it well when a large quantity of white crystals will appear; these are almost all potassium perchlorate. Leave it to cool to room temperature. Remove the crystals by filtration. The remaining liquid is mainly ammonium chlorate. Evaporate the mother liquor to about 30 ml. on a water bath. Cool it to room temperature and the ammonium chlorate will crystallize out as a crude product. Remove the crystals from the mother liquor. Dry the crystals leaving them at room temperature. The amount of ammonium chlorate thus obtained is about 19 grams. The yield is about 55~63% of the theoretical value.

This substance, NH_4ClO_3, decomposes gradually, generating a yellow-brown gas which smells strongly of chlorine. The degree of decomposition is about 30% of the original amount at an average temperature of about 26°C over 35 days. A quantity of ammonium chlorate thus prepared was stored in a glass bottle which had a loose filling rubber stopper and left at room temperature during the summer; in 48 hours it decomposed explosively, breaking the bottle.

Ammonium chlorate, NH_4ClO_3, alone explodes on strong impact, but it is not so sensitive to shock and friction in the absence of other combustible substances. A mixture of ammonium chlorate and shellac in a ratio 10:2 burns with a rate of 1.2~1.3 mm per second, producing a slight yellowish flame. This burning rate resembles that of potassium chlorate composition.

Ammonium perchlorate is decomposed by ultraviolet radiation, but not so much as potassium chlorate; to be precise 1/10 as much as the latter. According to Dr.Osada, ammonium perchlorate which is affected by ultraviolet radiation decreases its decomposition temperature to 210°C in 1000 hours of application. As in the case of potassium perchlorate, $FeCl_3$, $CuCl_2$, Cr_2O_3 , $K_2Cr_2O_7$ promote the decomposition of ammonium perchlorate, and decrease the decomposition temperature to 300°C, when it decomposes entirely.

Manufacture. The process is the same as that of potassium perchlorate except that ammonium chloride is used in place of potassium chloride for the double decomposition. As described above, the manufacturing process for perchlorate was developed in Sweden, which is blessed with electric power. In Japan the process was introduced in 1918 by S.Asano to produce it as the material of carlit and a factory was established at Minami-Senju in Tokyo. The factory was destroyed by the earthquake of 1923, and the new factory was established at Shibukawa in 1934.

Packing and volume for storage. A corrugated cardboard case which contains 25 kg of ammonium perchlorate. 1.47 m^3 per 1000 kg. This is the most bulky of all the oxidizers.

Quality. The moisture content is about 0.01%. 90% of it passes 80 mesh and 36% passes 270 mesh. Chromate can be detected in the mother liquor of the recrystallization process. An example of the specification is as follows: 99% minimum purity, 0.1% moisture, 80% passes 250 mesh[Handbook of Industrial Explosives, (Kyoritsu Sha) p.223(1966)].

13.2. Colour producing agents which serve also as an oxidizing agent

These materials are the nitrates or chlorates of strontium, sodium, barium etc.

(5) Strontium nitrate,

Molecular weight: 211.63, colourless tesseral crystals, specific gravity: 2.986 which is 1.4 times larger than that of potassium nitrate, and 1.2 times larger than that of potassium perchlorate. Thus the large density is one of the remarkable nature of strontium nitrate. It melts at 570°C, and decomposes on heating as follows:

$$Sr(NO_3)_2 \rightarrow Sr(NO_2)_2 + O_2$$

and then

$$Sr(NO_2)_2 \rightarrow SrO + NO + NO_2$$

Strontium nitrate is soluble in water; 40.1 grams at 0°C, 89.4 grams at 35°C, 93.4 grams at 60°C, 96.9 grams at 80°C, 104.9 grams at 105°C in 100 grams of water, i.e. a small amount of strontium nitrate dissolves in water even at room temperature, but the solubility is not too changeable with a rise in temperature and at about 100°C it is less than that of potassium nitrate. It is almost insoluble in ethanol or acetone.

A tetra-hydrate, $Sr(NO_3)_2.4H_2O$ also exists; it can be obtained by recrystallization from a solution in water but of course it becomes anhydrous over 100°C.

The solution of strontium nitrate in water is almost neutral; a pH value of 10 grams dissolved in 100 grams water was 7.0 at 25°C. The anhydrous salt is somewhat hygroscopic like ammonium perchlorate. A well dried sample passing 80 mesh absorbed 1.61% of moisture at 84% relative humidity. Powdered strontium nitrate gradually cakes, but not to the same extent as potassium nitrate or chlorate. When the caked strontium nitrate is heated to 200~300°C, it becomes a dry powder again.

Strontium nitrate alone does not explode even with a strong impact.

Strontium nitrate burns in combination with shellac in the ratio 10:2 producing a red flame, but it produces a large amount of solid ash. When the composition is charged in a paper tube and burnt, the ash remains like a stick in the burning position and disturbs the flame to the point of extinguishing it. In such circumstances the burning does not cease, but progresses without flame. The ash consists mainly of strontium nitrite, $Sr(NO_2)_2$.

When a mixture of strontium nitrate and magnesium in a weight ratio of 6:4 burns, the strontium nitrate decomposes perfectly owing to the high temperature of the flame and produces little ash. This is quite different from above. The decomposition may be as follows:

$$Sr(NO_3)_2 \dashrightarrow SrO + N_2 + 2.5\ O_2 - 92.15\ \text{kcal}$$

The oxygen produced by 1 gram of strontium nitrate amounts to 0.076 grams for the low temperature flame, but 0.189grams in the high temperature flame. Accordingly strontium nitrate is used only as a colour producing agent for low temperature flame compositions and as both colour producing agent and oxidizer, for high temperature flame compositions.

Strontium nitrate is an important colour producing agent for red flames. Some often recommend lithium nitrate for red flames, but the light from the flame is too weak for practical use as a replacement for strontium nitrate.

Strontium nitrate mixed with red phosphorus ignites from an impact between iron and iron or iron and brass, but it does not easily detonate. It is difficult to ignite it by impact with brass and aluminium.

A mixture of strontium nitrate and aluminium often degenerates producing ammonia and NO_x gas. This tendency is common with other nitrates except ammonium nitrate[see (31)]. Dust which contains strontium nitrate is inflammable, and the same precautions must be taken as they are with other oxidizers.

Manufacture. Strontium carbonate is prepared first[see(9)] and then nitric acid is added to it to produce strontium nitrate. Strontium and barium are similar chemically so the industrial purification of strontium nitrate is a difficult problem. At present there are three ways to separate the nitrates of strontium and barium[Ж. Прикл. Хим. 44(10) 2157~2161(71)]:

(a) By crystallization from strontium nitrate solution. In this case the barium is concentrated more in the crystals than in the liquor. Therefore the liquor is of greater importance.

(b) By adding sulphuric acid drop by drop to strontium nitrate solution in water to precipitate part of the strontium nitrate as strontium sulphate, in this case the barium impurity precipitates together with the strontium sulphate. The mother liquor gradually becomes higher in purity.

(c) The same process with (b), where only the difference is to separate as chromate instead of sulphate.

The quality in process (a) is not so good, but (b) can give an excellent value of Ba in strontium nitrate amounting less than 0.0002%. For (c) we have no exact value.

Packing and volume for storage. 20 kg in a tin or kraft paper bag, 1.00 m^3 per 1000 kg.

Quality. This material in commerce passes 80 mesh. Apparently there are variations in quality, especially in the Ba content which disturbs the red colour of a flame; the smaller it is, the better. It is not very often used for fireworks because of its hygroscopic nature, especially when good ignition is required. But it gives a very bright red to a flame, and could become more useful, if a greater resistance to water could be developed. At present it is used mainly for distress signals for roads, trains and at sea.

(6) Sodium nitrate, $NaNO_3$

Molecular weight: 84.99, colourless trigonal crystals, specific gravity; 2.257, melts at 308°C. It decomposes over 380°C generating oxygen to sodium nitrite:

$$2\ NaNO_3 \longrightarrow 2\ NaNO_2 + O_2$$

Sodium nitrate is soluble in water; 73 grams at 0°C, 80.8 grams at 10°C, 87.6 grams at 20°C, 148 grams at 80°C, 180 grams at 100°C in 100 grams of water. The solubility is 1.8 times larger than that of strontium nitrate. A sample on the market showed a pH value of 8.6 at 18°C. Its hygroscopic nature is not so large as some would suggest. A test showed that it absorbed 0.92% of moisture at 84% relative humidity over 10 days, which is less than that of strontium nitrate. It is slightly soluble in alcohol, very little in acetone.

Sodium nitrate powder is produced by crushing the crystals, it also cakes gradually but does not become as hard as potassium nitrate or chlorate.

Sodium nitrate alone does not explode from a strong impact. It burns well in combination with shellac in the weight ratio 10:2, producing transparent liquid drops at the burning surface which consist of mainly sodium nitrite. It burns in combination with magnesium in the weight ratio 6:4, when it is perfectly decomposed producing neither drops nor cinder. The oxygen available in the former case amounts 0.188grams and in the latter 0.424grams per 1 gram of sodium nitrate. The reaction of the latter may be

$$2\ NaNO_3 \longrightarrow N_2 + 2NaO + 2\ O_2$$

Sodium nitrate gives an intense yellow light, and latterly has been used for illumination. Especially in combination with magnesium it burns well without producing either cinder or sparks in wide range of the F/0 ratios; i.e. the ratio can vary from 3:7 to 8:2. This is a superior characteristic, which is not available for any other composition.

A mixture of sodium nitrate and red phosphorus is more sensitive to mechanical actions than that of potassium nitrate and red phosphorus. The former ignites or explodes from an impact of iron and iron. In the case of iron and brass it does not explode, but only burns; with brass and aluminium it is difficult to ignite.

A mixture of sodium nitrate and dust is very inflammable, and precaution must be taken to avoid fire.

Sodium nitrate occurs in nature. But this material is soluble in water, and is only obtained in desert regions where rainfall is low; in the desert spreading over the east coast of the Pacific Ocean in South America, 3hile, Peru and Bolivia. The layer, rich in sodium covering the earth, is called Caliche. This is a white mass which contains I5~8O% sodium nitrate, less than 60% sodium chloride, less than 10% sodium sulphate, other nitrates, calcium chloride, aluminium sulphate, calcium sulphate, magnesium sulphate, iodates etc. The product is called Chile Saltpeter.

Manufacture. In former times sodium nitrate was produced by the recrystallization of Chile Saltpeter. After the material was dissolved in hot water, the sodium nitrate was allowed to crystallize out; this contained many impurities and was hygroscopic. Next a saturated solution of this material in water was prepared and a quantity of nitric acid was added to it to allow the sodium nitrate to recrystallize out of the liquor as fine crystals; the nitric acid was removed by heating.

Sodium nitrate is now manufactured from nitric acid produced by the oxidation of ammonia gas. It is then neutralized by adding sodium carbonate.

Quality and use. The pure product is not as hygroscopic as described above. The main use for this material is for illumination in combination with magnesium.

(7) Barium nitrate, $Ba(NO_3)_2$

Molecular weight: 26l.35, colourless tesseral crystals, specific gravity: 3.24, which is 1.1 times larger than that of strontium nitrate, 1.5 times that of potassium nitrate and 1.3 times that of potassium perchlorate. The melting point is said to be 592°C, but a commercial sample salted at 552°C. When it is heated above its melting point, it decomposes as

$$Ba(NO_3)_2 \rightarrow Ba(NO_2)_2 + O_2$$

and

$$Ba(NO_2)_2 \longrightarrow BaO + NO + NO_2$$

Barium nitrate is soluble in water; 5.0 grams at 0°C, 6.7 grams at 10°C, 9.0 grams at 20°C, 27.2 grams at 80°C, 34.4 grams at 100°C in 100 grams of water. A *5%* solution of this material in water showed a pH value of 5.8. It is hardly hygroscopic and is similar to potassium chlorate; it absorbs 0.02% moisture in an average humidity of 84% and an average temperature of 25°C over 10 days. It is insoluble in ethanol, but slightly soluble in methanol; 0.07 grams at 0°C, 0.05 grams at 30°C in 100 grams of methanol.

Powdered barium nitrate cakes to form a very hard mass almost like stone and thus causes considerable inconvenience.

Barium nitrate alone cannot be ignited or caused explode even by a strong impact. A mixture of barium nitrate and shellac in the weight ratio of 10:2 burns well producing a slight green coloured flame. The colour may be due to the BaOH molecule in the spectrum; this green light is too weak to be used for fireworks. When the mixture is loaded into a paper tube and burnt, the flame is disturbed by a cinder which consists mainly of barium nitrite. However a mixture of barium nitrate and magnesium in the weight ratio 6:4 burns with whitish blue flame producing almost no cinder because of the perfect decomposition of the barium nitrate due to the high temperature of the flame.

$$2\ Ba(NO_3)_2 \longrightarrow 2\ BaO + N_2 + 5\ O_2$$

The oxygen produced in the former case amounts to 0.061 grams and in the latter case to 0.184 grams per gram of barium nitrate.

Barium nitrate is an important colour producing agent for green and white flames. For example, we obtain an intensive white light from a mixture of 65% barium nitrate and 35% magnesium which contains no chlorine. On the other hand, when 20%(additional) PVC is added to the mixture, it gives a brilliant green light due to the action of the chlorine.

Barium nitrate becomes a little sensitive when it is added to red phosphorus; it explodes on impact between iron and iron, it ignites with iron and brass, but does not easily ignite with brass and aluminium. Nevertheless, there are some occasions when it explodes; this means that barium nitrate is sometimes more vivacious than potassium nitrate or sodium nitrate when it decomposes. R.Lancaster gives a noise composition which uses barium nitrate as the oxidizer; 68% barium nitrate, 23% pyro aluminium and 9% sulphur[Fireworks, Principles and Practice, p.120(1972)]. This kind of composition utilizes the vivacious nature of barium nitrate.

Manufacture. Barite which mainly consists of $BaSO_4$. is reduced by carbon to barium sulphide and dissolved in nitric acid.

$$BaSO_4 + 4\ C \longrightarrow BaS + 4\ CO \qquad (1)$$
$$BaS + 2\ HNO_3 \longrightarrow Ba(NO_3)_2 + H_2S \qquad (2)$$

First the powdered barite is mixed with carbon powder. The mixture is heated in a crucible and the reaction(l) occurs, when barium sulphide is obtained as a reddish grey mass. The mass is crushed and added in small quantities to nitric acid when it dissolves. The solution is boiled and filtered. The filtrate is evaporated and the barium nitrate crystallizes out. The crystals are washed with water and dried.

Packing and volume for storage. 50 kg in a wooden case or 30 kg in a paper bag, 0.8 m^3 per 1000 kg.

Quality. Barium nitrate in commerce is generally in a caked state like a stone, but the moisture content is unexpectedly small, about 0.07%. When the caked mass is crushed and heated to 200~300°C it again becomes a fine powder. It passes 85 mesh.

(8) Barium chlorate, $Ba(ClO_3)_2.H_2O$

Molecular weight: 322.26, colourless, monoclinic crystals, specific gravity: 3.18, it becomes anhydrous at 120°C and melts at 414°C. When it is heated above the melting point, it decomposes, generating oxygen as follows:

$$Ba(ClO_3)_2 \longrightarrow BaCl_2 + 3\ O_2$$

Barium chlorate is soluble in water; 20.3 grams at 0°C, 33.8 grams at 20°C, 84.8 grams at 80°C, 105 grams at 100°C per 100 grams of water; its solubility in water is greater than that of potassium chlorate. It dissolves very little in either ethanol or acetone and is not hygroscopic. The powder cakes in much the same way as potassium chlorate.

Barium chlorate alone explodes on strong impact, but no reaction could be initiated with a No.6 detonator.

Barium chlorate burns well in combination with shellac in a weight ratio 10:2,producing a beautiful green coloured flame. The spectrum consists of three clear bands of BaCl molecules, thus it has the ability to produce green colour even in low temperature class flames (without magnesium as fuel), and consequently it is regarded as the most superior green colour producing agent. However more care must be taken when handling the material than with potassium chlorate. It is said that compositions which contain barium chlorate are more sensitive than compositions which contain potassium chlorate and sometimes cause spontaneous combustion in the sun.

The oxygen obtained on burning amounts 0.298grams per 1 gram of barium chlorate.

Acids, sulphur, realgar, red phosphorus and ammonium salts must not be mixed with barium chlorate.

Manufacture. It is obtained by passing chlorine gas into a solution of barium hydroxide in hot water.

$$6\ Ba(OH)_2 + 6\ Cl_2 \text{ --> } Ba(ClO_3)_2 + 5\ BaCl_2 + 6\ H_2O$$

Packing and volume for storage. 30 kg in a tin case, 1.00 m^3 per 1000 kg.

13.3. Colour producing agents

Colour producing agents give colour to flames by producing colouring atoms or molecules in the flame. These atoms or molecules are produced under correct conditions for chemical reaction in the flame, and not by vaporized materials in an original form in the composition. For example, a green flame is not obtained by adding barium chloride, $BaCl_2$, to the composition, but by the creation of BaCl molecules in the flame by some chemical reactions in presence of a barium salt and HC1 molecules.

As colour producing agents metal salts are generally used, but only rarely would metal powder be used e.g. copper powder for blue flames. The metal salts consist of a metallic ion(cation) and non-metallic ion(anion), but the colour donor is the cation, e.g. strontium gives red, sodium yellow, barium green and copper blue. The anion has almost no influence upon the colour. For example, $Sr(NO_3)_2$, $SrCO_3$, SrC_2O_4, $SrCl_2$ etc. show almost the same effect for colouring. However the anions do have an influence upon the flame temperature; generally NO_3^- increases the flame temperature, and accordingly increases the brilliancy of the light, but other anions decrease both the flame temperature and the brilliancy. The flame temperature is concerned with the excitation of the colour producing melecules; in general the higher the temperature, the greater the number of excited molecules, and the anions exercise an indirect influence on the colour of the flame through the temperature.

Therefore the amount of colour producing agent which is added to a composition, except nitrates, should be as small as possible unless the colouring effect decreases; the limit may be 10~20% weight of the composition.

Red colour producing agents

(9) Strontium carbonate, $SrCO_3$

Molecular weight: 147.63; colourless rhombic crystals or fine powder; specific gravity: 3.70; makes a transition at 920~927°C to the hexagonal system; melts at 1497°C at 60 at.

Strontium carbonate is hardly hygroscopic; it absorbed only 0.65% moisture in 10 days at an average temperature of 25°C and an average humidity of 84%. Strontium carbonate changes into strontium oxide when heated generating carbon dioxide gas. The oxide is a white amorphous powder which changes into strontium hydroxide:

$$SrCO_3 \dashrightarrow SrO + CO_2$$
$$SrO + H_2O \dashrightarrow Sr(OH)_2 + 14.7 \text{ kcal}$$

When a red star composition is burnt, the ash often becomes gradually wet; this is caused by the hygroscopic nature of this hydroxide, $Sr(OH)_2$.

Strontium carbonate can be mixed with chlorate.

Strontium carbonate is almost insoluble in water; 0.001 gram per 100 grams of water at 24°C. The solution is alkaline and the pH value was 8.9 at 35°C. If a composition consists mainly of aluminium and nitrates including strontium carbonate, such an alkaline mixture has a risk of spontaneous decomposition in wet state. Strontium carbonate dissolves in water as the bicarbonate, if the water contains CO_2.

Strontium carbonate in a composition produces carbon dioxide gas when it burns rather than oxygen. Too much of this material in a composition decreases the burning rate and brilliancy of the flame; a 10~15% content may be the best.

Manufacture. Strontium carbonate occurs naturally as a strontium ore, but the production is not large. Celestine(consisting mainly of $SrSO_4$ and containing Ca and Ba) is heated with sodium carbonate to form a melt, and the product is then washed with water to remove the strontium sulphate. This method however cannot remove the sodium impurity which disturbs the red colour of the flame. Strontium carbonate of high purity is obtained when ammonium carbonate is added to strontium nitrate solution to precipitate it. If Ca or Ba is present in the solution, it precipitates at the same time and the separation from the strontium carbonate is difficult.

Packing and volume for storage. A paper bag or a corrugated cardboard case etc.; 1.30 m^3 per 1000 kg. The heaviness is a special character of this material.

Quality. One analysis showed 98.45% purity, 0.81% alkaline carbonate, 0.003% iron. Material of good quality is a white, very fine powder; the reddish powder contains iron. We can test its quality as a colour producing agent from the flame colour by burning a mixture of well purified ammonium perchlorate and shellac in the weight ratio of 10:2, to which a 10% sample of the strontium carbonate is added. If the flame is deep red, the quality is good. A Japanese industrial standard, JISK 8623, requires first class material to have at least 95% of purity, less than 0.75% of alkali, less than 1.0% of calcium, less than 0.005% of iron.

(10) Strontium oxalate,

Molecular weight: 193.66; colourless crystalline powder; specific gravity: 2.08; almost insoluble in water, i.e. 0.0046 grams at 18°C, 5 grams at 100°C per 100 grams of water; almost insoluble in alcohol; slightly soluble in water which contains an ammonium salt. It contains one mol of water of crystallization per mol, but loses it at 150°C.

Strontium oxalate decomposes on heating as follows:

$$SrC_2O_4 \longrightarrow SrO + CO_2 + CO$$

In fact the product has a reducing action due to CO. Accordingly, it reduces the solid particles of MgO to magnesium gas in the flame produced by a composition which contains magnesium:

$$MgO(\text{solid particles}) + CO \longrightarrow Mg(\text{gas}) + CO_2$$

This decreases the continuous spectrum due to the solid particles and makes the flame clear for the production of good colour. In such a case strontium oxalate may be more useful than strontium carbonate, but where magnesium is not used it seems that strontium carbonate is superior.

Manufacture. It is obtained by precipitation adding oxalic acid to conc. strontium chloride solution in water.

Packing and volume for storage. Wooden case, 1.30 m^3 per 1000 kg.

Quality. The white material is the best quality, but commercial grades may be somewhat greyish in colour.

Orange colour producing agent

(11) Calcium carbonate (precipitated chalk), $CaCO_3$

Molecular weight: 100.09; colourless, amorphous and heavy powder; hardly soluble in water; 0.008 grams at 0°C and 0.005 grams at 20°C per 100 grams of water. If the water contains carbon dioxide, it is more soluble producing the bicarbonate:

$$CaCO_3 + H_2CO_3 \dashrightarrow Ca(HCO_3)_2$$

When calcium carbonate is heated, it generates carbon dioxide gas over 700°C, and at 900°C almost perfectly:

$$CaCO_2 \dashrightarrow CaO + CO_2$$

Calcium carbonate causes a reaction in contact with ammonium perchlorate quite slowly in presence of moisture:

$$CaCO_3 + 2\ NH_4ClO_4 \dashrightarrow Ca(ClO_4)_2 + 2\ NH_3 + H_2O + CO_2$$

Calcium carbonate gives an orange flame, and often is used for toy fireworks etc. as a substitute for strontium salts.

Manufacture. Carbon dioxide gas is blown into milk lime. It is filtered, dried and crushed to a fine powder.

Packing and volume for storage. Paper bags; 1.00 m^3 per 1000 kg.

Yellow colour creating agents

(12) Sodium oxalate, $Na_2C_2O_4$

Molecular weight: 134.00; Colourless crystalline powder; specific gravity: 2.34; soluble in water; 3.4 grams at 20°C, 6.3 grams at 100°C per 100 grams of water. The pH value of a saturated solution in water was 6.1 at 24°C. It is hardly soluble in alcohol. It causes no reaction with aluminium and a small reaction with magnesium; this is an important feature which is quite different from that of sodium chloride or sodium bicarbonate. A test showed that it absorbed no moisture at an average relative humidity of 84% and an average temperature of 25°C over 10 days.

Manufacture. It is obtained by neutralization by adding sodium carbonate to an oxalic acid solution in water, or by adding a mixed solution of sodium hydroxide and potassium hydroxide to sawdust, and allowing them to react at 250°C.

Packing and volume for storage. Paper bags; 1.60 m^3 per 1000 kg.

(13) Sodium carbonate, Na_2CO_3

Molecular weight: 105.99; colourless powder; specific gravity: 2.53; melts at 851°C. It is more soluble in water than the oxalate; 7.1 grams at 0°C, 21.6 grams at 20°C, 45.5 grams at 100°C per 100 grams of water. A pH value for 10 gram sodium carbonate dissolved in 100 gram water was 12.7 at 24°C, which is quite strongly alkaline.

Sodium carbonate absorbs a little moisture; a test showed that it absorbed 10.74% moisture at an average relative humidity of 84% and average temperature of 25°C over 10 days.

Sodium carbonate damages magnesium or aluminium in presence of moisture; accordingly it is not recommended to use it as a component of a composition which contain magnesium or aluminium. It does decrease the burning rate of the composition remarkably. Colouration with this material is so sensitive that we could use it as little as possible.

Sodium carbonate is quite strongly alkaline, and we cannot use it in compositions which dislike alkali.

Manufacture. Sodium carbonate is an important product of the alkali industry. It is obtained naturally by the purification of sal soda which is found in the water of lakes; Magadi of Kenya in East Africa, Owens of California in the USA etc. Inudustrially it is obtained by the Solvay process (ammonia-soda process); sodium chloride solution is saturated by ammonia which is forced into the solution. Carbon dioxide gas is then blown into the solution to form the bicarbonate($NaHCO_3$) and ammonium chloride(NH_4Cl). When the bicarbonate is separated and heated, water and carbon dioxide are driven off and sodium carbonate is obtained. The ammonium chloride is mixed with milk of lime and distilled to form calcium chloride and ammonia solution. The recovered ammonia is used repeatedly.

(14) Sodium bicarbonate, $NaHCO_3$

Molecular weight: 84.01; colourless monoclinic crystals; specific gravity: 2.2; forms sodium carbonate on heating, generating carbon dioxide gas; soluble in water; 6.5 grams at 0°C, 8.8 grams at 20°C, 13.8 grams at 60°C per 100 grams of water. Over 65°C in water it actively generates carbon dioxide gas to become sodium carbonate.

Sodium bicarbonate solution in water is slightly alkaline; the pH value of a saturated solution at 24°C was 8.1.

Sodium bicarbonate has been used in Japan for compositions which contain potassium chlorate. It does not decrease the burning rate as much as the sodium carbonate. In a wet state it reacts actively with magnesium and less actively with aluminium, generating hydrogen gas. Accordingly sodium bicarbonate cannot be used for compositions which contain magnesium or aluminium.

Manufacture. The process is the same as described in (13).

(15) Sodium chloride, NaCl

Molecular weight: 58.44; colourless tesseral crystals, specific gravity; 2.164; melts at 800.4°C; boils at 1413°C, soluble in water; 26.28 grams at 0°C, 26.37 grams at 20°C, 28.12 grams at 100°C per 100 grams of water; the solubility does not vary much with temperature. It is insoluble in alcohol or ether. The material on the market is rather hygroscopic due to impurity. The solution in water is a little alkaline; a pH value of a 10% solution in water was 9.6 at 25°C. The so-called "Table Salt" is not hygroscopic, but the pH value of a 10% solution was 10.8 at 26°C and contained some insoluble matter.

Sodium chloride loses its hygroscopic nature on heating, and can be used for firework compositions. But it is not recommended for compositions which contain metal powder or those which are used in a metal container.

Manufacture. Sodium chloride is obtained from sea water, rock-salt or salt rich lake water, but in Japan it is manufactured only from sea water. Sea water contains 3.5~4.0% inorganic substance, consisting of about 80% NaCl and about 20% other substances including $MgCl_2$, $MgSO_4$, $MgBr_2$, KCl, $CaSO_4$., $CaCO_3$. In Japan the saltern process has been popular, but recently the electrodialysis process using ion-exchange resin films has been developed. Sea water is introduced into an electric cell, which is divided into many portions with films of two kinds, namely a cation and an anion exchange resin alternately placed. When an electric current passed through it conc, and a dilute solution are obtained. The salt is obtained by vacuum distillation of the conc, solution.

Green colour producing agents

(16) Barium carbonate, $BaCO_3$

Molecular weight:197.35; colourless hexagonal crystals; the specific gravity: 4.43. It makes transition to tesseral crystals at 982°C, When it is heated to high temperature, it decomposes generating carbon dioxide gas, but the partial pressure of the gas reaches 1 at. at 1350°C. The solubility in water is small, but somewhat greater than that of strontium carbonate; 0.0022 grams at 18°C, 0.0065 grams at 100°C. A pH value of a saturated solution was 9.9 at 20°C; it is thus more alkaline than strontium carbonate.

Barium carbonate gives a pretty green flame in a composition which contains ammonium perchlorate as the oxidizer, and the colour is better than that produced by using barium nitrate.

Manufacture. Barite ($BaSO_4$) is mixed with carbon and heated to 600~800°C to form barium sulphide, BaS. This is extracted with water. Carbon dioxide gas is blown into the hot sulphide solution to obtain BaCOs as a precipitate.

$$BaSO_4 + 4\ C \dashrightarrow BaS + 4\ CO$$

$$BaS + H_2O + CO_2 \dashrightarrow BaCO_3 + H_2S$$

Another process is to add potassium carbonate to powdered barite, and then to heat it under pressure.

$$BaSO_4 + K_2CO_3 \dashrightarrow BaCO_3 + K_2SO_4$$

Blue Colour producing agents

(17) Copper acetoarsenite(Paris green), $3CuO.AS_2O_3+Cu(CH_3COO)_2$

It is also called "emerald green". It is a pretty clear green powder in very fine particles; insoluble in water; its wash water is slightly acid; stable against sunshine and weathering; soluble in acid, ammonia solution, decomposes by alkali; not hygroscopic.

Copper acetoarsenite is used in Japan in almost all blue compositions at present because it can produce very pretty blue. Note that the extra fine powder is easily scattered and is poisonous. Care must be taken not to inhale this substance.

Manufacture. One example is shown as follows: 300 grams of copper sulphate is dissolved in 1000 cc of water, to which 250 grams of glacial acetic acid is added; this solution is named "A". Then 200 grams of sodium carbonate and 200 grams of arsenious acid are added to 1000 cc of water and boiled to form a solution; this is named "B". B is added little by little to A with constant stirring. Carbon dioxide gas is generated with active bubbling. When all the solution B has been added, it is boiled for about 30 minutes, when copper acetoarsenite appears gradually as green perticles in the solution. The mother liquor is removed by vacuum filtration, and the green substance, copper acetoarsenite, is washed with water until the sulphate ion disappears; it is then dried. The yield is about 180 grams. Too little acetic acid spoils the colour of the product. The filtrate is also poisonous and it must be treated with great care. Manufacture is quite simple, but it is only possible to manufacture it in a chemical plant where the drainage system is adequate.

Packing and volume for storage. Tin case, 1.00 m^3 per 1000 kg.

Quality. It is difficult to tell the quality of Paris Green by its colour. Take a small amount of the powder and wash it with water. Add barium chloride solution to the washings. If the water becomes milky due

due to the formation of barium sulphate, the material is not good especially for use in combination with chlorates. Good material is not lumpy. The material should not smell of acetic acid, however the acid does not decompose chlorates.

(18) Copper arsenite, CUHASO3

Molecular weight:187.51; light yellow green powder of extra fine particles. Insoluble in water, but soluble in acid or ammonia solution. It colours a flame blue almost as well as copper acetoarsenite. It is almost unhygroscopic. It is also poisonous and care must be taken as in the case of the acetoarsenite. It can be used in combination with chlorates.

Manufacture. The process is the same as that of copper acetoarsenite, except that no acetic acid is used in the solution A. The last filtration is not so easy as that of the acetoarsenite, and the material cakes hard after vacuum filtration. It must be crushed to powder after it is well dried.

Packing and volume for storage. 1.43 m^3 per 1000 kg, paper bags or tin cases.

(19) Copper sulphate, $CuSO_4 \cdot 5H_2O$

Molecular weight:249.69; blue triclinic crystals; specific gravity: 2.286. When it is heated, it changes to a trihydrate at 30°C, the monohydrate at 110°C, and it becomes anhydrous at 150°C. The molecular weight of the anhydrous salt is 159.61. It is soluble in water or alcohol. This material is a strongly acid salt, and must not be used in combination with chlorates. A mixture of copper sulphate and red phosphorus in a wet state gradually rises in temperature to cause spontaneous ignition. It can be used in combination with nitrates or perchlorates.

Copper sulphate is rather cheaper than copper acetoarsenite and produces a pretty blue colour in combination with ammonium perchlorate which is almost as good as the colour produced by copper acetoarsenite. Another advantage is that it is not easily scattered, due to its density.

Anhydrous copper sulphate absorbs moisture strongly, and is also used as a desiccating agent, however it does not become wet.

Manufacture. Copper scrap is added to the waste solution during the refining of copper by electricity. The liquid is also heated by blowing air into it and filtered. The filtrate is concentrated, and the copper sulphate crystallizes out. Copper scrap can be added to sulphuric acid which contains a small amount of nitric acid, or an excess of sulphur is added to heated copper to form copper sulphide, which is heated further to oxidize it until it becomes copper sulphate.

Packing and volume for storage. Paper bags; 0.70 m^3 per 1000 kg.

(20) Copper powder, Cu

A reddish powder with pretty metal lustre. The atomic weight is 63.55. Specific gravity:8.9; it melts at 1083°C and boils at 2595°C Gradually it is coated with a film of basic copper carbonate in the wet state by the action of moisture and carbon dioxide gas in the air. When it is added to a composition which contains ammonium perchlorate, a pretty blue flame is obtained; 5% copper powder is adequate. Neverthless ammonium perchlorate reacts with copper powder generating heat and ammonia gas in the presence of moisture, and the composition must be well protected from the moisture.

(21) Basic copper carbonate, (I) $CuCO_3 \cdot Cu(OH)_2$,(II) $2CuCO3 \cdot Cu(OH)_2$

There are two kinds, I and II. In fireworks I is used at present. I has a molecular weight of 221.11, is rather dark green, consisting of monoclinic crystals. It has a specific gravity of 4.0, decomposes at 200°C, and is insoluble in water. The green coat on weathered copper consists of this substance. It occurs naturally as malachite. II occurs naturally as azurite. It has a specific gravity of 3.77~3.83 and varies from light blue to a deeper blue and because of its pretty colour is used as pigment.

Basic copper carbonate cannot produce such a good blue as copper acetoarsenite, but it is not easily scattered and is not so poisonous. It is well suited to ammonium perchlorate compositions or high temperature flame compositions, where HCl gas is produced in the flame.

Manufacture. It is obtained by gradually adding a calculated amount of ammonium carbonate to copper sulphate solution in water. At first various forms of blue green precipitates occur in the solution, but they gradually change to the crystaline form of basic copper carbonate II.

13.4. Combustion agents (Fuels)

(22) Shellac

The principal component of shellac is trihydroxypalmitic acid, $CH_3(CH_2)_{11}(CHOH)_3COOH$. This is a chain compound, but another kind of ring compound, $C_{15}K_{20}O_6$, is contained in shellac. One analysis showed that shellac contained 7.00% C, 23.87% O and 9.00% H, and a formula $C_{16}H_{26}O_4$ was applied to it.

The quite remarkable character of shellac is that the carbon content is smaller, and hydrogen content is larger than that of other fuels, e.g. rosin. Apart from the $4H_2O$ which should be formed at burning, it contains a further 9 H_2; consequently when it is burnt in combination with an oxidizer, lack of oxygen in the flame does not cause the generation of carbon particles. In addition a high flame temperature is obtained by the reaction of the hydrogen at combustion. This is the reason why shellac is regarded as a superior fuel for coloured flame compositions. It burns in combination with ammonium perchlorate at F/O = 2:10 creating a slight reddish orange flame.

Treated shellac is sold as yellowish orange flakes on the market. The melting point is not clearly defined, but it is softened at 50~90°C to a liquid state, and blackened at 180°C, losing its adhesive power. When heated moreover, it decomposes and is carbonaized with the generation of inflammable gas.

When a small grain of shellac is dropped on the surface of melted potassium nitrate, the nitrate directly reacts on the shellac at the contact surface. In this case the surface of the potassium nitrate begins to move radially from the grain(Fig.54).

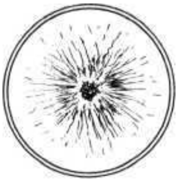


Fig.54. Decomposition of shellac on the surface of melted potassium nitrate

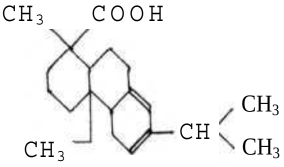
Shellac is insoluble in water, but soluble in alcohol, acetone and turpentine, it slowly absorbs paraffin and swells up. The solution in alcohol is popular as shellac varnish. It can be used in combination with chlorates. Shellac powder does not cake so much during storage over a long time; but a loaded composition which contains shellac and paraffin or oil degenerates or shrinks slowly, and it sometimes causes an unexpected rapid burning through the gap created between the composition and the container.

Manufacture. Obtained from the secretions of lac insects, which are parastic on the small branches of some kinds of wood, e.g. croton, in the districts of east India and Indo-China. These insects secrete resinous ratter due to stimuli from the females, and the branches are eventually covered by the substance; this is called Stick Lac". The substance is collected, selected and powdered. Then this is dipped in water and a clear red dye is extracted from it. The residue is called "Raw Lac". It is melted, filtered and crushed to powder or formed to flakes being melted. Further details are given by R.Lancaster[Fireworks, principles and practice, p.38 (1972)].

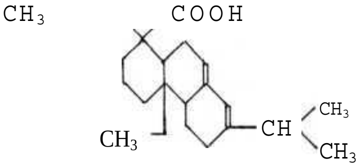
(23) Rosin(Colophony, Common rosin, Wood Resin-Pine, Resin-Colophony)

There are three kinds at present. One is called "gum rosin", which is obtained as the residue of the distillation of turpentine oil from pine resin, which is collected from pine woods. The second is called "wood rosin", which is obtained by extraction from chips of old pine stamps using a solvent. The third is the "tall oil rosin", which is obtained from the digester waste in the manufacture of kraft pulp. Rosin is produced in large amounts in America, Russia and China. At present wood rosin is mostly produced, and the tall oil rosin will gradually increase, but the production of gum rosin is decreasing. The most popular use of rosin is as size in paper production.

Rosin contains -COOH and double bonds in its molecular structure. Rosin contains mainly cyclic compounds as follows.



Laevoabietic acid



Dextroabietic acid

Rosin is slowly oxidized in the air, but it seems to give no trouble for firework use. It can be used safely in combination with chlorates.

There are many kinds of rosin products, each of which has a slight difference in burning character from the others. The two most popular items are described here.

Wood rosin FF. The so called "Yo-Chan", which means a foreign resin in Japanese is the most popularly used resin in Japan. It is a slightly yellowish mass. When it is powdered, it cakes gradually. It melts at 72°C, and keeps a clear liquid state up to about 200°C without any colour change. When it is further heated, it vaporizes without carbonization. Having such character, it melts and envelopes the surface of oxidizer particles to cause an interruption or irregularity or even delay in the combustion of compositions when it is used alone as fuel.

One analysis showed that it contained 75.77% C, 15.35% O, 8.81% H and

0.07% ash. In comparison with shellac, it has more carbon and less oxygen. The excess carbon produces a very bright flame which disturbs the production of colour. For example, it burns in combination with ammonium perchlorate at F/O = 2:10 producing a bright white flame. Accordingly this is used only as a partial substitute for shellac.

When small grains of the wood rosin FF are dropped one by one on aelted potassium nitrate, which is gradually heated to raise the temperature, the grains melt without ignition and are only vaporized up to 460°C; at higher temperatures they ignite. Clearly there are difficulties in the combustion of this material; in fact it is not combustible in a solid or liquid state, but only the vaporized state. This is where it differs from shellac. With potassium chlorate it ignites in excess of 404°C.

Combustion agent BL. This was named by H.Murai, who first introduced this substance into firework use in Japan after World War II. It is sold as a dark brown powder. It melts at 82°C and this melting point is 10°C higher than that of wood rosin FF. This material seems to correspond to a product sold by Hercules Inc. in the USA. Another chemical difference between this material and wood rosin may be in the acid value(the milligram number of potassium hydroxide wasted by neutralization of acid base -COOH contained in 1 gram of the material); the acid value of this material is about a half of that of wood rosin.

Powdered material does not cake during storage. From the melting point, 82°C, to 200°C it maintains a liquid state without any change, but when it is further heated, it is carbonized producing a combustible gas. These characteristics produce stable combustion in any composition, a superior characteristic which cannot obtained from wood rosin.

It is insoluble in water, but soluble in alcohol and especially in acetone. Wash water(100 grams of water per 10 grams of BL rosin) showed a pH value of 5.1 at 15°C.

It burns in combination with ammonium perchlorate at F/O = 2:10 rroducing a brilliant white flame. This shows that it contains a large amount of carbon. In the dropping test using melted potassium nitrate it is only carbonized up to 480°C and at higher temperatures it ignites finally. It can give a greater burning rate to compositions than shellac. On account of the high carbon content, it should be used in a quantity which does not disturb the colour of the flame.

(24) Pine root pitch

A black mass, which softens at 40~60°C and is glossy rather like coal pitch. It is insoluble in water, but partly soluble in alcohol. Owing to the low softening temperature, powdered pine root pitch cakes like wood rosin FF during storage.

One analysis showed that it contained 75% C, 17% 0, 7% H and 0.8% ash. The carbon content is somewhat less and the oxygen content is more than that of wood rosin FF. Pine root pitch therefore disturbs the flame colour less than wood rosin FF or the combustion agent BL. It burns in combination with ammonium perchlorate at F/O = 2:10 producing a white brilliant flame. When it is used even in combination with potassium perchlorate, it produces a large burning rate which is as large as that of chlorate compositions. It is therefore very much admired as a fuel for non-chlorate compositions for chrysanthemum stars.

Pine root pitch was obtained as a bi-product of the distillation of turpentine oil during World War II in Japan. After the war it was found to be useful for firework use, but the substance is not produced at present and is in short supply. When the reason why this material gives such a large burning rate to perchlorate compositions is better understood, it might surely be possible to produce such a substance by some other method.

(25) Kunroku (Amber powder)

"Kun" means smell and "Roku" came from the name of the district "Rikuchu" where this material is produced. It is used for incense sticks, and is called by such a name. It seems to be a fossil resin, but the quality is not as good as the Baltic amber. In English we call it "Amber Powder", but the chemical composition is said to be rather different from the Baltic amber. This material is yellowish or dark brown

(26) Accroides resin (Red gum)

This material is not yet popular in Japan, but the author was able to test it through the help of R.Lancaster. It is produced in Australia, and is cheaper than shellac. The burning rates comparing with shellac are as follows(Table 10).

Table 10. The comparison of burning rates between shellac and accroides resin

Oxidizer	Burning rate Shellac(20%)	 Accroides resin(20%)	Density
NH_4ClO_4 (80%)	1.6㎜/sec	2.0㎜/sec	1.23~1.26g/cc
$KClO_3$ (80%)	1.3	2.5	1.18~1.27
$KClO_4$ (80%)	incombustible	1.5	1.43~1.44

The sample composition were charged in a powdered state. The quite significant nature of the accroides resin is that it burns quite well with potassium perchlorate in comparison with shellac. The burning rate of the accroides resin is generally larger than that of the shellac as seen in the table. This is quite good for chrysanthemum stars.

(27) Wood meal

A slightly yellowish powder which smells of wood. The apparent specific gravity is about 0.18. The chemical composition is regarded as $C_7H_{11}O_5$, which is almost the same to that of cellulose or starch.

When heated, it is carbonized producing a combustible gas. It burns in combination with ammonium perchlorate at F/O = 2:10 producing a flame in which slight orange red lines are visible. The burning temperature is lower than that of shellac or rosin. Accordingly the brightness of the flame is not so large as in the case of shellac or rosin. It somewhat disturbs the caking of powdered composition during storage.

Wood meal is used for industrial explosives and also as an anticaking agent etc. It is quite cheap and does not disturb the colour of flames, and is used mainly for lance compositions. A standard test indicated: less than 13% moisture; 6.5~8.5 cc/g apparent specific volume; 97% of the meal passes 30 mesh; less than 1.4% ash[The Ind.Exp.S.J.: Handbook of industrial explosives, p.215(1966)].

(28) Charcoal

Charcoal is used for many purposes; e.g. to obtain an explosive force; as a fuel producing a large amount of heat and gas in combination with an oxidizer; to adjust the burning rate of compositions; to obtain sparks or fire dust; to modify the ignition character of compositions; to increase brightness of flames or simply as a combustion agent which helps the burning of compositions.

Charcoal is insoluble in any chemicals and does not melt. Charcoal, including the hemp coal later described, belong to the so called amorphous carbon allotrope. This material has many atoms in a parallel row. The main fine structure of the carbon is a plate on which carbon atoms are placed like a hexagonal net(one hexagon is 20~30 A in length) and these fine structures fold at random. The microstructure under the electron microscope consists of a mass which has many parallel small holes. Charcoal contains a small amount of hydrogen and oxygen. A highly carbonised charcoal is written as $C_{20}H_7O$, the weight ratio of the elements, C:H:O, amounting to 91:3:6.

Manufacture. Industrially on a large scale charcoal is manufactured by dry distillation in an iron vessel. In Japan for firework use it is produced in an earth oven. Firework manufacturers build this oven to obtain a charcoal which suits their own taste.

It is better to use sloping ground to build the oven, and the surface of the ground must always be dry. Water and clay must be easily obtained near the place as the water is especially necessary to knead the clay. When the scale of the production is not large the oven can be built in the yard of a house, but in large scale production the place must be selected near the wood supply to reduce the labour of carrying the wood. The place must not be windy, because the progress of the wood carbonization ±B known by the colour of the smoke generated from the oven, and this is often disturbed by a strong wind.

There are many kinds of oven for charcoal production, but for small scale production the simple round form may be used(Fig.55).

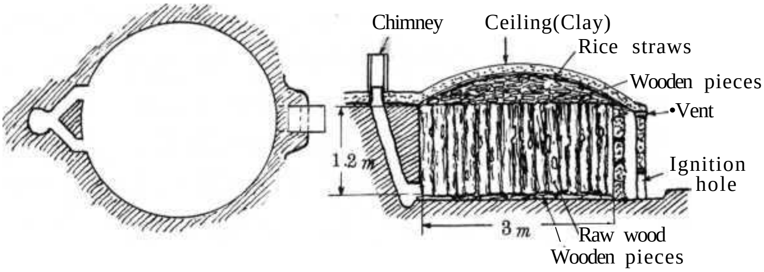


Fig.55. Charcoal oven

First the round wall is constructed and then small pieces of wood are laid down all over the floor; these pieces are mainly wooden branches. The raw wood which is cut to a suitable length is taken into the oven piece by piece and stocked vertically and closely on the floor. The raw wood is then covered by many small pieces of wood to form a spherical surface on top. It is covered with straw-mats or rice straws and then with moist clay, which is consolidated by beating it; this completes the oven. Then wood is burnt for a long time (about one day) at the ignition hole to ignite the raw wood. When a large amount of white smoke comes out of the chimney and the temperature of the smoke is so high that one cannot keep a hand in it at the chimney outlet, it shows that the raw wood is ignited. At this stage the ignition hole is closed and a small vent is left pen. In four or five days the smoke becomes light and somewhat violet. The time this takes differs according to the diameter of the raw wood. The vent is then opened further to make the carbonization perfect. Finally the vent and chimney are closed. The clay ceiling generally cracks but this is painted out with a mixture of ash and clay in water. The ceiling is not very strong, and so there is a risk of it collapsing and starting a fire. Naturally therefore repair of the clay ceiling is dangerous, but the most important operation in charcoal manufacture. Cracks which appear at any other place must be perfectly closed by the same method to shut out the air and prevent it from entering the oven. After three or four days when the oven is perfectly cooled a part of the wall at the ignition hole is removed and the charcoal is taken out of the oven piece by piece. The clay ceiling is re-used in later processes, and it must be protected from snow or rain by a roof which is constructed over it; this is necessary to eliminate labour in subsequent processes. The yield of charcoal thus obtained varies according to the degree of carbonization, but generally it is about 15~20% of the raw wood.

Pine charcoal. A fine easily scattered black powder, which has an apparent specific gravity of about 0.37 g/cc. The adsorption power of dye in water is quite small which may show that it is not so porous. One analysis showed that it contained 7.07% moisture, 1.05% ash. The pH value of the wash water(5 grams of charcoal/ 30cc of water) was 7.7. Pine charcoal burns in combination with ammonium perchlorate at F/O = 2:10 producing a yellow flame, but no sparks or fire dust. A mixture of pine charcoal, sulphur and potassium nitrate in the weight ratio 30:10:60 burns producing pretty orange red fire dust. This characteristic is generally seen with other charcoals but pine charcoal produces the most pretty fire dust of all. On the other hand, the phenomenon shows that pine charcoal does not complete the reaction and produces less gas in black powder-type compositions. Therefore pine charcoal is used to produce fire dust and not to obtain force.

Pine charcoal on the market generally passes 300 mesh.

Paulownia charcoal. A light powder, which is easily scattered and has an apparent specific gravity of 0.12 g/cc. This value is the lowest for all the kinds of charcoal at present available. The dye adsorption power in water lies between pine charcoal, and hemp coal which has the largest. One analysis showed that it contained 4.9% moisture and 2.5% ash. The pH value of the wash water(5 grams of charcoal / 30cc of water) was 7.5. A mixture of the paulownia charcoal, sulphur and potassium nitrate burns as well as the pine charcoal, but it produces less fire dust than the pine charcoal.

Paulownia charcoal is one of the most superior kinds of carbon particle as a black powder component for producing power, but it is not cheap, and for some time it has been replaced by hemp coal. Recently paulownia coal has recovered its use again because of the decrease in the culture of hemp.

(29) Hemp coal

A black fine powder which has a somewhat hygroscopic feeling. The apparent specific gravity is 0.22g/cc. The dye adsorption power is the largest of all the kinds of plant coal. A mixture of hemp coal, sulphur and potassium nitrate burns to produce a violet flame and less fire dust than pine charcoal. It is used to obtain a large force of explosion as a component of black powder or in combination with potassium chlorate or perchlorate for the bursting charge of chrysanthemum shells.

It is more hygroscopic than the pine charcoal; this may be caused by a phosphorus compound which is found in cultivated plants in general. One analysis showed 9.15% moisture and 8.64% ash, and the carbon content may be less than 82%. Such a small carbon content is a defect of this material and the ash contains Si, Cu, K, Al and phosphorus compounds. The wash water(5 grams of hemp coal / 30cc of water) showed a pH value of 10.5, and changes the colour of phenolphthalein to red. The purification of hemp coal by washing it with water takes much time, because the filtration is very slow due to its alkaline nature. The particle size of commercial hemp coal is less than 20 microns, but it is better to sieve it before use to remove foreign matter.

Manufacture.The following method is typical: An oven is constructed with stones in the shape of a well. The inside diameter of the oven is determined so that the hemp caules can be easily inserted. At first some of the hemp caules are ignited and thrown into the oven, and then the remainder of the caules are heaped on the fire step by step at intervals so that the material thrown in at first does not become ash. Finally, water is poured on the hemp to extinguish the fire. The hemp coal thus produced is dried by itself from the remaining heat. Finally it is crushed to a fine powder and sieved to remove coarse grains and foreign matter.

(30) Lampblack (Pine black)

The lampblack used in Japan is obtained by the incomplete burning of pine wood, and consists of very fine easily scattered particles. It contains a small amount of tar, and when water is added to the powder, it floats on the water and the two cannot be easily mixed together. A mixture of lampblack, sulphur and potassium nitrate in the ratio 25:15:60

burns producing a reddish violet flame, but no sparks or fire dust. As a component of black powder it produces quite a large force of explosion. The particles are so fine that it spreads well into a mixture, even if the amount is small. This characteristic is a great advantage as an ignition agent. As a component of the Senko-Hanabi composition, it creates a big spark with many branches, and has been used for this from old times. The high price is the major defect.

Manufacture. Rape oil, resin, pine root or pine wood is burnt in an oven and the generated soot, which is caught on the wall of the oven, is subsequently collected. It is said that the quality varies with the place where the soot is caught.

Carbon black used for industry is different from the lamp black. It is made from natural gas, acetylene gas, anthracene or coal tar. This material has a high specific gravity(1.8~2.1 g/cc) and contains carbon with a graphite structure; the crystalline nature can be observed by X ray techniques, It is rather difficult to burn it in the air and it did not produce sparks in Senko-Hanabi when it was tested by the author.

(31) Aluminium, Al

Atomic weight: 26.982. Pure aluminium has a specific gravity of 2.699; it melts at 660 C and boils at about 2270°C. The heat of combustion in excess of oxygen is 7130 kcal per 1 kg. This value is 690 kcal smaller than that of carbon, which generates 7820 kcal of heat per 1 kg. But aluminium does not produce as much gas as carbon, and the heat is well concentrated on the product to obtain a high temperature.

Aluminium powder is used in Japan in two forms; the flake aluminium which looks brilliant silver and consists of small flat plates, and the atomized aluminium which looks whitish grey and consists of spherical or pebble-like grains. The latter is less ignitable than the former, and only the former is popular in fireworks. The former reflects infra red and ultraviolet rays.

Aluminium is chemically stable in the air, because its surface is covered by a film of aluminium oxide which protects aluminium from corrosion. It is also stable in water or weak acid at the room temperature, because the surface is covered by a film of its hydroxide $Al(OH)_3$. But when wet aluminium powder is kept at a higher temperature, it suddenly causes a violent reaction over a few hours (Table 13), because the film of the hydroxide is broken as it dissolves into the water. In strong acid aluminium dissolves, except in the case of an oxidizing acid like nitric acid which makes a film of oxide on the metal surface which protects it from the corrosion. Aluminium is easily corroded by alkaline substances, e.g. by sodium carbonate (but there is little corrosion with sodium bicarbonate).

Aluminium reacts with nitrates in presence of water to produce H_2, NH_3, and NO_x, gas, except with ammonium nitrate. The reaction proceeds slowly at ordinary temperatures,but when the temperature rises to about 80°C it becomes tremendously violent. In this case a large amount of heat is generated and it accelerates the reaction even more, and sometimes it causes spontaneous ignition. A mixture of aluminium powder(flake) and a nitrate in the weight ratio 50:50, to which 55 additional % of water is added, seems to be the most reactive. When a weak acid like boric acid is added to the mixture to keep its pH value at 4.7~5.1, the reaction is suppressed. Potassium nitrate, strontium nitrate, barium nitrate or sodium nitrate cause the most violent reaction in combination with aluminium, but as it has been stated above, ammonium nitrate does not cause such a reaction. [See Table 13. in (65) Boric acid].

Aluminium reacts with potassium chlorate or perchlorate in presence of moisture to generate hydrogen gas. The reaction proceeds very slowly at room temperature, but is accelerated over 85 C. This reaction is not so violent as that of aluminium and a nitrate. Aluminium does not react with ammonium perchlorate or starch, e.g. glutinous rice starch.

The flake aluminium on the market generally contains an oily impurity such as stearine. Insoluble matter after digestion in hydrochloric acid must be hardly detectable. The mesh size of the aluminium is selected according to use. For "report" compositions very fine flake aluminium is used. For fire dust, coarse flakes are often used; the size of flakes has an influence upon the life of the fire dust. The flake aluminium on the market passes 170~270 mesh and the thickness of a flake is about 2.0~0.3 microns.For waterfalls flakes of about 5 mm in diameter are added to the ordinary flake aluminium.

Manufacture. (1) Stamp process. Aluminium foil scrap is put into an iron mortar with rape oil, beef tallow or olive oil etc, crushed by a hammer which moves up and down and then it is sieved. The contents of the mortar are then transferred to a cylindrical drum, to which some lubricant like stearic acid is added, and the drum is then revolved for glazing to take place. (2) Ball mill process. Aluminium scrap or foil is charged into a ball mill with some lubricant or benzine, and crushed. In some cases an inert gas is introduced into the mill in place of benzine. (3) Atomizing process. Melted aluminium is scattered by spraying molten metal in a jet of air to produce fine particles.

Quality. Aluminium on the market is sometimes mixed with a filler like mica powder etc. One analysis showed that it contained 96.18% pure aluminium, 1.03% was extracted by acetone and there was a 0.34% weight loss by drying.

(32) Magnesium, Mg

Atomic weight: 24.312; pure magnesium has a specific gravity of 1.74, it melts at 650°C and boils at 1107°C. Magnesium is lighter than aluminium in specific gravity, has the same melting point and a lower boiling point. Magnesium burns well in combination with an oxidizer, even if the oxygen content is not enough for complete combustion, because magnesium is easily vaporized and burns as a large long flame catching the oxygen in the air. The flame is easily coloured by a colour producing agent, i.e. the flame temperature is so high that the colour producing atoms or molecules in the flame are highly excited to produce a clear and pretty colour. It can produce coloured flame even in combination with a nitrate only; this is peculiar to magnesium.

The amount of combustion heat per 1 gram of magnesium is 6000 kcal; it is not as high as that of aluminium.

Magnesium powder is slowly oxidized at the surface and loses its metallic lustre. Cold water reacts very slowly with magnesium, but it is quite active with hot water; when the water is cold, magnesium hydroxide formed on the surface protects the metal from corrosion, but in hot water, the hydroxide is dissolved off to cause the reaction:

$$Mg + 2\ H_2O \dashrightarrow Mg(OH)_2 + H_2$$

At the room temperature alcohol or acetone does not react with magnesium, but they react slowly with heat.

Magnesium is violently attacked by various kinds of acid and even by a weak acid, e.g. boric acid or acetic acid. This is quite a different property from aluminium. Strong alkali, e.g. sodium hydroxide, reacts with magnesium very slowly and even with heat there is little activity. It is thought that a film of magnesium hydroxide formed on the surface of the metal disturbs the reaction.

Magnesium is attacked by various salts or sulphur in moisture or water. According to the order of reactivity, first we mention copper sulphate, which reacts on magnesium violently generating hydrogen gas. Ammonium nitrate or ammonium perchlorate also reacts on magnesium violently generating ammonia gas. In this case, quite hygroscopic magnesium nitrate or perchlorate is formed. If a composition contains magnesium and ammonium perchlorate or nitrate, it is rapidly destroyed in presence of moisture. But in well dried state,the reaction scarcely occurs and the composition can be stored for long time. Sodium bicarbonate is a weakly alkaline salt, but it reacts considerably on magnesium generating hydrogen gas. Sodium carbonate is more alkaline than the bicarbonate and less active than the bicarbonate against magnesium. Sodium oxalate is unexpectedly reactive with magnesium. Sulphur quite slowly attacks magnesium generating H_2S gas.

Potassium chlorate or sodium chloride reacts rather actively on magnesium; potassium perchlorate less actively than the above; potassium nitrate very slowly and at room temperature it looks as if no reaction occurs at all; barium nitrate, strontium nitrate or potassium bichromate cause no reaction.

It has already been suggested that the above reactions do not occur in practice if the materials are well dried. Therefore, compositions which contain magnesium as a component must be kept very dry if they are to be stored for a long time.

Magnesium is attacked also by some organic materials, especially by organic acids which are dissolved in alcohol or acetone. Wood rosin FF is the most reactive, but shellac, accroidea resin(red gum) or BL combustion agent cause almost no reaction.

Coating of magnesium powder. When we use magnesium powder as a component of firework compositions, we protect it from the actions of moisture and chemicals by coating the grains with a suitable material. We must use in this case a proper ratio of the material to the magnesium powder to avoid coagulating the powder. We generally take 2～5% additional weight of the material. The coated magnesium powder is sieved one or two times before the coating material becomes hard. Table 11 shows the degree of resistance obtained by coating various materials against chemicals.

Table 11. Chemicalproof nature of magnesium coatings
(Tested in wet state at room temperature)

	pH	No coating	Linseed oil (4%)	Paraffin (5%)	Cashew (5%)	Polyester (7%)	Potassium bichromate
Water	5.8	X	0	0	0	0	0
N/10 HCl	-	xxxx	0	0	xxx	x	xxxx
1N. NH_4ClO_4	4.8	xxxx	xxxx	xxxx	xxxx	xxxx	S
N/2 $KClO_3$	5.5	XXX	0	xx	xx	S	S
1.5N/100 $KClO_4$	5.6	xxxx	0	xx	xx	S	S
N/100 $Ba(NO_3)_2$	5.5	xxx	0	S	S	0	S
1N. $Sr(NO_3)_2$	5.1	xxx	0	S	0	S	S
1N. KNO_3	5.6	xxx	0	S	S	S	S
1N. $NaNO_3$	6.4	XXX	0	0	S	xx	S
1N. Na_2CO_3	-	-	XX	0	XXX	xxxx	0

Note: The symbols are as follows:
o: No reaction occurs.
S: Very slightly attacked and useful in practice.
X: Attacked slowly.
XX: Attacked considerably.
XXX: Attacked actively.
XXXX: Attacked violently.

Coating with potassium bichromate is carried out as follows:
50 grams of potassium bichromate is dissolved in 300cc of hot water. 1000 grams of magnesium powder is heated to about 100°C in an air oven for one hour. It is placed in a large aluminium bowl and the hot solution of potassium bichromate is added to it. It is quickly mixed stirring by hand with gloves until the powder colours uniformly brown. Then the powder is spread on a kraft paper and dried well in the sun. When dried., it is passed through a 30 mesh sieve. The dust must not be inhaled because potassium bichromate is poisonous.

According to the table, any kind of coating is effective against moisture or water. Against chemicals, the resistance depends on the kind of the coating material. Against ammonium perchlorate only the potassium bichromate coating is practically used.This is almost perfectly chemical-proof. The linseed oil coating is quite effective for almost all chemicals except ammonium perchlorate. The paraffin coating is also unexpectedly useful. The polyester coating is not so effective as the paraffin coating; even when the amount of the polyester is increased to the additional ratio of 25 weight %, the resistance remains almost unchanged.

Manufacture. First the anhydride of magnesium chloride is prepared by means of dehydration from solid bittern, which contains mainly $MgCl_2.6H_2O$. This is melted at 700°C and electrolysed with iron cathodes and graphite anodes under 5~8 volts. The magnesium is formed at the cathodes.

Quality. Magnesium on the market sometimes contains a small percentage of aluminium. Magnesium of low purity decreases the intensity of the light for illuminants. The purity is required to be not less than 99.8% as a powder. Recently it has been easier to obtain good quality powder. In general we use ground powder, but in the USA they use an atomized powder spherical in shape.

(33) Magnalium

Magnalium is an alloy of aluminium and magnesium. It is a silver mass, which is easily crushed to powder with an iron mortar. The magnalium powder which is obtained in commerce at present contains 50% aluminium and 50% magnesium. This is solid solution of Al_3Mg_2 in Al_2Mg_3. Its specific gravity is about 2.0. It melts at about 460°C. We call it 50/50 magnalium.

Magnalium is also attacked by various salts in the wet state or in the presence of moisture, but the degree of attack lies in general between those of aluminium and magnesium. Table 12 shows the comparison.

Table 12. Comparison of the resistance of aluminium, magnalium and magnesium against various salts in the wet state at room temperature

	Aluminium	Magnalium	Magnesium
Distilled water	0	s	x
NH_4ClO_3	0	x	xxx
KNO_3	s(xxxx)	x	xx
$Ba(NO_3)_2$	s(xxxx)	x	xx
NH_4NO_3	0(0)	0	xxx
$KClO_3$	0	x	xxx
$KClO_4$	0	s	xxxx
$Na_2C_2O_4$	xx	xxx	xxxx
NaCl	s	xxxx	xxxx
$CuSO_4$	s	xxxx	xxxx
$NaHCO_3$	s	0	xxxx
Na_2CO_3	xxxx	xx	xxx
NaOH	xxxx	xx	xxx
H_3BO_3	0	xx	xxxx
CH_3COOH	0	xxxx	xxxx
$K_2Cr_2O_7$	0	0	0

Note: (1) Symbols are the same as those in Tabele 11.
(2) Samples were used in a powdered state,
(3) 50/50 magnalium was used,
(4) ( ) denotes the resistance when heated at about 60°C . It also often occurs spontaneously at room temperature in summer.

50/50 magnalium powder gives pretty yellowish white sparks, which branch like pine-needles, when it is mixed in a black powder-type composition and ignited. It burns smoothly in combination with chlorate or perchlorate, producing a brilliant flame and a small amount of fire dust sparks. With nitrates however magnalium does not burn smoothly, but vibrationally especially with barium nitrate or strontium nitrate. Therefore, it is difficult to use this item to an illuminant, but it is admired as material for spark or stars with vibrational burning.

(34) Iron filings, Fe

Iron filings are used for producing sparks. The branching of the sparks is different according to the carbon content of the iron. The carbon burns explosively in melted iron; this causes the branching of the iron particle into a spark. When the carbon content is less than 0.20%, the sparks occur seldom. As the carbon content increases up to 0.7~0.8%, the iron particles are activated more and more to produce many large sparks. A greater carbon content is not so effective. [Kawai: Metallic materials, p.91(1960), Nakaya and Sekiguchi: Riken Report, 6, (1927)]. The melting point of iron which contains 0.7% carbon is about 1300°C.

When iron filings are used as a component of a spark composition, the corrosion is an important problem; i.e. the occurrence of sparks decreases as the time passes during storage. This is promoted by acid, but decreased by alkali. But the corrosion does not occur without air and moisture. Therefore the composition must be kept in a dry state as far as possible, and the filings must be coated by some material. In this case Table 11 may be helpful for the purpose.

(35) Titanium, Ti

Titanium has an atomic weight of 47.90, it melts at about 1800°C and boils at 3262°C. Titanium filings are quite stable against water, moisture or the various other chemicals that we use. The filings are quite reactive at high temperatures (over a red heated state)and produce pretty yellowish white sparks, when they are mixed with a black powder type composition.The front page photos show the sparks in comparison with others caused by aluminium and magnalium. (The author owes the tests to R.Lancaster.) The compositions consist of 70% black powder(in a powdered state), 4% pine charcoal and 26% metal powder.

In Japan a Ti-Fe alloy in various mesh sizes which contains more than 80% of titanium is recently used.

Titanium produces brilliant fire dust sparks having a relatively long life which cannot be obtained by other materials.

SUPPLEMENTS TO 13.1 and 13.2:(1),(5),(6),(7):

In general, a mixture of nitrate and charcoal or of nitrate and some organic material (shellac or accroides resin etc.) produces carbonate (K_2CO_3,$SrCO_3$, or $BaCO_3$, etc.) which forms a large volume of ash when burning. Nitrite is also found in the ash when the nitrate consists of coarse grains. A mixture which contains nitrate and sulfur produces sulfate (K_2SO_4., $SrSO_4$ or $BaSO_4$ etc.) in the ash burning with a flame of fairly high temperatures.

(36) Silicon, Si

Atomic weight: 28.06. Three kinds are produced; amorphous, crystalline and graphite-type. The crystalline form has a conc. black gray metallic lustre and specific gravity of 2.4; the graphite-type form is black and has a specific gravity of 2.7. All of them have the same crystal structure. Silicon melts at 1420°C and boils at 2335°C. Insoluble in water. The amount of heat generated at oxidation is 7300 kcal per 1 kg of silicon, which is equal to 0.9 times the amount per 1 kg of carbon. This is almost the same as that of aluminium, but it is not used for thunder reports, because the noise is quite small. Silicon is stable against acid, but attacked by alkali generating hydrogen gas. Silicon is used for red thermit in combination with minium, e.g. in a weight ratio $Pb_3O_4:Si=7:3$.

Silicon conducts electric current as well as graphite; the electric resistance decreases as the temperature rises.

Manufacture. This is obtained by reducing silica sand with carbon in an electric furnace(amorphous silicon), or by reducing potassium silicofluoride with metallic aluminium, potassium or sodium(crystalline silicon).

(37) Ferro-silicon

The powder has black gray metallic lustre. This is reactive with alkali solution and dissolves in it, generating hydrogen gas. Stable against ordinary acids.

Ferro-silicon is used for red thermit as an ignition composition. The more the silicon is present, the more the heat of combustion increases.

Quality. JIS standard G2302 shows that the first class material has 88~93% silicon content and it is used for explosives(carlit) or generating hydrogen gas in combination with sodium hydroxide. From the second to the fifth class, the silicon contents are defined as 75~80%, 43~47%, 25~30%, 20~25% respectively, and these classes are used as the deoxidation against in iron manufacture or the silicon supply for manufacturing silicon steel plate etc. The sixth class has 15~19% silicon content and is used for acid-proof iron vessels. For firework use(for the red thermit) the first class is recommended.

(38) Zinc dust, Zn

A grey powder, the particles of which are somewhat oxidized at the surface. Pure zinc has an atomic weight of 65.37, melts at 419°C and boils at 907°C. Its specific gravity is 7.34.

Zinc dust is stable against water or moisture, because the film of zinc hydroxide, $Zn(OH)_2$, or basic zinc carbonate, $2ZnCO_3.3Zn(OH)_2$., formed on the particle surface protects the metal from corrosion. It is not easily soluble in sodium hydroxide solution in water, but it is soluble in a weak alkali solution such as sodium carbonate or bicarbonate generating hydrogen gas. It is also easily soluble in ammonia solution to form a complex salt, $[Zn(NH_3)_4](OH)_2$. Zinc is attacked by chlorides,but not by ammonium perchlorate. The main use for zinc is in white smoke, which is created by zinc chloride particles. Zinc dust is quite reactive with hexachloroethane in presence of moisture or water, and it often causes fire when manufacturing smoke composition. It is thought that a trace of hydrochloric acid in the hexachloroethane causes the reaction.

<u>Manufacture</u>. (1) Metallic zinc is evaporated, collected, cooled and sieved. (2) The residue, which is produced in the manufacture of zinc oxide(metallic zinc is burnt in the air) contains zinc and is crushed to a fine powder.

<u>Packing and volume for storage</u>. A strong wooden case, the inside of which is covered with zinc plate. 0.62 m^3 per 1000 kg of zinc dust. Quite a heavy powder.

<u>Quality</u>. The zinc dust of commerce is a fine powder which passes 150 mesh. It contains some matter insoluble in hydrochloric acid solution. Examples of analyses are shown as follows: Made by manufacturer A: metallic zinc: 69.62%, total zinc: 84.69%; made by B: metallic zinc: 77.91%, total zinc: 86.79%; made by C: metallic zinc: 81.02, total zinc: 87.13%.

<u>(39) Starch</u>, $(C_6H_{10}O_5)_n$

A white powder. If brownish, it may contain some impurities such as an iron salt etc. Moisten the samples with a small amount of water or alcohol and observe them through a microscope, and it will be found that all of them consist of small grains which differ from each other in shape and size according to the kinds of starch. For example the grains of potato starch are egg shaped, which is 0.06~0.1mm in diameter(0.07 mm in average). The grains of wheat starch are spherical and 0.01~0.04mm in diameter (0.028mm in average). When heated, it burns without melting. It is insoluble in cold water, but soluble in hot water or hot alcohol to form a paste. The temperature of the solution in water is about 66~80°C and over, but differs according to the kind of starch.

There are many kinds of starch; potato, sweet potato, corn, wheat, rice, adder's tongue lily, bracken etc. For fireworks potato or wheat starch is used as a combustion agent, especially as the low temperature combustion agent for smoke compositions. (Rice starch is used as a binding agent, but is described later.) It must be noted that starch on the market is sometimes mixed with a trace of ultramarine for the pure white look.

The heat of combustion of starch amounts about 3400 kcal per kg, which is almost equal to half of that of carbon or aluminium. Although the heat is so small, it is favoured for low temperature combustion, i.e. it allows the smoke composition to burn below about 500°C to avoid the decomposition of dyes.

The amount of moisture contained in starch becomes larger as the grain size of the starch increases; potato starch contains about 15% and wheat starch about 14% of moisture. When the humidity increaes to a higher value, the moisture content increases further; 20~30% in potato and 18~27% in wheat starch at 80~90% relative humidity(Handbook for manufacturing of confectionery, p.27(1968)).

(40) Milk sugar, $C_{12}H_{22}O_{11} + H_2O$

This is contained in milk; the solid matter in milk contains about 40% milk sugar. This is called lactose also. There are two forms of the molecular configuration; α and β. The ordinary milk contains α and β in the ratio 4:3. The molecular weight: 360.32; specific gravity: 1.525; melting point: 202°C(α) and 252°C(β); moisture content: about 5% and increases to about 7% at high humidity. Soluble in water, but not so much as other sugars; almost insoluble in alcohol. When it comes in contact with heated potassium chlorate, it reacts on the chlorate at 322°C, which is lower than the melting point of the chlorate, 368°C. The temperature is somewhat higher than that of cane sugar, but lower than that of wheat or potato starch. For this reason lactose is favoured more than wheat or potato starch as a combustion agent for coloured smoke compositions.

(41) Cane sugar, $C_{12}H_{22}O_{11}$

It is also called sucrose. It consists of colourless monoclinic crystals; specific gravity: 1.558; softened like wheat-gluten at 160°C and caramelized at 200°C. Cane sugar contains about 1% moisture and at high humidity absorbs more moisture and at last dissolves to a liquid state. Easily soluble in water; dissolves in an amount of water of 1/3 of the weight of the sugar. Insoluble in alcohol or acetone. When it comes in contact with heated potassium chlorate, it reacts with the chlorate at 307°C, which is the lowest of all carbohydrates used at present for fireworks. Cane sugar therefore is quite useful as a combustion agent for coloured smoke compositions to produce good coloured smoke. The only defect of cane sugar lies in its hygroscopic nature, and at present it is used less than milk sugar.

(42) Dextrine, $(C_6H_{10}O_5)n \cdot xH_2O$

White or yellowish powder or grains; soluble in water, but not in alcohol or ether. The brownish material is sometimes sold also on the market. Dextrine is uncrystalline and always contains some insoluble starch, not so much in the yellowish dextrine, but a little in the white.

Dextrine does not have a large cohesive power with the consequence that it is not widely used as the binding agent of firework compositions in Japan, but it is used as the combustion agent for coloured smoke compositions. When it comes in contact with heated potassium chlorate, it reacts with the chlorate at 342°C, which is higher than that of milk or cane sugar. Dextrine burns more easily than starch.

Manufacture. Dextrine is obtained by heating starch from wheat, corn (maize), potato or sweet potato in powder form to 200~270°C. Or 0.15~0.3% of nitric acid or 0.4~0.5% hydrochloric acid is added to the starch uniformly, which is well dried and heated to 100~120°C. The former product is called *calcinatory dextrine* and is brownish; the latter is called *acid process dextrine* and white or yellowish.

Quality. Dextrine of good quality is white or slightly yellowish and has no black or dark spots. The moisture content amounts 5~12% or less; the ash content amounts less than 5%. The sand or earth content shall be less than 0.2%. The acidity must be small; if more than 5 ml of 1 normal alkali solution is spent for neutralizing 100 grams of sample solution in water, it is not of good quality. Dextrine has a special smell, but it is very slight in general. The starch or sugar content should be low. If it contains a little amount of insoluble matter and becomes quite glutinous by heating in water, the quality is not good. One analysis of a sample on the market showed that it contained 8.98% moisture, 0.5% ash, within the JIS limit of starch content.

(43) Sulphur, S

Atomic weight: 32.06. There are two or three allotropes. The sulphur used at ordinary temperature and pressure is α, which has yellowish rhombic crystals and has a specific gravity of 2.07. α sulphur makes a transition to β sulphur at 95.5°C. β sulphur has yellow brown monoclinic crystals, with a melting point of 118.95°C and a specific gravity of 1.96. There are two kinds of liqiud state; λ and μ . Sulphur boils at 444.55°C. The molecules of the vapour state are S_8, which change to S_2, at 1000°C.

Sulphur does not conduct electricity but it is easily electrified. For firework use the sulphuric acid content must be low especially if it is used in combination with chlorate. The acidity is tested with blue litmus paper to see whether the wash water of the sulphur changes its colour to red or not.

Sulphur ignites at 223°C in the air. This relatively low ignition temperature is often used for firework compositions for ease of ignition. Sulphur is used as a raw material for black powder in combination with potassium nitrate and charcoal and it is also used for white smoke compositions.

The composition which contains sulphur and some oxidizer is generally sensitive to shock and friction. The highest degree of sensitivity is in combination with chlorate; next with ammonium perchlorate; with potassium perchlorate the third; and with nitrates less sensitive than above. With any oxidizer sulphur gives a higher ignition sensitivity than charcoal.

The combustion heat amounts 2162 kcal per 1 kg of sulphur, which is 1/3 as large as that of carbon.

Manufacture. For firework use, natural sulphur is melted, separated from sand and earth matter, solidified to a mass and crushed to powder. Or the natural crystals, material of good quality, are selected and crushed by a ball mill to powder. Flowers of sulphur which is made from raw sulphur by distillation contains sulphuric acid, and is not used for firework compositions.

Recently sulphur as a bi-product of the oil industry is finding use in the place of natural sulphur.

Packing and the volume for storage. Paper bags. 1.62 m^3 per 1000 kg.

Quality. For firework use the acid content must be especially low. This item on the market passes 70 mesh. One analysis of natural sulphur showed that it contained 0.05% sulphate, 0.003% chloride, 99.80 pure sulphur.

(44) Realgar, As_2S_2

Monoclinic crystals, the fracture of which has a fat-like lustre.The powder of realgar is orange. Specific gravity: 3.4~3.9; melting point: 308~320°C, boiling point: 565°C. It makes a transition from α(red) to β(black) at 267°C. α has a specific gravity of 3.506 and β 3.254. The heat of formation amounts 40.3 kcal per mol. It is slowly oxidized by the air especially in the sun producing orpiment, As_2S_3, and arsenious acid,

As_2O_3. Namely

$$3\ As_2S_2 + \frac{3}{2}O_2 = 2\ As_2S_3 + As_2O_3$$

In this case the realgar powder changes its colour from red to yellow.

Realgar is insoluble in water, but when it is boiled in water, it changes to As_2S_3 generating hydrogen sulphide gas. When it is treated with dilute bromine water, it becomes arsenious acid, and with iodine solution in carbon disulphide, AsI_3. When it is boiled in nitric acid, it become arsenic acid and sulphuric acid. With dilute ammonia solution no change occurs, but with conc. ammonia solution the crystal surface is attacked. It is only slightly soluble in carbon disulphide or benzene.

When realgar is mixed with an oxidizer, it becomes generally quite sensitive to shock and friction to cause an explosion. But the degree differs very much depending upon the kinds of mechanical action, i.e. shock or friction and the kinds of oxidizer. In combination with potassium chlorate it is quite sensitive both to shock and friction. When an amount of water is added to the mixture, it suddenly loses the sensitivity, but even up to 15% water content(a muddy state) it is not perfectly safe for handling. Alcohol cannot lower the sensitivity. In combination with potassium perchlorate it is sensitive to friction, but not so sensitive to shock; with ammonium perchlorate, on the contrary, it is sensitive to shock, but not so sensitive to friction; the difference between the two is quite clearly observed. With potassium nitrate it is generally not so sensitive to either kind of action, shock or friction, and the sensitivity to shock is almost the same as that of potassium perchlorate.

Realgar is used for report compositions for relatively small pieces utilizing the high sensitivity in combination with chlorate. It is also used for yellow smoke compositions, because it boils at a relatively low temperature as described above.

Manufacture. Realgar occurs naturally in the USA(in the State of Washington, Utah, Wyoming), it contains 20~30% As_2S_2 in combination with silica. The ore is crushed to a proper size, placed in an iron oven and heated to 350~400°C. The melted realgar flows out of the oven and sets into a mass, which is crushed to powder. This process has a defect in that the product often contains acid. Recently in Japan realgar has been produced by crushing natural crystals imported from China.

Packing and volume for storage. Tin case. 1.10 m^3 per 1000 kg.

Quality. Acid content, especially of sulphuric acid, is thought to often cause the accidents and spontaneous explosions in the compositions which contain realgar and chlorate. Realgar on the market generally has two sizes; the coarse passes 80 mesh and the fine 140 mesh. The former is used for yellow smoke, and the latter for report compositions. One analysis showed that it contained 97.70% pure realgar, 1.29% arsenious acid, 0.80% free acid(as sulphuric acid) and 0.80% sulphur.

Realgar should be kept in a dark place during storage so that it does not change colour due to the action of sunlight.

It is said that pure realgar is not poisonous, but generally the realgar of commerce contains a trace of As_2O_3 which is soluble in water, and it is better to handle it with care as with other poisonous substances

(45) Antimony trisulphide, Sb_2S_3

Molecular weight: 339.70. It is stable in the form of rhombic prismatic crystals, which have a black grey metallic lustre. It has a specific gravity of 4.64; melts at 548°C; dissolves in alkali sulphide, conc. hydrochloric acid and alkali. It has another unstable form, an orange red amorphous substance, which has a specific gravity of 4.64, melts at 548°C and dissolves in ammonium sulphide and potassium sulphide. When it is heated to 200°C in carbon dioxide gas, it changes to the stable form.

The combustion heat is about 1000 kcal per 1 kg of antimony trisulphide, when Sb_2S_3 is oxidized to SO_2, and Sb_2O_3; this is equal to about a half of the heat of sulphur. The maximum purity of natural antimony trisulphide is about 88%, and the practical heat of combustion may be lower than that.

Antimony trisulphide burns in combination with ammonium perchlorate producing a slightly green flame(in the case of sulphur a slightly red flame) and can generate red brown smoke in combination with potassium nitrate and charcoal.

When antimony trisulphide is dropped little by little on the surface of potassium chlorate, the temperature of which raised gradually by heating, it ignites as soon as the chlorate begins to melt at about 360°C. (Realgar has the same tendency as antimony trisulphide and sulphur ignites less instantaneously as this, even at 500°C.) Therefore it may be said that antimony trisulphide is more ignitable than sulphur.

A mixture of antimony trisulphide and an oxidizer is generally sensitive to shock and friction. Roughly speaking antimony trisulphide is less sensitive than sulphur or realgar to shock, but it has a higher friction sensitivity than sulphur and a lower friction sensitivity than realgar. Generally we must consider the friction mainly in the ordinary handling of firework articles, and from this point of view it may be thought that antimony trisulphide lies between sulphur and realgar in sensitivity. (With potassium chlorate it is sensitive to both shock and friction; with potassium perchlorate it is sensitive to friction, but quite insensitive to shock; with ammonium perchlorate, on the contrary, insensitive to friction, but sensitive to shock as in the case of chlorate; with potassium nitrate it is insensitive to both, shock and friction.)

Manufacture. Antimony trisulphide is obtained from stibnite which occurs naturally in Bolivia, China, Hungary, Southern Africa.

Packing and volume for storage. Tin case. 0.70 m^3 per 1000 kg.

Quality. Examples of analysis: 87.20%, 92.52% in purity.

(46) Red phosphorus, P

A red brown powder, which has no smell, but if it contains yellow phosphorus, it smells like ozone. The specific gravity amounts 2.20. It ignites at 260°C. It melts at about 550°C, when it is rapidly heated in the absence of air. Insoluble in water or carbon disulphide. Dissolves in nitric acid to become phosphoric acid.

Red phosphorus is not poisonous. Commercial material generally absorbs moisture and slowly becomes wet; this shows that the red phosphorus contains a trace of yellow phosphorus, which is poisonous. The yellow phosphorus is gradually oxidized by the oxygen in the air to phosphoric acid. It is better to purify it before use by the process later described.

When a drop of 90% nitric acid is added to red phosphorus, it ignites instantaneously. Red phosphorus reacts on copper sulphide in presence of moisture generating heat, which causes spontaneous ignition. Red phosphorus does not react on dilute or conc. sulphuric acid. Also it is unreactive with other sulphides; K_2SO_4, $KHSO_4$ etc.

The most safe and practical process for the purification of red phosphorus is to wash it with hot water and to filter away the impurities with the wash water while it is hot, because the yellow phosphorus contained in red phosphorus as an impurity has a low melting point of 44.1°C, and it easily melts and it is removed from the red phosphorus. Another method is as follows:

7% sodium hydroxide solution in water is added to red phosphorus: it is boiled for 24 hours and then the red phosphorus is washed in cold water until the water indicates no alkali. It is dried in a vacuum with phosphorus pentoxide and stirred, being sealed hermetically. This is very dangerous process, which is only acceptable in a laboratory etc., where the ventilation arrangements are adequate. It has been recommended that red phosphorus is exposed to the air for a long time so that the yellow phosphorus contained in it as an impurity is oxidized to phosphoric acid, and then washed and dried well. But this is a paper argument; this could only applied to the treatment of a small amount, because with large quantities it often causes a partial temperature rise leading to spontaneous ignition.

Red phosphorus is said to be a mixture of violet phosphorus, imperfect violet phosphorus and amorphous phosphorus(T.Chitani: Inorganic Chemistry, p.691(1964).

Red phosphorus burns in the air producing a pretty yellow flame, at the top of which the white smoke of phosphorus pentoxide is generated. With this property it is used for a day and night signal. (The flame spectrum probably occurs from PHO molecules; $\lambda\lambda$ 6436-4879 Å; R.W.B. Pearse and A.G.Gaydon: The identification of molecular spectra, p.271, 4th edition (1976)).

Red phosphorus alone is ignited by a strong impact in the air. Red phosphorus becomes quite sensitive especially to friction and ignites or explodes easily when it is mixed with an oxidizer. This property is more distinctive than that of realgar, and it is used for matches. Table 13 shows a series of qualitative tests.

Table 13. A series of qualitative tests for mixtures of red phosphorus and an oxidizer to determine sensitivity to impact and friction using a hammer and anvil in different kinds of metal

	Hammer:	Iron	Iron	Iron	Brass
Oxidizer	Anvil :	Iron	Aluminium	Brass	Aluminium
KNO_3	Impact/Friction=	O E/no	OE/no	OE/no	no/no
$KClO_3$	Impact/Friction=	OEEE/BBB	OEEE/BBB	OEEE/BBB	OEEE/BBB
$KClO_4$	Impact/Friction=	OEE/BB	oEE/no	OEE/no	OEE/no
NH_4ClO_4	Impact/Friction=	OEE/B	OEE/no	OEE/no	o EE/no
$Ba(NO_3)_2$	Impact/Friction=	O E/no	B/no	no/no	no/no
$Sr(NO_3)_2$	Impact/Friction=	E/no	E/no	no/no	E/no
$NaNO_3$	Impact/Friction=	Δ E/no	Δ E/no	E/no	Δ E/no
R.T.	Impact/Friction=	ΔB/no	ΔB/no	ΔB/no	ΔB/no
MnO_2	Impact/Friction=	BB/no	B/no	no/no	B/no

Note:(1) Iron hammer: a 255 gram block 20mm in diameter with a 300mm long handle, brass hammer: a 140 gram block 20mm in diameter with a 300mm long handle.

The impulsive force of impact: corresponds more or less to that of a 1 kg drop hammer from a height of 18cm. The pressure of the friction test amounts to about 1 kg.

(2) Sample: the ratio of red phosphorus to oxidizer is about 1:5 in weight.

(3) Symbols: no: no explosion or no burning. E: sometimes explodes. EE: frequently explodes. EEE: always very sensitively explodes. B: sometimes burns. BB: frequently burns. BBB: always very sensitively burns. O : with a loud noise. Δ : with a low noise. R.T.: red thermit(8o% red lead +20% iron silicate).

Care must be taken since $KClO_3$, $KClO_4$ and NH_4ClO_4 are quite sensitive to friction and shock with red phosphorus.

Red phosphorus which is scattered on the floor cannot be removed perfectly by washing with water because of the fine particles and insolubility in water. Accordingly we must have a workroom which is used exclusively for red phosphorus. The same care must be taken with tools, furniture, fixtures, clothing etc.

A trace of yellow phosphorus tends to become phosphoric acid in the air absorbing moisture during storage. This acid corrodes many kinds of metals, cotton and other materials. Stainless steel(18-8 chrome-nickel) can be effectively used without corrosion for red phosphorus.

<u>Manufacture</u>. Yellow phosphorus is heated for a week at 260°C in the air. A brittle reddish violet mass is obtained and this is boiled with sodium hydroxide solution to remove the yellow phosphorus, and dried.

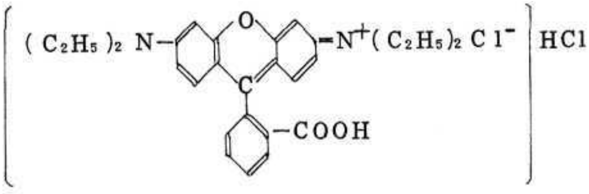
<u>Packing</u>. In tin cases.

<u>Quality</u>. One analysis showed that 99.612% pure red phosphorus, 0.009% yellow phosphorus, 0.03% H_3PO_4, 0.049% insoluble matter in nitric acid, 0.325% moisture, trace of SO_4^- ion.

13.5. Dyes

Dyes are used mainly for smoke, but often for colouring firework pieces also. The dyes for smoke should be in a solid state at ordinary temperatures, have a relatively low boiling point(200~400°C) and be thermostable.

(47) Rhodamine B



The base of the dye is a red powder, which is insoluble in water, but soluble in alcohol producing a red solution. The HC1 salt, which is sold on the market as "Rhodamine B", is a very fine violet black powder with yellow green fluorescence; soluble in water to produce a deep red violet colour; also soluble in alcohol producing a red solution; melts at 270°C, boils at 310°C, but it begins to smoke gradually with the temperature rise from the melting point and is carbonized partly without vaporizing. The smoke particles of rhodamine B from a smoke composition are insoluble in water.

The solution of rhodamine B is acid, the pH value being 2.5~3.0 for a 1% solution in water, but its use in combination with chlorate does not cause any trouble. This dye has a serious defect in that it stains everything that comes into contact with it.

The base, which is insoluble in water, can be used for smoke in place of the HC1 salt, but it burns less easily than the smoke composition which contains the HC1 salt. Moreover the base is not as cheap as the HCl salt because the manufacturing plant has to be modified for the purpose.

The smoke colour of rhodamine B is violet red.

Manufacture. Rhodamine B is obtained by condensation of diethyl-m- aminophenol with phthalic anhydride.

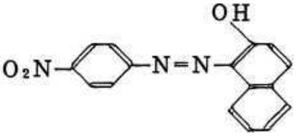
Packing. Tin cases or wooden casks.

Quality. One manufacturer uses the following standard: (1) Appearance: Crystalline powder with a green metallic lustre which is almost the same as the standard colour. (2) Moisture: Weigh out accurately about 1 g of the sample in a weighing tube and dry it at 70~75°C until it has a constant weight. The loss in weight is regarded as the moisture content, which should be less than 5% of the sample. (3) Ash: Weigh out accurately about 1 g of the sample in a porcelain crucible of known weight and heat it with a gas burner, slowly at the beginning and finally quite strongly to a dark red, until it is burnt out and becomes a constant weight. The matter left in the crucible is regarded as ash, which must be less than 1% of the sample, (4) Solubility: Dissolve 0.5 g of the sample in 100 cc of water. The solution shall be transparent without any remaining insoluble matter. (5) Dyeing test(here omitted).

One analysis showed that it contained 1.20% of moisture and 0.27% of ash.

The additive name "B" means "blue" and this dye which contains no filler is called often "Rhodamine B conc".

(48) Para red (p-nitroaniline red)



This is a kind of naphthol dye which contain one azo base, -N=N-, in the molecule. It is a bright red powder, insoluble in water and alcohol, it melts at 210°C, vaporized from about 230°C, and boils at 280°C being partly carbonized. As a component of smoke compositions it is easily damaged by heat even at relatively low temperatures; this is a defect of this dye and it may be caused by the NO_2, base contained in the molecule.

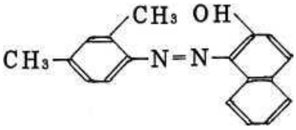
The smoke colour of para red is orange red, and generally it is not used alone, but in combination with rhodamine B for red smoke.

Manufacture. Para-nitroaniline is diazotized and coupled with β naphthol.

Packing. A wooden cask or a paper bag.

Quality. An example of analysis showed that it contains 0.6% moisture, 0.47% ash and 0.60% soluble matter in water.

(49) Oil red



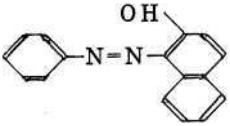
The dyes which are soluble in oil are popularly prefixed with the word "oil" for the commercial name.

Oil red is also a naphthol dye which contains one azo base, -N=N-, in the molecule like para red. It is a bright red powder, insoluble in water, soluble in alcohol and in acetone producing an orange red colour, it melts at 165°C, begins to vaporize at 270°C, and boils at 330°C. Oil red is more stable than para red against heat and is not so easily damaged.

The colour of the smoke of oil red is orange red, and to obtain a good red smoke it is used in combination with rhodamine B.

Manufacture. Mononitro-metaxylene is diazotized and coupled with β naphthol. The process is the same to that of para red.

(50) Oil orange



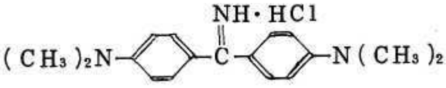
This is a dye which is soluble in oil, and belong to the same class as para red or oil red. It is a reddish orange or dark orange powder, insoluble in water, soluble in alcohol producing an orange colour, soluble also in acetone producing an orange colour; it melts at 100°C, begins to vaporize at 200°C and boils at 270°C. Oil orange is more stable than para red against heat.

The substance sometimes causes an eruption on the skin. Perhaps it comes from the fact that it dissolves into the fat of humans since other kinds of dyes, which dissolve in oil, genrally have such a character.

Manufacture. Aniline is coupled with β naphthol. It is the most simple and representative manufacturing process of this kind of dye and described as follows:

Dissolve 9.3 g of aniline in 30 cc of conc, hydrochloric acid and 100 cc of water. Then pieces of ice are added to the solution to reduce the temperature to 0°C. Prepare sodium nitrite solution by adding 7.2 g of sodium nitrite to 35 cc of water. Add this solution to the aniline solution slowly, and diazotization occurs. Test the solution with potassium iodide starch papers, to avoid excess of sodium nitrite solution. The point is determined by the colour change of the test paper to a slight blue. Add pieces of ice to the solution during the diazotization to keep the temperature at about 5°C. On the other hand, dissolve 15 g of sodium hyroxide in 200 cc of water and then dissolve 14.4 g of β naphthol in this sodium hydroxide solution and cool it. Add the diazotized solution to the β naphthol solution, stirring below 15°C. The mixed solution must be alkaline. Continue the stirring for about one hour, keep it still, and the dye crystallizes out. The dye is separated from the mother liquor by filtering and it is then well dried.

(51) Auramine



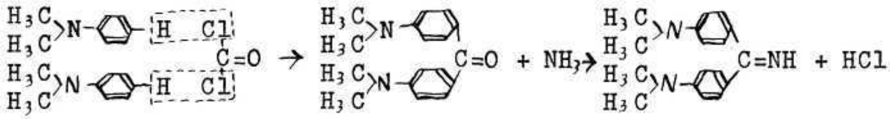
A representative diphenylmethane dye. It melts at 25O°C and begins to vaporize, boils at 290°C and is partly carbonized. This material on the market is generally hygroscopic.

Auramine gives smoke of pure yellow, and is used alone or in combination with other dyes to obtain green or other coloured smokes. When it is used alone for yellow smoke, it looks somewhat weaker than realgar in yellowness.

The HCL salt of auramine is soluble in water.

The smoke composition which contains auramine and potassium chlorate is said to cause spontaneous ignition(Yamanaka and Mitsuo, Showa Kaseihin Co.), but when the composition is in a well dried state there should not be such a problem. The reason is not clear, but it may come from the ammonium chloride which is used for manufacturing auramine and which remains in it as an impurity. As described before, the mixture of an ammonium salt and potassium chlorate creates ammonium chlorate which easily decomposes.

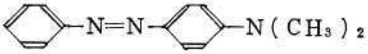
Manufacture. First Michler's ketone(tetra methyl diamido benzophenone) is prepared by the condensation of dimethyl aniline and phosgene in the presence of a catalyst such as zinc chloride. Then the Michler's ketone is melted at 150°C with ammonium chloride and zinc chloride. This material is sold on the market as the HCl salt.



Dimethyl aniline Phosgene Michler's ketone Auramine base

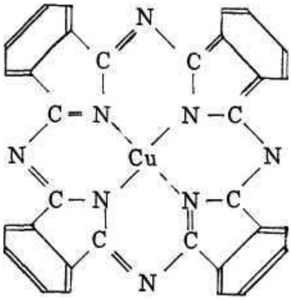
Packing. Tin cases.

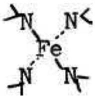
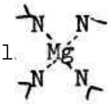
(52) Oil yellow.



This is used for smoke, and is a somewhat reddish, but pretty yellow, and is used in the place of auramine. It is insoluble in water, but soluble in oil. The name "Butter Yellow" comes from the fact that it is used for colouring margarine. Soluble in alcohol or acetone, it melts at 105°C, begins to vaporize at 200°C and boils at 350°C.

(55) Phthalocyanine blue



This substance resembles hemin which is contained in haemoglobin as  or in chlorophyll  in molecular structure.

A bright cobaltic blue powder, which has a specific gravity of 1.6. It is quite stable, and is generally used as a pigment. Insoluble in water or alcohol, very slightly soluble in acetone producing a yellow colour. When heated it is not easily decomposed and sublimes over 500°C. When heated for a long time below 500°C it decomposes slowly to generate white smoke.

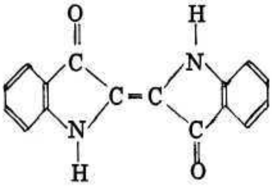
This gives smoke of a very pretty bright cobaltic blue. The daylight firework display has become remarkably pretty from the use of this dye in place of indigo, which gives only a dark blue smoke.

Phthalocyanine blue is well vaporized by using only a strong heat producing agent, e.g. a mixture of carbohydrate and potassium chlorate in quite a large quantity, because it is not so easily vaporized. Accordingly care must be taken because fire often remains in the cinder after the smoke composition has burnt out. If a weak heat producing agent such as celluloid is used in combination with this dye, it produces only a low temperature decomposition which generates white smoke only.

This substance contains copper, and burns in combination with ammonium perchlorate with a blue flame.

Manufacture. This is synthesized by melting phthalic acid and ammonia together in presence of metallic copper.

(54) Indigo pure



The title "pure" means the artifical indigo rather than the natural one. This is a dark violet powder, has a specific gravity of 1.39, and sublimes over 300°C generating violet red vapour. In this case the dye on the market leaves a small amount of black residue. It is insoluble in acetone but soluble in benzene.

Indigo pure is a stable dye, which gives a blackish blue smoke, but when the burning temperature of the smoke composition is too high, it is decomposed to generate yellow grey smoke.

Manufacture. There are many ways of manufacture. In practice it is made from phenylglycine, naphthalene or diphenyl thiourea.

Packing.Tin cases.

13.6. Other chemicals

(55) Red iron oxide, Fe_3O_4

This is a fine red powder with a molecular weight of 159.69; it has a specific gravity of 5.24, and melts at 1550°C. Insoluble in water, soluble in hydrochloric acid reacting with it, but it is hardly soluble in other acids.

A mixture of red iron oxide and aluminium burns generating sparks at a high temperature (about 2400°C), leaving melted iron and melted aluminium oxide, as described in Chapter 5 on page 26.

Manufacture. Obtained by heating iron(II)sulphate, $FeSO_4.7H_2O$, at 650~700°C. There are other several processes(from ores or some bi-products, which contain iron sulphate, iron hydroxide or iron(III)oxide).

Packing.Paper bags.

Quality. There are various kinds of quality. JIS provides for following kinds of purity. Made from iron sulphide, the special No.1 is more than 90% pure and special No.2 is also more than 90%; made from iron(II)sulphate, No.1 is more than 95% pure, No.2 more than 85%, No.3 more than 70%, No.4 more than 60%, No.5 more than 35%.

(56) Minium, Red lead, Pb_3O_4

Molecular weight: 685.57. Clear yellowish red powder or crystals, which have a specific gravity of 9.07; it decomposes generating oxygen over 500°C. Insoluble in water, but soluble in acetic acid, nitric acid and hot hydrochloric acid, reacting with them.

For pyrotechnic use it is combined with ferro silicon under the name of "Red Thermit", which is used as a first fire composition for compositions which are difficult to ignite. Or it is also used to display orange fire dust in combination with other compositions. The red thermit is said to generate no gas in the burning reaction, but truly a small quantity of gas is generated.

Minium has an unusual characteristic in that it can produce "second burning". For example, if paper is dipped into a fire-proof solution, partly painted with minium and dried, it will be found that when the paper is put into a flame it is at once carbonized and then the minium burns alone leaving no carbon, i.e. the minium causes the carbon to burn completely after a while.

Manufacture. Metallic lead is melted and heated to 335 C, to obtain yellow lead monoxide, PbO, being oxidized by the air. Then this is heated at 400~450°C for a long time, we obtain red plumboplumbic oxide(minium), also being oxidized by the air. When the temperature is too high, it decomposes to become PbO again and thus the temperature range of the formation of this material is very narrow.

Packing. This item in commerce has various qualities and we cannot select it by the colour only. It is tested by adding hot hydrochloric acid to it and heating it. The smaller the amount of insoluble matter there is, the better the quality.

(57) Zinc oxide, ZnO

Molecular weight: 81.37. A white powder of quite small particles or hexagonal crystals. It has a specific gravity of 5.47~5.78, and occurs naturally as zincite in the district of Franklin Furnace in the USA. It melts at 1800°C, sublimes at 1700°C under normal atmospheric pressure, changes the colour to yellow at about 300°C, but when it is cooled, becomes white again. Almost insoluble in water and alcohol, but soluble in dilute and conc, alkalis.

This is used for white smoke composition in combination with zinc dust and hexachloroethane. It seems that the higher the purity is, the whiter the smoke colour is. The smoke composition is generally packed in a tin case, and the apparent specific volume is important in manufacture; if it is too small the can is not filled and if it is too large, the case cannot be filled with the amount defined in the specification. The apparent specific gravity of this material on the market lies between about 0.5 kg and 1.0 kg per litre.

Manufacture. French method: Metallic zinc is heated in a crucible to about 1000°C, and vaporized. Hot air is introduced into the zinc vapour to oxidize it to zinc oxide, which is cooled and collected. American method: Coal is added to zinc ores and heated to generate zinc oxide vapour, which is cooled and collected. Heating the nitrate or carbonate of zinc: Sodium carbonate is added to the solution of a zinc salt to create basic zinc carbonate, which is washed with water and heated at 600°C.

Packing and volume for storage. Paper bags, 2 m^3 per 1000 kg (a little bulky).

Quality. There are various kinds of quality. One of the ones used as a component of smoke composition showed that it contained 0.19% moisture, 0.01% soluble matter in water, 0.15% lead, 99.35% of pure zinc oxide.

(58) Potassium bichromate, Potassium dichromate, $K_2Cr_2O_7$

Orange red crystals; molecular weight:294.21; specific gravity: 2.7; melting point:398°C. It decomposes at 500°C, dissolves easily in water; 4.8 grams at 0°C, 10.97 grams at 20°C, 20.83 grams at 40°C, 42.2 grams at 80°C, 94 grams at 100°C in 100 grams of water. It is insoluble in ethanol. It is poisonous and corrosive to the skin and mucous membrane. When iron sulphate is added to the bichromate solution, the hexavalent chromium is reduced to the trivalent form with a loss of colour and the poisonous nature is decreased.

When potassium bichromate is heated to a high temperature, it decomposes as follows:

$$4\,K_2Cr_2O_7 \dashrightarrow 4\,K_2CrO_4 + 2\,Cr_2O_3 + 3\,O_2$$

Potassium bichromate can therefore be used as an oxidizer, but its oxidizing power is very weak compared with other ordinary oxidizers.

Potassium bichromate promotes the burning reaction of potassium perchlorate composition when it is added to it in small amounts. For example, a test showed that the burning rate of a composition which consisted of potassium perchlorate and hemp coal in a weight ratio 75:25 increased 1.55 times when 4～5% potassium bichromate was added to it.

Potassium bichromate suppresses the corrosion of magnesium especially with ammonium perchlorate. Place a small amount of a magnesium powder into a test tube which contains potassium bichromate solution in water. Heat it for a short time, remove the solution and wash the powder with water several times.Add a saturated solution of ammonium perchlorate to the magnesium powder in the test tube, and it will be observed that no bubbles are generated. This phenomenon confirms that the magnesium powder has become anticorrosive. After a while however it begins bubbling actively. Next add a small amount of the potassium bichromate solution to the mixture and shake it, and it will be seen that the bubbling suddenly stops and the reaction ceases. This shows that potassium .bichromate suppresses the corrosion of magnesium powder against ammonium perchlorate.

It is difficult to ignite or to explode a mixture of potassium bichromate and red phosphorus or sulphur even by impact between iron surfaces.

Potassium bichromate is used in small amounts in match compositions. It may be to suppress the violent burning reaction caused by potassium chlorate (Yoshinaga and others: The study of the combustibility of a match composition, J. Industrial Exp. Society, Japan, p.192, volume 38, No.4(1977)).

Manufacture: Finely powdered chromate, $FeO.Cr_2O_3$, is mixed with sodium carbonate and slake lime. It is heated and melted in a rotary kiln to 1000~1300°C. Water is poured into the product and sodium chromate is extracted as a solution. Sulphuric acid is added to the solution until the pH value becomes about 3, thus producing sodium bichromate, $Na_2Cr_2O_7$, Insoluble matter is removed and the solution is concentrated by vacuum evaporation. A theoretical amount of potassium chloride is added to the solution and it is cooled to obtain raw crystals of potassium bichromate, $K_3Cr_2O_7$, which are purified further by recrystallization.

(59) Boric acid, H_3BO_3

It occurs as white flaky crystals. Molecular weight: 61,83; specific gravity: 1.4; it melts at 185°C; solubility: 2.70 grams at 0°C, 4.65 grams at 20°C, 12.96 grams at 80°C, 27.5 grams at 100°C in 100 grams of water; 11.8 grams at 25°C in 100 grams of ethanol; 28 grams at 20°C in 100 grams of glycerine. As described in Lancaster's book boric acid is quite effective to suppress the decomposition of a composition which contains aluminium by its buffer action and it is superior to acetic acid or gum arabic as shown in Table 14. But it must be noted that boric acid corrodes magnesium.

Table 14. Comparison of the suppressing effect of weak acids for the decomposition of wet aluminium powder and wet compositions which contain aluminium(100 grams of samples in a warm state)

Composition	Acid added (additional %)	Water added to 100 grams of sample	Temperature for test	Waiting time for commencing decomposition
100%Al	no acid	50cc	70-79°C	3,05(h,m)
90%Al,10%GRS	"	"	65-80	3,00
"	0.5%AA	"	65-80	2,00
"	1.0%BA	"	65-80	∞
26%Al,64%$KClO_3$,10%GRS	no acid	"	70-73	9,30
"	1.0%AA	"	70-73	3,00
"	1.0%BA	"	70-73	∞
23%Al,68%$KClO_3$,10%S,9%GRS	1.0%BA	"	70-73	∞
29%Al,62%$KClO_3$,9%S	6.0%GA	"	60-70	3,30
40%Al,50%$KClO_4$,10%GRS	no acid	"	70-84	2,65
"	0.25%AA	"	70-84	3,45
"	1.0%BA	"	70-84	∞
40%Al,50%KNO_3,10%GRS	no acid	"	72-77	1,42
"	0.25%AA	"	68-79	6,05
"	1.0%BA	"	72-77	∞
40%Al, 50%$Ba(NO_3)_2$,10%GRS	no acid	"	72-77	1,48
"	0.5%AA	"	68-75	1,28
"	1.0%BA	"	72-77	∞

Note: Al=fine flake aluminium, GRS= glutinous rice starch, AA=acetic acid, BA=boric acid, GA=gum arabic

The symbol ∞ in Table 13 shows the composition did not decompose when heated for a long time. It must be noted that wet aluminium powder decomposes without other chemicals when it is heated for a long time. Glutinous rice starch does not react with aluminium.

Manufacture:It is produced naturally in Toscana in Italy as a component of steam issuing from the earth; this is condensed to a 0.5% boric acid solution. Generally it is manufactured from borax by adding sulphuric acid to it:

$$Na_2B_4O_7 + H_2SO_4 + 5\ H_2O \rightarrow Na_2SO_4 + 4\ H_3BO_3$$

(60) Boron, B

Atomic weight: 10.811. Two kinds are produced; amorphous and crystalline, but only the amorphous boron is used for fireworks. It has a specific gravity of 2.35, melts at 2160°C, boils at 3650°C. When amorphous boron is touched it feels as if it were somewhat hygroscopic. It absorbs moisture to about *6%* and it is sometimes necessary to protect it against moisture. According to an American analysis (K.M. Chemical Corporation) the purity of amorphous boron cannot exceed 92%. It is a dark brown powder of very fine particles.

Amorphous boron burns in oxygen and reacts with sulphur at 600°C, but it is stable against many chemicals. It does not react with conc. HCl solution or HF even in a hot state. With conc, nitric or sulphuric acid it reacts in small amounts to produce boric acid.

A mixture of amorphous boron and potassium nitrate in a ratio 75:25 burns rapidly with a brilliant green flame at very high temperature. The green colour comes from BO_2 band spectrum. The boron mixture is used as an ignition composition in place of thermit, and the difference between the two lies in that the former ignites other compositions with its high temperature flame but the latter mainly with its high temperature liquid cinder. Amorphous boron is very expensive commercially, but it is very useful when the ignition surface of a composition cannot be pasted with thermit as in the case of a rocket propellant which must start without a delay. The boron mixture ignites very well from a relatively weak heat source such as a black powder flame.

Manufacture. Boric oxide, B_2O_3, is reduced with magnesium to form fine particles smaller than 2 microns.

(61) Ultramarine. $Na_2S_2,3NaAlSiO_4$(?)

A beautiful blue powder. It is easily attacked by acids, but has considerable resistance to alkalis. It is stable in the sun or in hydrogen sulphide, H_2S, and withstands heat.

As Lancaster wrote (Fireworks, Principles and Practice, p.35(1972)), there are very few ingredients which produce yellow flames without any storage problem. Ultramarine is, however, one of them and it is suitable for ammonium perchlorate based compositions especially when they contain magnesium(s. p,219). An experiment showed that there was no degeneration when the composition was stored for two years without moistureproof containers. Under the same condition $NaNO_3$, Na_2SO_4, $Na_2Ca_2O_4$ or cryolite etc. caused degeneration by moisture. The only defect of ultramarine is that the yellow of the flame is rather weak and when it is used for chlorate or perchlorate based compositions, it produces much ash.

(62) Chlorinated isoprene rubber, Parlon(in the USA), ADEKA rubber (in Japan)

A white powder. It is known as a chlorine donor for producing coloured flames. It contains 66-67% chlorine and is easily soluble in acetone, but it is insoluble in alcohol(s. Lancaster's book p.34).

Chlorinated isoprene rubber and also PVC which is described next react not only as a chlorine donor, but also as a fuel. They are, however, different from each other regarding the extent of their reaction as a fuel. According to experiments it may be assumed in practice that the rubber is only a chlorine donor, but PVC is both a chlorine donor and a fuel when they are used for chlorate or perchlorate based compositions.

(63) Carbon hexachloride, Hexachloroethane, C_2Cl_6

Molecular weight: 236.74. Colourless crystals, which slowly sublime at room temperature producing an odour. It melts at 182~187°C. Insoluble in water, but soluble in ethyl alcohol, ether and acetone. This is a solid chlorine producing agent and 89.8% chlorine. It may be used as a colour deepening agent for flare compositions, but at present it is not used because of its volatility. It is used for white smoke composition, as described in 31., which is sealed in a tin case.

A mixture carbon hexachloride and zinc dust generates a large amount of heat when it is moistened. It is said that it comes from a trace of acid contained in the carbon hexachloride.

Manufacture. First carbon tetrachloride, $CCl_2:CCl_2$, is prepared by an alternate reaction between chloride and slake lime on acetylene. The carbon tetrachloride is then chlorinated with chlorine gas under light beams.

Packing and volume for storage. A wooden case with inner paper bag. 1.5 m^3 per 1 kg of the material.

Quality. The material on the market often has coarse grains of 3~5 mm in size. The difference in the crystal size does not seem to have much influence upon the duration of the smoking. But it is better to use it after crushing it to pass 16 mesh to avoid delay in the initiation of the smoke composition.

One analysis showed that it contained 0.03% moisture, 0.02% insoluble matter in alcohol and 0.03% acid. The melting point was 184.0~186.5°C.

(6k) Polyvinyl chloride, PVC, $CH_2:CH.Cl$

A white powder, with a grain size which varies according to the manufacturing process; 0.2~2µ by milk polymerization and 20~150µ by grain polymerization. The specific gravity is 1.35~1.45 and the softening point 70~80°C. It is not attacked by water or alkalis and by strong acids; it dissolves in tetrahydrofuran, methyl ethyl ketone or cyclohexane. Polyvinyl chloride in the ordinary state degenerates slowly generating HCl gas, becoming discoloured. This reaction is promoted by the air, especially by oxygen, or by sun beams. Therefore, a stabilizer like the stearate of zinc or calcium is added to polyvinyl Chloride when it is used for plastic. But in the case of coloured flame compositions, which contain magnesium and polyvinyl Chloride being shaped into etars, it was not possible to find any generation of HC1 at all in spite of a long storage for two or three years. This may depend on the suppressing effect of magnesium hydroxide, which is produced in small amounts in the composition, thus avoiding degeneration. (Anyhow such compositions show a small amount of strong alkalinity; pH values of about 10 in distilled water.)

When polyvinyl Chloride is heated, it dissociates at about 170°C being carbonized to generate gas which is mainly HC1. Polyvinyl Chloride, therefore, is used quite favourably as an HC1 gas producing agent to deepen the colour of flames. Too rauch however causes the generation of soot which decreases the light intensity and sometimes spoils the colour of the flame. Therefore 10~15% by weight % of the polyvinyl Chloride for the compositions which contain magnesium and less than 4% by weight for other compositions may be the most adequate except when it is used as a Fuel. Polyvinyl Chloride contains carbon which allows the flame to become transparent by the reduction of the metal oxide particles in the flame, and is used also as a reducing agent.

Manufacture. The monomer of polyvinyl Chloride is gas at room temperature and has a boiling point of -13.9 C. The monomer is manufactured in two ways: (1) Acetylene and HC1 gas are allowed to pass over active carbon and to react with each other at 150—200 C; (2) chlorine gas is allowed to react on ethylene to produce $C_2H_4Cl_2$(EDC) at 200~350°C to produce vinylchloride and HCl gas. These are separated by distillation. The monomer is then polymerized in a pressure vessel; the mixture of water and liquid monomer is stirred violently. Benzoyl peroxide is used as a catalyzer and polyvinyl alcohol as a dispersion agent for the reaction. The conditions are 10 atm, 40°C and 50 hours.

Packing. Kraft paper bags.

Miscellanea. Polyvinyl Chloride powder is quite easily charged, with electricity during operations and it adheres to every thing. Rather coarse grains give less light intensity than the fine grains.

The burnt polyvinyl Chloride cover of electric wire has a little electrical conductivity which is not found in the case of cotton, silk or enamel covers. This phenomenon is applied to an electric heat relay in some pyrotechnics.

(65) BHC, Benzene hexachloride, $C_6H_6Cl_6$

Six isomers are separated from industrial products; α, β, γ, δ, ε, η. They have slightly different physical characteristics. Only the γ BHC is effective as insecticide. Industrial products generally contains 55~80% α BHC and only 8~15% γ BHC. The γ BHC which is separated from the industrial products to more than 99% purity is called "Lindane". It is best to use the bi-product from the manufacture of Lindane for firework material.

BHC has white crystals which have a specific gravity of about 1.9. γ BHC has the lowest melting point, 112~113°C, and β the highest, 309~310 C. All the isomers are insoluble in water, but soluble more or less in alcohol, ether or acetone.

When BHC is heated, it vaporizes without carbonization. It is difficult to ignite BHC or its vapour in the air, but when once ignited, it burns generating soot and HC1 gas. Therefore it is used as an HC1 producing agent and reduction agent for coloured flames. But it is not as effective as PVC. But in the case of twinklers BHC is used for the compositions in place of PVC, because BHC does not disturb the flickering of the flame.

Manufacture. Chlorine gas is introduced into benzene under sunlight or a fluorescent lamp. The reaction temperature is 25~40°C. Or chlorine gas is introduced into 1~2% sodium hydroxide solution in water, on which benzene is floated. Lindane is manufactured by the purification of industrial products by methanol.

By JIS standards it is required that γ BHC must be more than 12% of the total BHC, the weight decreases on drying should be less than 1.0%, the insoluble matter in acetone less than 1.0%, hydrochloric acid less than 0.1%.

(66) Anthracene, $C_{14}H_{10}$

Molecular weight: 178.24. It has a specific gravity of 1.250, melts at 216.2 C, boils at 342°C Insoluble in water, and hardly soluble in alcohol(0.076 g per 100 g of ethanol at room temperature). Purified anthracene has pure white snow-like crystals, but is generally somewhat yellowish. In summer it sometimes causes trouble with workers by producing skin eruption but this varies with constitution. It is used for compositions of black smoke.

Manufacture. (1) Crystallized from crude anthracene oil and the impurities of phenanthrene, carbazole etc. are removed. (2) Distilled in an iron retort, in which crude anthracene oil is charged together with an alkali carbonate. The distilled matter contains phenanthrene, which is removed by carbon disulphide.

Packing. In tin cases.

Quality. It is tested by heating it in a porcelain crucible. If tar-like matter remains, a small amount of impurity is contained in the anthracene. For firework use it must be of good quality, otherwise the burning surface of the smoke composition is often covered by the tar-like matter which extinguishes the fire. The material on the market passes 25 mesh. An example on analysis showed that it contained 0.50% ash, had a specific gravity of 1.23 and a melting point of 210~212 C.

(67) Naphthalene, Tar camphor, White/tar, $C_{10}H_8$

Molecular weight: 128.18; specific gravity: 1.168; melting point: 80.05°C; boiling point: 217.96°C. Colourless crystals, which are insoluble in water, soluble in benzene, absolute alcohol and ether, slowly sublimes at room temperature.

From early times it has been used for black smoke in combination with potassium chlorate. The composition cannot be stored for a long time, because the naphthalene sublimes, but the black colour of the smoke is so clear, that it is quite popular in use even at present. Care must be taken because there is often a risk of changing the ratio of the components spontaneously to form a dangerous composition due to the sublimation of the naphthalene.

Manufacture. Obtained by crystallization from naphthalene oil, which is obtained by the fractional distillation of coal-tar, and then purified by sublimation.

Packing. In tin cases.

(68) Picric acid, Trinitrophenol, $C_6H_2(NO_2)_3OH$

Molecular weight: 229.11; specific gravity: 1.767; melting point: 122.5°C. 1.2 g of picric acid is soluble in 100 g of cold water and 7.2 g in 100 g of hot water; soluble in alcohol, ether or benzene. It forms picrates, which are sensitive to shock and friction, in combination with lead, iron, copper or other salts.

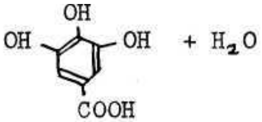
Picric acid contains oxygen, and is a strong explosive. It burns in the air with a flame generating a small amount of soot, which is caused by the insufficiency of oxygen in it. It is used for increasing the brilliancy of a flame by the radiation of the carbon particles, but for this purpose it may be replaced by lampblack or camphor. It is said that picric acid in combination with potassium chlorate or potassium nitrate produces chloric acid or nitric acid, which can cause spontaneous ignition.

Picric acid is used for manufacturing potassium picrate for whistles. It is sometimes used as a combustion agent for black snakes. When handling picric acid ordinary metallic containers or tools must be avoided.

Manufacture. (1) Chlorobenzene is nitrated with a mixture of sulphuric acid and nitric acid to produce dinitrochlorobenzene, which is synthesized to dinitro-sodium phenolate under reaction with sodium hydroxide. This is further changed to dinitrophenol with hydrochloric acid and then the dinitrophenol is nitrated by a mixture of sulphuric acid and nitric acid to trinitrophenol, picric acid. (2) Phenol is mixed with conc. sulphuric acid and heated to obtain phenol-sulphonic acid. This is nitrated with a mixture of sulphuric acid and nitric acid to trinitrophenol.

Packing. It is forbidden to use metallic containers. A wooden cask is best.

(69) Gallic acid, $C_6H_2(OH)_3COOH + H_2O$



Colourless needle shaped crystals; molecular weight: 188.14; specific gravity: 1.694; melting point: 222°C(becomes pyrogallol).

$$\underset{\text{Gallic acid}}{C_6H_2(OH)_3COOH} \rightarrow \underset{\text{Pyrogallol}}{C_6H_3(OH)_3} + CO_2$$

It is soluble in water or alcohol. This is a raw material for blue-black ink, but for fireworks it is used in combination with potassium chlorate as a whistle composition, which is quite sensitive to shock and friction.

Manufacture. This substance is found naturally in tea. Also it occurs as tannin in galls. Gallic acid is obtained by the hydrolysis of the tannin.

(70) Guanidine nitrate, $NH:C(NH_2)_2.HNO_3$

An organic molecular compound of one molecule of guanidine and one molecule of nitric acid. Molecular weight: 122.09; colourless grainy crystals; specific gravity: 1.44; soluble in water, 12.5 g at 20°C, 41 g at 50°C and 99 g at 80°C in 100 g of water; soluble in methanol or ethanol in small amounts; insoluble in ether or acetone. The purity of this material on the market is about 95% and white insoluble matter remains undissolved in water. It melts at 208 C and begins to decompose at 235°C, generating ammonia gas actively, leaving a yellowish substance which is insoluble in acid. It is difficult to ignite the gas, but when guanidine nitrate is suddenly heated to 400~500°C, it ignites and burns furiously with an orange flame. Red phosphorus, charcoal powder, copper powder, copper compounds(copper oxide, copper sulphate, basic copper carbonate etc.), compounds of chromium or of manganese have catalytic action to decompose guanidine nitrate into ammonia gas. The material on the market looks hygroscopic, but actually the moisture content is as small as 0.4%, which is observed at a relative humidity of 90%(left for ten days).

Guanidine nitrate is stable to ordinary mechanical actions, shock and friction. But when it is initiated by a strong booster like RDX, it detonates partially, but perfect propagation of the detonation is difficult (Y. Mizushima: Initiation test of ammonium nitrate, its mixtures and nitrates of organic bases, Journal of the industrial explosive society, Japan, p.23, volume 33(1972)). A mixture of guanidine nitrate and red phosphorus, antimony trisulphide or sulphur cannot be ignited or exploded by shock or friction, and cannot continue burning, even when it is ignited by some heat source. A mixture of guanidine nitrate and potassium chlorate cannot continue burning.

Guanidine nitrate which is mixed with a catalyzer and consolidated into small cylinders is sold in England as a fuel for toy airplanes under the name of "JETEX". It is rather difficult to ignite this fuel. But when it is once ignited, it burns at a much lower temperature than other rocket fuels; the burnt gas is about 250~300°C.Guanidine nitrate is also used for the compositions of some special smoke generators like insecticidal smoke or gas generators.

13.7. Paste and binding agents

Recently synthetic resins have been very much developed as pastes or binding agents, but unfortunately these are often damaged by heat. Further these resins or their vapour often permeate into compositions slowly during long storage to degenerate them. When they are used as a binder for some compositions, they become generally difficult to ignite. The vapour of synthetic resins is not good for health and for this reason the paste or binding materials naturally produced are still quite important.

The characteristics of binding agent which are required for firework use are as follows:

(a) The binding agent must have a strong cohesive power, but threading must be avoided if possible. When the cohesive power is very large, even the smallest amount allows the composition to consolidate well and it does not decrease the burning temperature very much.

(b) The binding agent must give strong water or solvent resistance to the composition when it is consolidated. Otherwise when the composition comes in contact with another slurry composition as in the case of the manufacture of round stars, the water or solvent in the slurry destroys the composition or it passes deeply into the grains of the composition and remains in it to cause burning problems.

(c) The binding agent must produce a composition which is very hard on consolidation. The hardness is necessary to protect itself from the shock caused by the bursting charge.

(d) The binding agent must not disturb the drying of shaped compositions.

(e) The binding agent must not cause cavities in the composition when it is dried.

(f) The binding agent should be soluble in water or solvent even in a cold state. If it is soluble in a cold state, we can generally add it to the composition in an accurate ratio before consolidation.

(g) The binding agent must allow a kneaded composition to be easily formed into a shape or cut with a knife.

(h) The binding agent should be more or less neutral in solution in water and cause no reaction with other chemicals in the composition,

(i) The binding agent must not disturb the ignition or burning of a composition.

(j) The binding agent must not cause degeneration during long storage.

(k) The binding agent should not be hygroscopic.

(1) The binding agent must not disturb the colour of the flame of a composition.

Table 15 shows a comparison of various kinds of binding agents which are soluble in water and which were tested by manufacturing 10 mm cubic stars.

Table 15. Comparison of the characteristics of water soluble binding agents used for 10mm cubic stars

	Comp.	M.S.	C.P.	W.R.	H(kg)	DTR(h)	DT50(h)	C.F.	S.W.	Cut.	Acid.	B.R. (mm/s)	D.C.
GRS	C	Pow.	○	○	6.0	61	-	○	○	△		2.1	×
"	"	Pas.	◎	◎	9.0	64	-	○		△	△	2.3	×
"	P	Pow.	○	○	7.5	-	5.9	○	○	△	△	1.5	×
"	"	Pas.	◎	◎	7.7	120?	9.0?	○		△	△	-	×
ORS	C	Pas.	△	△	6.5	67	-	○	×	○	△	2.1	×
"	P	"	△	△	13.5	110?	2.4	○		○	△	1.2	×
WF(w)	C	"	△	×	6.5	56	-	○	×	△	△	2.3	×
"	P	"	△	×	10.0	41	1.2	△		△	△	1.0	×
WF(s)	C	"	△	×	8.0	75	-	○	×	△	△	2.1	×
"	P	"	△	×	12.5	54	1.4	○		△	△	1.1	×
WS	C	"	△	○	-	50	-	○	×	△	△	2.0	×
"	P	"	△	△	8.0	57	3.6	○		△	△	1.3	×
DEX	C	Pow.	×	×	8.0	42	-	×	○	×	△	2.4	×
"	P	"	×	△	18.0	31	1.9	×		×	△	1.2	×
GA	C	Pas.	×	×	3.0	42	-	×	○	×	○	2.4	×
"	P	"	×	×	14.5	27	0.9	×		×	○	1.3	×
CMC	C	Pow.	△	×	10.5	-	-	○	○	△	△	3.4	×
"	P	"	△	△	12.5	64	1.1	○		△	△	2.1	×

Note: Comp. = Composition.
M.S. = Mixing state of the composition.
C.P. = Cohesive power of the kneaded mass.
W.R. = Water resistance of the dried stars.
H(kg) = Hardness in kg(the maximum loaded weight when a star is crushed between an iron anvil and a plastic pestle(ABS) with a flat head 3mm diameter).
DTR(h) = Drying time at room temperature(hour).
DT50(h) = Drying time at 50°C in a drier.
C.F. = Cavity formation in composition.
S.W. = Solubility of the raw material in cold water.
Cut. = Easiness of cutting kneaded composition.
Acid. = Acidity in water solution.
B.R. = Burning rate of composition in 1 atmosphere.
D.C. = Disturbance of flame colour.
GRS = Glutinous rice starch.
ORS = Ordinary rice starch.
WF(w) = Wheat flour(weak).
WF(s) = Wheat flour(strong).
WS = Wheat starch.
DEX = Dextrine.
GA = Gum arabic.
C = Potassium chlorate base composition(67% potassium chlorate, 14% combustion agent, 13% strontium carbonate, 6% binding agent).
P = Potassium perchlorate base composition(67% potassium perchlorate, 14% BL combustion agent, 13% strontium carbonate, 6% binding agent).
Pow. = Powder.
Pas. = Paste.
O mit Punkt = The largest or easiest of all.
O ohne Punkt = Large or easy.
Dreieck = Middle or neutral.
X = Small, weak or difficult.

(71) Soluble glutinous rice starch (Mizinko)

There are two kinds; glutinous rice starch is parched and then ground into a powder, which is called "Quick Starch"; glutinous rice starch is steamed or further pounded into a cake, parched and ground into a powder, which is called "Parched Starch". At present the material on the market is not the latter, but the former, but for firework use the latter, parched starch, is better than the quick starch.

The glutinous rice starch contains about 80% carbohydrate, about 7% albumin and about 14% moisture. The carbohydrate consists of only amylopectin, which is a group of long branched chains of grape sugar molecules. (On the contrary the group of long but unbranched chains of the sugar molecules is called amylose. These are detected by adding iodine solution in alcohol to the solution of these substances; amilopectin gives red violet, but amylose blue indigo colour.)

When a small amount of water is added to the glutinous rice starch and kneaded, it becomes like rice cake and quite cohesive. But when we add a large amount of water to the starch and boil it for long time, the cohesive power of the starch decreases; this shows that the amylopectin changes to amylose.

The cohesive power of glutinous rice starch is very strong; this is seen clearly by comparing this starch with others like dextrine. Add ten times as much water to glutinous rice starch and stir well. Test it between the fingers, and it is clear how far more cohesive it is than a dextrine solution which is prepared in the same way.

This cohesive nature of glutinous rice starch is quite important especially for preparing round stars, because the essential point of the process lies in that the composition must be pasted in a wet state on the core using as little paste as possible. Accordingly a paste which has a strong cohesive power satisfies the requirement well. For this reason glutinous rice starch is quite superior for manufacturing round stars. In other words, it is not too much to say that the Japanese round stars are widely developed only by the presence of the glutinous rice starch.

However the cohesive power of the paste of glutinous rice starch generally changes as the time passes when it is mixed with chemicals or compositions. For example, an experiment in the summer season is set out in Table 16.

Here 20 cc of distilled water was added to mixtures of 2 g of glutinous rice starch and 20 g of other chemicals. The mixture were stirred well and the viscosities were observed at definite time intervals.

Table 16. The influence of chemicals upon the viscosity of soluble glutinous rice starch

	15 hours after	24 hours after
- Blank	**S**	s
$KClO_3$	ss	ss
$KClO_4$	w	ww
$NH4ClO_4$	www	wwww
KNO_3	ww	www
$Sr(NO_3)_2$	ww	ww
$Ba(NO_3)_2$	**0**	**0**
$Na_2C_2O_4$	**0**	**0**
$CuS0_4$	ww	ww
Black powder	**0**	**0**
S	**0**	**0**
Pine charcoal	**0**	**0**
Na_2CO_3	sss	sss
Realgar	s	ss
Al (Powder)	s	s
Sl_2S_3	w	**0**
Red phosphorus	w	ww
Shellac	s	ss
Rosin	w	ww
$NaNO_3$	ww	ww

Note: s : The mixture does not change in viscosity and somewhat flows.
SS '• The viscosity increases and the mixture hardly flows.
SSS : The viscosity increases greatly.
W '• The viscosity somewhat decreases and the mixture flows fairly.
WW : Soft and flows well.
WWW : Quite soft and can be ruffled by shaking,
WWWW: Quite low viscosity which is hardly felt.
O : Quite low viscosity like water.

The above table shows that the starch alone does not change in viscosity. Sodium carbonate and potassium chlorate increase the viscosity. Realgar and aluminium have almost no influence upon the viscosity. Other substances generally decrease the viscosity. Sodium oxalate, barium nitrate, black powder, sulphur and charcoal particularly cause the starch to lose its viscosity. Ammonium perchlorate also has a large influence.

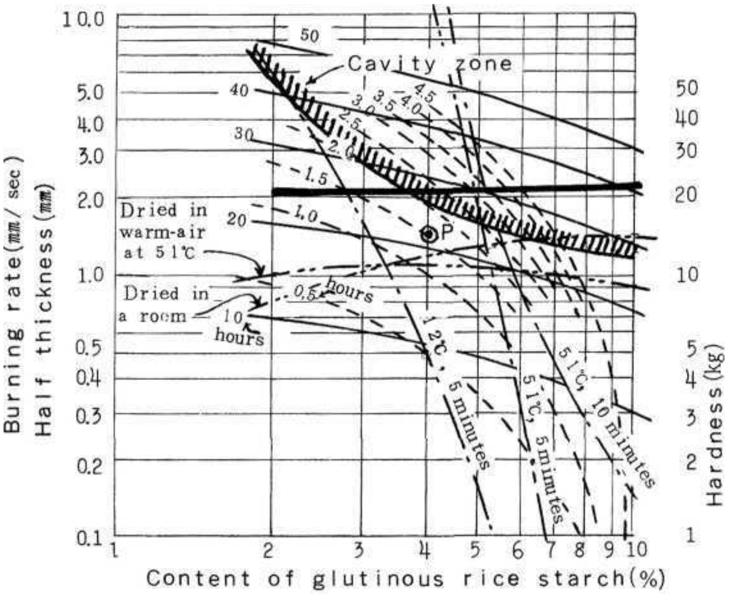
The decrease in the viscosity caused by sodium oxalate or black powder, which are the most powerful, was more precisely observed. In the first one or two hours it looks as though there is an increase in the viscosity, and then the viscosity slowly decreases; after five or six hours the viscosity is not so different as that at the beginning. This property of glutinous rice starch does not cause any trouble in manufacturing stars, but the paste of a composition which contains glutinous rice starch must not be left more than half a day.

Glutinous rice starch has the smallest hygroscopic degenerative nature of all popular starches, but for long storage it is preferable to place the product which contains glutinous rice starch in dry conditions as far as possible, and at more than 5°C if possible, because the degeneration of starches occurs most easily at 30~60% moisture and a temperature of 2~3°C. Careful kneading is also effective for avoiding degeneration.

Fig.56 and 57 shows the influence of glutinous rice starch upon a chlorate composition and a perchlorate composition respectively when stars are manufactured with it as a binder. The symbols are as follows:

——— : dried thickness over a given period at room temperature,
------ : dried thickness over a given period at 50°C in a warm-air drier,
—·—·— : thickness which absorbs water over a given period when the star is dipped in water (water resistance curve),
—··—··— : hardness, the values show the maximum load when a 10 mm cubic star is not crushed (s.note(2) in table 13-),
━━━ : burning rate at 1 at.

For example, a 3 mm cubic cut star of the chlorate composition containing 4% glutinous rice starch is denoted by a point P in Fig.56 (the half thickness of the star is 1.5 mm). We know from the lines that the star is dried in 1.5 hours in a warm-air drier at 50°C or in 22 hours in a room at normal temperature. It takes more than 5 minutes at room temperature to completely soak it with water. The hardness of the star is 12 kg if it is dried in a room at a normal temperature and 10.5 kg in a warm-air drier at 50 C. The burning rate of the star is 2 mm/sec. A star of perchlorate composition corresponding to the above is denoted also by a point P in Fig 57, and shows that the drying time is 1.3 hours in a warm-air drier, 35 hours in a room at a normal temperature, the water soaking time 8 minutes, the hardness 7.4 kg and the burning rate 1.1 mm/sec. In manufacture it is necessary to avoid the cavity zone in Figs. 56 and 57.



al 1 2 3 1| 5 6 Y 8 9 '10
Content of glutinous rice starch(%)

Fig.56. Content of glutinous rice starch and the characteristics of a chlorate composition(67 parts potassium chlorate, 14 parts BL combustion agent, 13 parts strontium carbonate and x parts starch by weight).

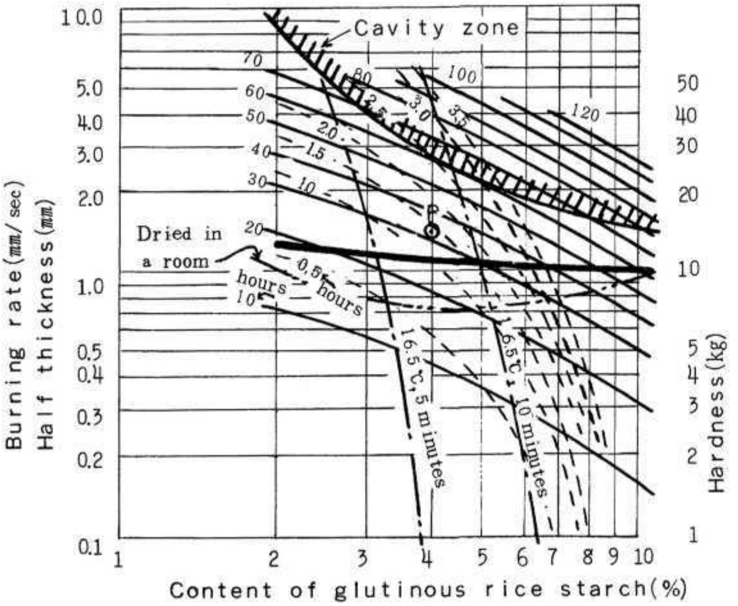


Fig.57. Content of glutinous rice starch and the characteristics of a perchlorate composition(67 parts potassium perchlorate, 14 parts BL combustion agent, 13 parts strontium carbonate and x parts starch by weight).

Manufacture. (1) Parched glutinous rice starch: Glutinous rice is polished and soaked in cold water for a week. This is then steamed in a steam basket and pounded into a cohesive mass. The mass is stretched into a thin plate like a squashed cake, which is parched at a suitable temperature. The parched cake is ground into a fine powder. The powder is somewhat brownish, but has a large cohesion power and is perfectly gelatinized in combination with water. This is the most useful binding agent for firework stars. (2) Quick glutinous rice starch: Glutinous rice is polished, parched and ground into fine powder. To keep a good appearance, it is not heated as much as the parched starch, and it is less cohesive than the parched starch.

Packing. Paper bags.

(72) Wheat flour

This material varies in character according to the kind of wheat and the method of manufacture. For example, the soft wheat flour produced in the USA has a milling yield of 80%, contains 8.8% alubumen, 88.6% carbohydrate, 1,4% fatty material, 0.5% cellulose, 0.7% ash and the effective heat of combustion value is 339 Kcal per 100 g (J.Ozaki, Y. Sakurai and N.Watanabe: Handbook of manufacturing confectionery, p.31 (1965)). With lower yields the amount of carbohydrate increases. The particular character of the wheat flour lies in that it contains a small amount of gluten, which corresponds more or less to the alubumen content and it is insoluble in water, however it becomes elastic as water is absorbed. Wheat flour which contains a large amount of gluten is called "strong flour" and as the amount decreases it is called "middle flour" and then "weak flour". Strong is a slightly yellow colour and weak flour is white. For firework use, especially for pasting paper shells, weak flour is recommended, because its paste spreads well on paper. All of them can be used as combustion agents.

As a combustion agent it generates a combustion heat of about 800 kcal per 1 kg of mixture of wheat flour and potassium chlorate; this value is the largest compared to other materials such as milk sugar, cane sugar and dextrine etc.

Generally wheat flour contains about 14% of moisture.

(73) Wheat starch

This material must not be confused with wheat flour described above.

This is a starch which is obtained by separating the gluten from wheat flour.

Paper articles used in fireworks, such as figures, flags or parachutes, which are folded into a shell, must open perfectly in the air after the shell is burst. When wheat starch is used for pasting paper sheets, the pasted part is soft and flexible, and this allows the paper pieces to open well. This material is used for pasting shells also.

To prepare wheat starch paste, add about ten parts of water to one part of starch by weight and heat it, stirring until it looks slightly bluish. Cool it to the gelatinized state, put it into cold water and leave it in the water for four or five days. Before use, it is filtered with a cloth.

Manufacture. Add sodium chloride solution in water to wheat flour and knead it well until it becomes cohesive. Put it into a cambric bag, soak it into water and rub it until the starch comes out of the bag through the texture and settles on the bottom of the vessel. This is wheat starch and the cohesive substance which remains in the bag is gluten,

(74) Casein

Casein is a phosphoprotein. It is the main protein of milk, and the name "casein" often refers to milk casein. Pure casein is white, but it is sold on the market as creamy or slightly greyish brown grains. It is insoluble in water, alcohol or ether, but it slowly dissolves in alkali, carbonate and strong acid. The material which passes 60 mesh is the best for paste.

Casein glue is inferior to synthetic resins in durability and resistance to water, but it is very cheap and not detrimental to health, and is still popularly used at present.

Manufacture. The natural zymotechnics process (lactic acid fermentation): When lactic acid is formed in milk by the action of lactic acid bacilli, the casein coagulates due to the acidity of the lactic acid. There are several other methods.

Quality. One analysis was as follows (Kanamaru: Cohesion and cohesive materials, p.80 (1935)).

Manufacturing process	Moisture %	Fatty matter %	Ash %	Nitrogen %	Acidity (1/10 N NaOH) cc/g
Lactic acid fermentation	7.87	0.27	2.16	14.84	8.7
Sulphuric acid process	7.81	0.35	4.05	14.46	7.6
Hydrochloric acid process	7.10	0.16	5.74	14.32	6.7

(75) Gelatine

Gelatine is generally used in match composition. The purpose may be to give good ignition and to maintain fire.

Gelatine is colourless and forms transparent glass-like sheets or grains, which are tasteless and swell absorbing 5~10 times as much cold water. It is easily soluble in hot water, but insoluble in alcohol or ether. The solution in water is neutral or slightly acid. The solution sets as it cools like Japanese isinglass. The solution in water forms a white precipitate with tannin acid. The jelly, which is obtained by adding potassium bichromate to a hot gelatine solution in water, becomes insoluble in water when it is placed in the sun. When formalin is added to gelatine solution in water, it increases the gelling power, and makes the film tough after drying.

Successive heating and cooling of gelatine solutions decrease the gelling capacity, but they can be gelled again by adding formalin to them.

There is no clear distinction between gelatine and glue. There are also many products due to the varied raw materials and manufacturing processes. Gelatine is the name of a product of good quality produced by using good raw material and a rational process. The items are selected according to the purpose for which they are needed; cohesive power, the nature of the gelatine or gelling power.

Manufacture. Skins, bones or tendons, which contain collagen or ossein, are heated in water. The solution is purified according to the required use.

(76) Nitrocellulose, Cellulose nitrate, Nitrocotton,

$$[C_{12}H_{14}O_4(OH)_4(ONO_2)_2]_x \sim [C_{12}H_{14}O_4(ONO_2)_6]_x$$

A white powder which is very easily scattered in a dry state, or a cottonwool-like matter. Molecular weight: 426.4~594.3. In practice the nitrogen content varies from 9.0% to 13.4% and 11-12% is the most popular commercially for firework use. Nitrocellulose is soluble in acetone, ethyl acetate, amyl acetate etc. Nitrocellulose which contains less than 12% nitrogen dissolves in a mixture of ether and ethanol in a ratio 2:1 by volume. This solution can produce a stronger film of nitrocellulose than one in acetone.

Nitrocellulose is a nitric ester. In a well dried state it ignites explosively at 160-180°C, when burnt in 1 at. it produces a gas which consists of e.g. 25% No_x, 42% CO, 18% CO_2, 8% H_2, 6% N_2, 1% CH_4 by volume;

it explodes on sudden heating or with a strong shock or friction. It is unstable and decomposes above 70°C generating NOx gas even when the quality is good. It decomposes slowly even at room temperature especially if there is a trace of acid or an impurity. These characters increase as the nitrogen content increases. To suppress spontaneous decomposition we add a small amount of diphenylamine, about 1 g per 100 grams of nitrocellulose, in a nitrocellulose solution.

It is important to keep it in a wet state with water or ethanol during storage. Never scatter it because it becomes a dangerous inflammable dust floating in the air. It is used as a solution in acetone or amyl acetate and is known as "NC paste", for the consolidation of compositions which contain magnesium.

Manufacture. Linter or cotton waste is purified by boiling it in a dilute NaOH solution and well dried. It is dipped into a mixed acid which consists of sulphuric and nitric acids in a weight ratio about 7:3. The ratio of the cotton linter to the mixed acid is about 1:50 by weight. It is kept at room temperature for 2.5 hours and the linter is then nitrated to the nitrocellulose. The required nitrogen content is obtained by adjusting the water content in the mixed acid; for example, about 17.5% H_2O is adequate to obtain 12% N. The nitrated linter is separated from the mixed acid. It is washed with water and boiled in a 0.01% Na_2CO_3 solution in water for about two days renewing the solution several times in order to remove traces of acid. Lastly it is beaten in water with a beater to form fine particles and finally washed with hot water until it passes a heat resistance test.

Quality. JIS standard (K 6703) shows two grades of nitrogen content, L: 10.7~11.5% N and H: 11.5~12,2% N which are easily obtained on the market. They are further classified by viscosity into various kinds and denoted by figures such as 1/4, 1/2,. . . . .60, 120, 200, which show a falling time in seconds of a 2 gram iron ball between two levels 254 mm apart from each other in a nitrocellulose sample solution (mainly 12.2% nitrocellulose). For example, we often use H60 where H means the 11,5~12.2% nitrogen content and 60 means the falling time in sec.

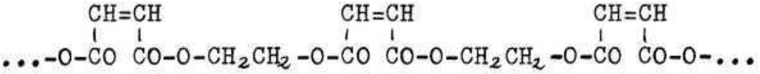
The standard requires that the nitrocellulose shall contain less than 0.03% acid as H_2S0_4 (or less than 0.04% acid for viscosities ***1/4,*** 1/8, 1/16) and less than 0.3% ash; the heat resistance shall be more than 7 minutes at 80°C by Abel's heat test; the ignition point shall be higher than 180°C.

Packing and volume for storage. 1 kg in a moistend state with more than 20% ethanol in a tin case. 6 Liter per 1 kg. Take care to store it in a cool place.

(77) Polyester (unsaturated polyester)

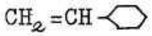
The representative polyester on the market is a solution of polyethylene malate(ester) in styrene monomer in various ratios to obtain various hardnesses.

Polyethylene malate consists of very long molecules which contain many double bond. Styrene monomer consists of short molecules which contain one double bond. (In place of the styrene monomer methyl metaacrylate or diallyl phthalate are also used.)

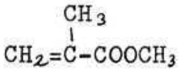


$$\cdots\text{-O-}\overset{\text{CH=CH}}{\text{CO}\quad\text{CO}}\text{-O-CH}_2\text{CH}_2\text{-O-}\overset{\text{CH=CH}}{\text{CO}\quad\text{CO}}\text{-O-CH}_2\text{CH}_2\text{-O-}\overset{\text{CH=CH}}{\text{CO}\quad\text{CO}}\text{-O-}\cdots$$

(1) Polyethylene malate

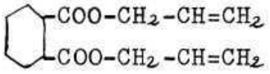


(2) Styrene monomer



$$\text{CH}_2\text{=}\overset{\text{CH}_3}{\text{C}}\text{-COOCH}_3$$

(3) Methyl metaacrylate

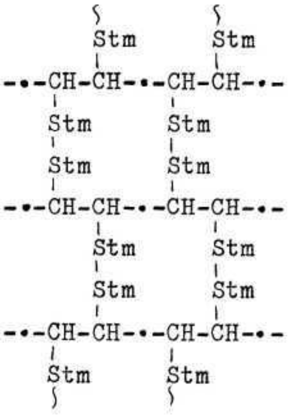


(4) Diallyl phthalate

The melting and boiling points of above substances are as follows:

	Melting point	Boiling point
(2) Styrene monomer	-31°C	146°C
(3) Methyl metaacrylate	-	157
(4) Diallyl phthalate	-50	101

These long and short molecules combine with each other at the double bonds in three dimensions by an initiation of a catalyzer to a solid mass as follows:



Stm: from styrene monomer, -•-CH-CH-•-CH-CH-•-: from polyethylene malate. When we use a proper catalyzer the reaction is initiated at room temperature and it is accelerated by a temperature rise owing to the heat of reaction.

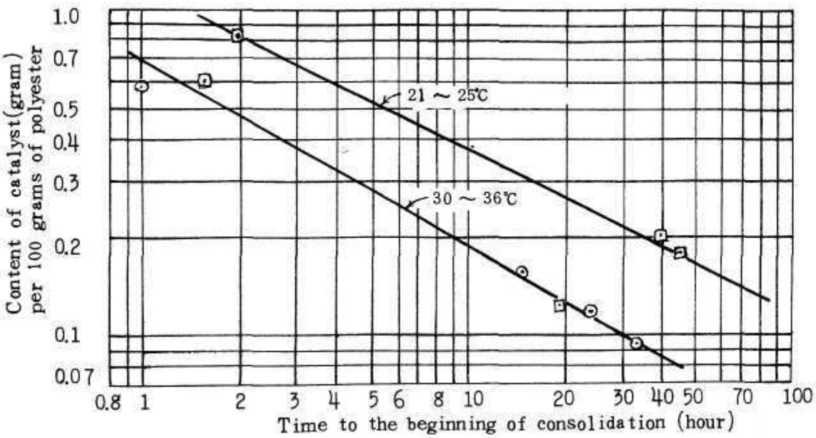
Benzoyl peroxide, $C_6H_5CO\text{-}O\text{-}O\text{-}COC_6H_5$, or methyl ethyl ketone peroxide, $CH_3C_2H_5\text{-}C(O\text{-}O)_2CC_2H_5\text{-}CH_3$ is used as a catalyst. To initiate the reaction at room temperature it is necessary to add another substance such as cobalt naphthenate, $(C_{10}H_7C00)_2CO$, or dimethyl aniline, $C_6H_5(CH_3)_2$, to produce an initiator, e.g. free radicals $C_6H_5C{:}00$(benzoil radical).

Consolidated polyester shows different physical characters owing to the ratio of the quantity of the ester to that of the monomer; the specific gravity is 1.2~1.4, tensile strength 350~700 kg/cm^2, compressive strength 850~1700 kg/cm^2-. Generally it is hard and brittle. Its resistance to inorganic acids and alkalis is weak.

Polyester is used as a binder as well as a fuel for a composition. For example, a flare composition which does not contain magnesium can contain about 20% polyester by weight and it can be cast into a container. In this case the composition shrinks in diameter on consolidation and between the composition and the container it produces a gap which often causes a quick fire problem. The diameter of the container is therefore generally limited to a maximum of about 25 cm. For a composition which contains magnesium the quantity of polyester is kept to the minimum; about 2~5% by weight to prevent the flame temperature dropping. In this case the composition does not flow and it is pressed into a container with quite a high pressure. Stars which are consolidated with polyester as a binder have a high density, low ignitability and a small burning rate. Naturally they cannot be used for shells which require the opposite characteristics.

Composition which contains magnesium and is consolidated with polyester is not really as waterproof or moistureproof as it is thought. This may be perhaps due to the fact that the polyester has a weak resistance to acids and alkalis. The coating effect for magnesium powder is not as good as that of paraffin.

The amount of catalyst which is added to polyester for consolidation may vary according to the purpose but for a commercial sample it is generally limited to a maximum of *1%* to avoid too great a temperature rise and rapid consolidation as these are both dangerous and produce an inferior quality. It is thought that a small quantity of catalyst produces the best effect. Moreover the time of consolidation differs according to the brand, the quantity of the catalyst and the temperature. An example for the consolidation of a composition is shown in Fig.58.



0.8 1 2 5 \ 5 6 8 10 20 50 1|0 50 70 100
Time to the beginning of consolidation (hour)

Fig.58. An example of consolidation of a firework composition which contains polyester.

In this case over 30°C a viscous matter oozes from the composition and covers its surface or it oozes out of the paper container. It may be caused by the separation of the monomer from the ester. Sometimes it damages the product, and it is recommended to keep the room temperature below 20°C.

Many substances which are used for firework composition more or less have an influence upon the time of consolidation; sulphur, sulphide or organic fuels particularly delay the consolidation.

The toxicity of the polyester comes mainly from the vapour of the monomer, but it is said that the toxicity is slight or moderate and does not produce serious physical impairment (N.Irving Sax: Dangerous properties of industrial materials, 4th. edition(1975)).

Manufacture. The ester, e.g. polyethylene malate is derived from maleic anhydride, O=(CO-CH=CH-CO), and ethylene glycol, $HOCH_2CH_2OH$. Here the ethylene glycol is obtained from an oil industry. The ester is dissolved in a monomer, e.g. styrene, in a ratio which gives the desired hardness.

13.8 Paper

Paper is used for flags, figures or parachutes, which are contained in a shell as display pieces, or for making various containers, shells, paper mortars etc. The type of paper is selected to suit a particular purpose.

The special property of paper may be set out as follows: Fragments of a paper shell do not damage people or things due to the small apparent specific gravity and softness of the paper. Paper has strength to some extent and it can keep a definite form. Paper is pervious to air or moisture and does not accumulate gas; this allows us to manufacture dangerous firework items by a wet process. Paper is easily cut, pasted, bent, nor is it softened by heating. Paper hardly disturbs the colour of flames, but it has weak resistance to water and fire often causing trouble. Paper expands and contracts due to the action of moisture. Thick paper can be shaped under pressure in a heated mould.

When we use paper skillfully, it is economically and technically quite useful.

(78) Kozo-paper

This paper will be gradually replaced by kraft-paper due to its high price, but it is important as one of the fundamental materials.

Kozo-paper is soft, easily folded and has a large tensile strength; 270~280 kg/cm^2 with the fibres arranged in parallel and 150~160 kg/cm^2 arranged vertically. Recently we have sometimes found a lower value of 100~150 kg/cm^2 in parallel and 40~80 kg/cm^2 in vertical due to a deterioration caused by mixing with other fibres. The thickness depends upon the uses, but it is 0.1~0.05 mm on average. Kozo fibres are somewhat rough and the paper shows large pores with thicknesses less than 0.03 mm.

Kozo-paper is weak in water, and very porous. The pores can be easily observed with a microscope of small magnification. Care must be taken because small particles of compositions may leak through the mesh of the fibres.

The difference between the parallel strength and the vertical one is quite large, so it must be used with the fibres in the right directions. Starch paste is quite reliable for pasting pieces of this paper.

Manufacture.The word "Kami" which means paper in Japan comes from the time of Emperor Suiko(610). In the year of 606 a Korean buddhist Doncho came to Japan and instructed people how to manufacture Kozo-paper. However the paper was weak in strength, and it was modified by Prince Shotoku resulting in manufacture of a good strong paper which was distinctively Japanese. The process has continued until today without much modification (T.Nishi: Comments on the manufacture of Japanese paper, p2(1928), F.Jugaku: A topography of Japanese paper (1947)).

During the winter season, Kozo plants(Broussonetia kazinoki) are cut and collected. These are steamed in a large pot, and the barks are removed and dried. These are called "Black Barks". The black barks are soaked in the water of a pool or river, and then stamped by foot or shaved with a knife to remove the black coats; then they are dried naturally for a few days. These are called "White Barks".The white barks can be stored for many years. These are soaked in water until they swell and then boiled in lye for an hour to remove non-fibrous matter. Immediately after this process, they are soaked in clear water and washed until the lye is removed, and then bleached in cold and clear running water in a river for two days and nights in winter. The material is then selected, removing knars, foreign matter and stains. Kozo fibres are too long to be pulped by a pump machine;i.e. 1.5~10.0 mm, and 5~6 mm on average and from early times the pulping has been done by hand. The white barks are put on a stone or a wooden stump where they are beaten to a pulp. A pulp vat is filled with water and a quantity of the pulp and a pasting material called "Tororo" are added to it and stirred well. The Tororo is a sap obtained from the root of a plant called Tororo-Aoi or Oshokki. A quantity of the liquid in the vat is placed in a mould which is fixed with a bamboo hurdle. The vat is horizontally shaken by hand for a time while the water is filtered out of the bottom, where the fibers are found intertwined with each other. In due time the mould is inclined, and the remainder of the liquid overflows out of the mould. The working time is adjusted in order to obtain a proper thickness of paper, i.e. the essence of manufacturing paper by hand lies in the shaking and overflow of the liquid. Next the wet sheets of paper thus made are piled one by one on a bench, drained and pressed with a weight. These are torn off one by one, placed on wooden plates and dried in the sun.

The processes described above has been used for centuries, but it needs a lot of time and labour. Needless to say there is a modified process, which uses sodium hydroxide for the boiling the fibres, calcium hypochlorite for the bleaching and hot air for the drying process etc. However for firework use the strength of the paper is the most important factor, and the modified process is not recommended.

Standard. For firework use a large sheet 6o6mm x 909mm is popularly used. The thickness varies according to the use.

(79) Gampi-paper

This is a thin paper which has a slight lustre and makes a sound when handled like metal foil. This paper has the highest transparency compared with other Japanese paper, and a high tensile strength. The fibres are very fine and strong. This paper has a reasonable wet strength. It looks slightly yellowish.

This is the best kind of paper for making flags, figures or parachutes, but the price is so high it has been gradually replaced by copying paper which is manufactured mechanically. However for figures other kinds of paper may be difficult to use. Gampi-paper is so thin, that it is easily burnt.

Manufacture(T.Nishi: Comments on manufacturing Japanese paper, p.12 (1928)). Gampi-paper is made of Gampi fibres. Gampi is a plant which is also known as ; Gyo-ka, Mo-ka, Ji-wata or in a certain dialect as Yamakago. This is a perennial shrub which belongs to Thymelaeaceae and grows to a height of more than 3 m. It is said that this plant is difficult to cultivate and in practice the wild plant is collected. This plant is distributed in warm climates, e.g. South Asia, Japan, Pacific islands; in Japan: in Ogasahara islands, Kanagawa, Wakayama, Kochi, Fukui, Hiroshima and Kyushu.

Gampi fibres can be pulped by a pulping machine and this is different from Kozo fibres. Generally the fibres are boiled, pulped, bleached and manufactured into paper almost in the same way as Mitsumata-paper.

Standard. For example, the item manufactured at Gifu has a size of 570mm x 820mm and a thickness of 0.020~0.015mm.

(80) Mitsumata-paper

Mitsumata-paper is soft and of close texture, but not to the same extent as Gampi-paper. It is not as strong as Gampi-paper, and a large parachute cannot be made from this paper. The paper is porous, and fine particles of powder pass through it. On the other hand the price of this item is cheaper than Gampi-paper, and it is popularly used in place of Gampi-paper.

Manufacture. Mitsumata is a perennial shrub, which belongs to Thymelaeaceae. It has a single trunk in the first year, but branches into three at the top during the second year. Each of the three branches again split into three at the top in the third year and so on. Mitsumata is naturally distributed in Asia, but it is only cultivated in Japan.

Mitsumata-paper has been in existence for some time; earlier than 1594. The manufacturing process is almost the same as that of Kozo-paper, but in this case a pulping machine can be used.

(81) Tengujo-paper

Kozo fibres are used as the main raw material. This is a thin, soft, pretty paper which has been manufactured in Gifu. Tengujo-paper is used for the core of hand-made fuses, when it is sprinkled with black powder. Popularly it has been used for packing valuable articles like silver or gold.

(82) Kraft paper

A pale or darker brown paper of high tensile strength, the values of which are 200~300 kg/cm^2 in parallel and 140~180 kg/cm^2 in a vertical direction in an old cement bag for example. New paper had values of 300~400 kg/cm^2 in parallel and 140~180 kg/cm^2 in vertical. Old cement bags are often used because they are so cheap. (The kraft paper for gun cartridges is made so that it has the same tensile strength in the parallel and vertical directions.

Manufacture. Sodium sulphate is used for making wood pulp when the lignin is removed by boiling. The pulp is then put through the paper machine.

Kraft paper is sold generally in a size of 765mm x 1085mm. For firework use the optimum thickness is 0.10~0.16 mm.

(83) Cardboard

Yellow cardboard is a plate paper which is made from rice straw. Brown cardboard, coloured cardboard or white cardboard is made from pulp and waste paper as the raw material. Yellow cardboard has the greatest tensile strength, with a value of 80~90 kg/cm^2- on average. There are imitations of yellow cardboard on the market which look yellow on both sides,but a grey weak material is sandwiched between the surface layers.

(8k) Other paper

Copy paper. A thin paper of good quality, which is made of a mixture of Mitsumata-pulp with suitable ratio of Manila hemp pulp. The quality is varied. It is used for flags or parachutes in place of Gampi-paper.

Lustre paper. A coating liquid is painted on one side of a paper which is made of sulphite pulp mixed with a small amount of wood pulp, dried and lustred with a lustre machine. This is used for toy fireworks etc.

Metalfoil paper. Gum, gelatine, or albumen is pasted on one side of paper and a metal foil is placed on top and pressed; this is the old method. At present metallic foil powder is used and it is manufactured in the same way as lustre paper. Aluminium foil is used for silver and bronze foil for gold. There is sometimes an imitation which uses aluminium foil on which varnish is painted. This is used for decorating products or packing of toy fireworks to make them moistureproof or airproof. In practice the point must be made that the metal foils have pinholes and they can be porous.

(85) Hollow paper spheres

These are used to make round bomb shells and are sold as hemi-spheres of various sizes. There are two kinds at present; newspaper sphere and yellow strawboard spheres. Recently spheres made of plastic resin have appeared, but they may have defects in that there is no air ventilation; the injurious effect of the splinters may also be quite large and the waste plastic spheres do not degrade naturally when exposed to the weather.

It is said that the newspaper hemi-spheres are the most suitable for shell manufacture. (At present they are not used for export, but only for the shells displayed in Japan.) The reason is that they have a moderate tensile strength and they split more uniformly than the straw board spheres. The tensile strength value of newspaper generally sold in Japan is about 70~80 kg/cm² in parallel and about 45 kg/cm² in vertical, which is 1/3 of the Japanese Kozo paper. A sphere is manufactured by pasting newspaper pieces one on top of the other on a round hard wooden core until it gains an adequate thickness. This is dried and cut with a sharp knife along its diameter into two hemi-spheres, which are removed from the core and dried again in the sun. Before the cutting, one or two joint symbols are marked around the diameter; the two hemi-spheres are sold as a pair. The strawboard spheres are made of yellow strawboard and sold as hemi-spheres; they are made on pressing machines(R.Lancaster: Fireworks, Principles and Practice, p.143(1972)). Japanese made strawboard spheres are not very uniform, e.g., the hemi-sphere varies in thickness especially in the middle and at the edge. Two hemi-spheres must be prepared by grinding them so that they are united to make a perfect sphere. These strawboard hemi-sphere are used for shells which are mainly exported.

The grades of the paper hemi-sphere on the market are set up in Table 17.

Table 17. Grades of paper hemi-spheres

Newspaper hemi-sphere			Strawboard hemi-sphere		
Grade number	Outside diameter (mm)	Thickness (mm)	Grade number	Outside diameter (mm)	Thicknes (mm)
(Large)			(Large)		
No.2.5	-	-	3 inch	68	2
3	83	2	4 "	93	4
3.5	97	3	5 "	120	4
4	113	2.5	6 "	140	4
5	142	3	8 "	195	5.5
6	170	3	10 "	235	7
7	200	3	12 "	280	7
8	225	3.2	(Small)		
10	275	3.5	For small		
15	370	8	flowers	16	1.5
20	534	12	"	21	"
(Small)			"	24	"
2.5	65	2	"	27	"
3	80	2	"	33	"
4	107	2.5	3 inch	67	2
5	135	3	4 "	90	3
6	165	3	5 "	114	4
7	193	3	6 "	135	4.5
8	220	3	8 "	185	6
10	270	3	10 "	225	7
15	-	-	12 "	275	7
20	518	9			

In this table "Large" is used for Poka and "Small" for Warimono (Chrysanthemum). Warimono is manufactured by pasting many layers of paper on the sphere and the completed shell has a thicker wall than that of Poka. It is necessary to manufacture both Poka and Warimono with the same external diameter since they are both used in the same size of mortar.

13»9» Explosives and pyrotechnic pieces

These articles have been manufactured from early times by pyrotechnists, but this tradition is gradually being relinquished. However the propellant, black powder, industrially made is much more reliable than that which is hand made.

(86) Black powder, Gunpowder

Irregular angular black grains of 0.5~2 mm is the only grade popularly used in Japan. Hunting powder has a lustre due to polishing with graphite, but for fireworks unpolished powder is used to maintain good ignition. According to a Japanese industrial standard the apparent specific gravity is 0.88~0.96 and the moisture content is 0.6~0.9% in weight; black powder does not degenerate with such a small moisture content. The true specific gravity is 1.58~1.84 and generally about 1.75. The burning rate in the open air is quite large. The deflagration velocity is said to be 400 m/sec, when it is initiated by another booster(Military Explosives(USA)). The value is about 1/10 that of high explosive. The force of explosives, f(= NRT, where N is the number of mols of gas generated by 1 kg of the explosive, R the gas constant, T the explosion temperature), is about 1/3 that of smokeless powder. (It is said that black powder has the best ignition with a moisture content of about 1%. An American Bureau of Mines test showed a curious result in that wet black powder, which contains moisture of less than 7%, is more sensitive than the dry powder to static electricity(Brown, F.W., st al.: Sensitivity of explosion to initiation by electrostatic discharge, U.S. Department of interior, Bureau of Mines, Report No.5002, September p.5(1953)). It is true that black powder has quite a low sensitivity to shock and friction compared with other general firework compositions. Attention must be paid to the fact that it can ignite or explode from strong mechanical action. Grinding black powder grains with an iron mill at the same time adding a small amount of water is still popular in Japan for making fine powder, but it is quite dangerous, and in place of the iron mill a gun metal mill should be used, When a large amount of water is added to black powder, the potassium nitrate contained in it dissolves in the water, and the powder loses its explosive nature.

At low temperatures the ignitability of black powder is quite good, but at low pressure less than 1 atm. it becomes uncertain.

Black powder burns with a great burning rate even at 1 atm. This allows us to fire a shell in a loose mortar in spite of little clearance between the shell and the mortar.With a smokeless powder,which burns only quite slowly below 1 atm, we cannot fire the shell unless we use a thick and heavy mortar and close the clearance entirely to raise the interior pressure to allow the smokeless powder to burn quickly, but it is not practical.

Black powder is quite stable at room temperature or even at lower temperatures, but the grains gradually coagulate over 70°C.

Black powder corrodes copper, bronze and iron in the presence of moisture. When this powder comes in contact with ammonium perchlorate, it creates ammonium nitrate and becomes wet, because the ammonium nitrate absorbs moisture extraordinarily.

Quality and standard. There is a standard, JIS K 4805 Black Powder, but the product under JIS is not sold commercially. One analysis showed that it contained 74.20% potassium nitrate, 9.62% sulphur, 16.18% charcoal and 1.16% moisture. The true specific gravity was 1.77, but when it was manufactured, the ratio of the component materials when it was mixed was, potassium nitrate: sulphur: charcoal, 74:10:16.

Packing. It is marketed in a tarlined paper bag. Six bags are contained in a corrugated cardboard case. One bag contains 5 kg of the powder. The volume is 1.8 m^3 per 1000 kg of black powder.

(87) Fuses

In Japan there have been three grades of Bickford fuse, No.1, No.2 and No.3. Vinyl covered fuse and universal fuse are also sold on the market. Fuses have been designed ordinarily for coal mining, mining, quarrying and other public works. Fuse No.1 has the strongest cover which consists of jute, asphalt and paper tape, and it is waterproof. This is 5.0 mm in diameter, which is the largest of them all. It is hardly damaged by handling, and is used mainly for coal mining. No.2 has a weaker cover, and as the burning proceeds the smoke escapes through the cover. This fuse is 4.8 mm in diameter, and is almost as waterproof as No.1; it is used for mining and other public works. For fireworks No.2 is most widely used. Fuse No.3 has the thinest cover of the three and is 4.6 mm in diameter. When it burns,it produces smoke through the cover and is less waterproof than the others. This is used for quarrying and public works above ground.

The black powder used for the three kinds of fuses mentioned above contains 60~70% potassium nitrate, 15~20% sulphur, 10~20% charcoal. The fuses contain more than 3.5 g of the powder per 1 m. The burning rate lies between 100 sec and 140 sec per 1 m. Asphalt is generally used for waterproofing, but the asphalt slowly soaks into the black powder during long storage and prolongs the burning rate, this consolidates the powder and finally prevents ignition. It is wise not to use old fuses. Moreover the asphalt absorbs the vapours of various organic solvents and damages the fuse. This is quite important because organic(synthetic) pastes are becoming very popular for fireworks manufacture.

Recently firework fuses which are modified types of the industrial Bickford fuse have appeared on the market. For example, the products of Nippon Kayaku Co. are as follows: The main fuse for shells is 5.5 mm in diameter, with a burning rate of 4~6 sec per 5 cm; thunder report fuse is 4,9 mm in diameter, the burning rate being the same as that of the main fuse. The main fuse is being modified so that no loose powder falls off; this is superior to other ordinary Bickford fuse at the point where it is cut. The burning rate of these fuses is somewhat faster than that of ordinary Bickford fuse and so they can be conveniently used for manufacturing shells.

Another simple fuse called "Green Fuse" is made in the USA;it is **used for** toy fireworks. It can be ignited from the outside of the cover with match. However it is more dangerous since the fire communicates laterally.

13.10. Other firework materials

(88) Cotton and hemp string

Cotton string is very ignitable, and once ignited, the fire is not easily extinguished. Hemp string is also ignitable, but it seems to be less so than cotton string. In view of the inflammable nature of cotton there may be some situations where it might contribute to fire and so it is wise to make the thread fireproof. To do this, the string is dipped in a solution of an ammonium salt in water and dried. Ammonium sulphate, ammonium chloride or ammonium phosphate can be used for example. But this does not particularly protect the string from fire, but only disturbs the progress of the fire along the string.

According to JIS, the grade of cotton string is expressed by a hank number(1 hank=840 yard=768 m) per 1 pound(453.6 g) with an authorized moisture content; the grade of hemp string by fibronumber(1 fibro=300 yards=274 m) with a similar moisture content. The authorized moisture content is 8.5~12% by weight of the dry sample(JIS 1 1008, 1011).

(89) Cotton seeds

These are used as a spacer or filler in a shell, or as cores for the bursting charge grains in shells. Cotton seeds are obtained during the manufacture of cotton. The seeds are white and woolly and vary in diameter between 4.3 mm for the small size and about 7.5 mm for the larger one. The apparent specific gravity is about 0.45. The seeds serve as a buffer and the surface is quite suitable to receive the bursting charge composition as a slurry.

The seeds must be well dried before use. It is said that seeds which have been stored for more than a year and which have lost their germinating power are the best to use. Commercial seed contains a small amount of cotton and dust which must be removed with a suitable sieve. This is important to avoid residual fire sparks among the seeds and to obtain good bursting charge grains.

As the cultivation of cotton in Japan is declining there is a shortage of cotton seeds on the market, but of course a large amount of cotton is produced in the USA, India and China. At present, in place of the cotton seeds many of the fireworkers use rice chaff for small or medium shells and Japanese cypress seeds for large shells.

(90) Rice chaff and immature rice

Rice chaff is used also for the packing material in shell or as cores for the bursting charge. These contain a small amount of dust, and must be sieved before use. Immature rice is said to be better than rice chaff. This material can be coated with a large amount of composition than it is possible with cotton seeds. The loading density of the bursting charge of a shell can also be increased, but the composition does not adhere so well to this material as it might do with cotton seeds because of the lack of downy wool.

SUPPLEMENTS TO (43) and (86): When sulphur is mixed with some nitrate a strange effect other than those of ordinary fuels. For example, a propellant of black powder which contain too much excess of sulphur is used for a rocket, it produces a high temperature to melt the iron nozzle. Sulphur is often used with some nitrate as a long time flare which burns slowly producing a coloured flame of high temperatures and a large amount of ash. The ash consists of mainly a metal carbonate.

14. Unit processes

14.1. Preparations

Preparation of materials. Materials are prepared for mixing into compositions by several processes; pulverizing, sieving, drying etc. Pulverized barium or strontium nitrate consolidates into a hard mass over a period of time. These substances are dried above 100°C and stored in a moistureproof container, e.g. a steel drum. Nitrates are sometimes placed in a iron pan and heated over a direct heat with constant stirring. It is not dangerous unless a combustible material is added to it. It should be stirred with a spatula made of incombustible material such as aluminium.

Preparation of compositions. There are two kinds of processes, dry and wet. The wet process is only applied to very sensitive compositions. The dry process is the most popular, because it is possible to maintain the component ratio correctly.

(1) Dry process of mixing materials

The well dried powders are mixed together by passing them through a sieve several times.

Before mixing, materials are prepared, i.e. coarse grains are finely ground in a mill, wooden roller or ball mill etc. For potassium nitrate or barium nitrate a wooden roller will do. But hard stone-like masses need to be ground in a suitable machine. Each of the materials should be passed once through the sieve in order to make the mesh size uniform and to remove foreign substances. In practice it is common to find unexpected matter; nails, pieces of metal, sand etc. which are present in the materials even though they look as if they are pure.

A sieve which is used for mixing a sensitive composition, containing for example, potassium chlorate or barium chlorate, should be made of hair. For compositions which are not so sensitive a brass sieve can be used. For most of the insensitive compositions such as some smokes we can use a sieve made of iron wire coated with zinc. A 40~60 mesh sieve is convenient for normal mixing, but other mesh sizes are used for special purposes.

Materials which easily consolidate like potassium chlorate, potassium nitrate(these two are also sold as free flowing powders as described in chapter 13), barium nitrate, ammonium perchlorate and rosin etc. should be ground and sieved immediately before the mixing.

The dry mixing by hand is carried out as follows: First prepare a work table, vessels, sheets of kraft paper, a balance, a scoop, a sieve and a composition formula. A wooden work table with a duralmine plate on the top is best, if possible. This is to prevent the chemicals from soaking into the wood of the table and it can be useful for avoiding electrostatic charges during the operation. It is also useful for crushing lumps of chemical with a wooden roller. The paper should only be kraft paper and it should be renewed for each type of composition. A balance with sliding weights is quite convenient and safe, but spring balances are not accurate, and often need re-calibrating with known weights. Put the kraft paper on the table and weigh out materials on to the paper according to the composition. When the same operations are repeated, it is convenient to use one vessel for each component. The component materials are then mixed on the kraft paper by hand. People have different views about the order in which component materials are added to one another, but in practice the materials are mixed together at the same time, slowly and gently by hand as well as possible until the mottles of the composition vanish. Pass the mixture through the sieve at least three times. Whether the mixing is complete or not, we can see from the colour of the mixture whether it is uniform or not. It is a rule not to force through with fingers any material which remains on the sieve. Some materials, e.g. rosin or lampblack cohere to the mesh of the sieve and cannot be sieved on their own. However these materials pass the sieve quite well when they are accompanied by other materials; they should therefore only be sieved after hand mixing. Weigh the total amount of the mixture after mixing to test whether the operation has been carried out correctly or not.

The amount of mixture should be about 5~10 kg at a time, depending on the kind of composition. A sensitive composition ought to be limited to less than 5 kg. The completed composition is stored in a wooden box, on which there is a note of the kind of composition, the components, their ratio, the date and the name of the worker. After it is labelled it is placed in an expence magazine or a store. The finished composition must not remain in the mixing room.

A V-type mixer is conveniently used for mechanical mixing(Fig.59). A V-type container revolves slowly on a horizontal axis. Materials should occupy less than 1/3 the volume of the container. They are mixed by an up and downward movement of the materials, causing a constant separation and collection. This mixer looks quite safe to handle, but accidents have occurred. The author experienced a self ignition when the container was opened at the end of the operation; it contained a sensitive smoke composition.

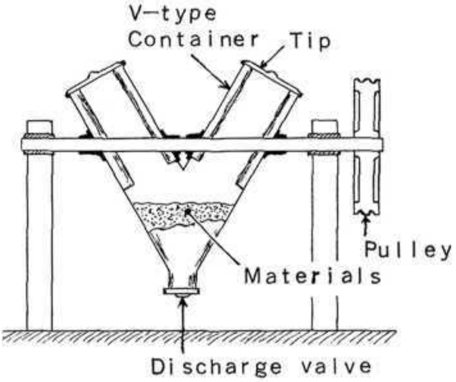


Fig. 59. V-type mixer

The author also heard of another accident which occurred using this type of mixer; the construction of the tips and the furnishing of the shaft may be the problem. This type of machine has come into firework manufacture from other industries, but it is not very safe. A modified type for the exclusive use of firework compositions must be used. In this case it must be remembered that the mixer degenerates gradually due to the biased load and this may cause dangerous cracks in some parts.

We often use an I-type mixer consisting of one cylinder. This is simpler, but it does not function as well as the V-type.

A safe composition like white smoke, which consists of hexachloroethane, zinc dust and zinc oxide, can be mixed with a mixer like the one used for concrete. In this case, the light zinc oxide is placed first into the mixer, then hexachloroethane and lastly the heavy zinc dust.

A light bulky composition like coloured smoke is apt to cohere to the wall of the mixer. This disturbs the mixing. In this case an enclosed vessel with a revolving metal paddle is very useful, but for compositions which contain chlorate mechanical stirring cannot be allowed.

In general it is necessary to leave more than 2/3 of the total volume empty in the mixing chamber in the case of the drum-type, V-type and cylindrical type as they take heavy compositions of small volume. On the contrary, the mixer with the revolving paddle only requires a small air space and is suitable for mixing bulky materials.

(2) Wet process for mixing materials

For quite sensitive compositions the wet process is used. In this case an amount of water is added to the materials when they are mixed, so that they lose their explosive nature. It is also possible to add an organic solvent, but in this case it is impossible to perfectly suppress the explosive nature. The wet process is not effective for materials such as picric acid salts, which are generally sensitive even in the presence of water.

The solubility in the water differs according to the kinds of material and the temperature. Accordingly the ratio of the components might be changeable during the wet process, and it is often necessary to stir the composition well. Generally 40~50 g of water would be added to 100 g of a composition. With a mixture of red phosphorus and potassium chlorate, 30 g of water per 100 g of the chemicals will not suppress the explosiveness and ignitability, and at least 50 g of water would be necessary. In this case the mixed chemicals form a slurry. If realgar, sulphur or antimony trisulphide is added to potassium chlorate, 20 g of water per 100 g of the chemicals is not sufficient, but more than 30 g of water is effective; in practice 40 g of water per 100 g of chemicals should be used for safety.

The wet process is operated as follows: Dissolve a quantity of the binding material like gelatine etc. in the water. Weigh out an amount of well sieved oxidizer, add it to the solution in small amounts, stirring it well. Then add the red phosphorus powder, realgar or other fuels in small quantities to it to obtain a slurry. This slurry is pasted onto some supporting material in small quantities and these are packed with thin paper one by one. The pieces are dried naturally to recover their explosive nature, but the composition is now separated into small amounts and is safe to handle.

During the wet process gelatine helps to prevent the chemicals from sedimentation, but some compositions are manufactured without such a binder.

The wet process cannot be used of course for compositions where the components react with each other in presence of water.

Wet compositions are generally used in conjunction with paper with the result that the components partially soak out to change their ratio. In view of this an excess of the oxidizer etc. should be used in mixing.

The wet process is used for manufacturing cracker balls(the composition consists of realgar and potassium chlorate), paper caps (red phosphorus, sulphur and potassium chlorate) and pull-igniters (red phosphorus, antimony trisulphide and potassium chlorate).

The process for manufacturing matches, quick-match, Senko-Hanabi, sparklers or searchlights, which utilize relatively insensitive compositions dipping them on to sticks, string or pieces of paper, may be described as a wet process, but the purpose lies not so much in safe mixing, but rather in the manner in which the composition is held, and in this case the wet process is not always necessary for the mixing of the component materials.

14.2. Shapes

Compositions manufactured by the dry process are shaped into fireworks or parts in three states; as powders, kneaded mixtures and slurries; as follows:

Compositions made by the dry process	Powder	Twisting(for twisted pieces or fuses)
		Loading(for report, smokes or lances)
	Kneaded mixture (with water or a solvent)	Tapping(for tapped stars)
		Pumping(for pumped stars)
		Cutting(for cut stars or igniters)
		Pushing out (for some flares or toy-fireworks)
		Granulation(for bursting charge or smoke)
	Slurry (with water or a solvent)	Pasting(for round stars or powder pasted paper)
		Dipping(for sparklers, Japanese Senko-Hanabi)

In this table the processes are arranged so that there is an increase in the amount of water or solvent used.

Twisting involves twisting a piece of paper tape with a compos'ition in the core. This is applied, e.g., to a kind of Japanese sparkler Senko-Hanabi or some fuses. Loading involves filling a container with a composition lightly, e.g., in the case of reports in which the composition is filled with an apparent specific gravity of about 0.6 to allow it to explode perfectly, or in the case of lances, where the composition is consolidated rather better to avoid explosion. No water or solvent is added to the composition, and there is no need for drying, but they are always charged in containers such as paper tubes. Kneading requires the addition of water, solvent or a binder to form various shapes; grains, cylinders or tubes. Drying is necessary except in the case of a self-consolidating binder. The smaller the amount of additional material, the higher will be the necessary consolidating pressure, but the drying time will be less. Moreover, a large amount of the additional material causes considerable shrinkage and cracking. Accordingly it is only used for granulation or small items. Slurry contains a larger amount of water or solvent than the kneaded compositions. In the manufacture of round stars, grains of composition are first pasted with slurry and then sprinkled with powder of the same composition as they are rolled around in a circular pan. The grains grow in a spherical form. Other methods of pasting involve the painting of a slurry composition on to pieces of paper, cloth(called powder pasted paper or cloth) or string(quick match). Dipping utilizes pieces of wire or stick which are dipped into a slurry compositions and then dried. This is repeated until they gain an adequate coating of the composition. The important processes are described as follows.

(l) Cut stars

Grains of one cubic cm in size are popular in Japan, but in other counties, e.g. in the USA, larger cut stars are also used. The operation is simple, but care must be taken to avoid cracks when the grains are dried.

As a binding agent soluble glutinous rice starch is mostly used in Japan, because this is soluble in cold water and can be added to a composition in a right ratio, and because the cohesion power of the starch is greater than that of other forms of starch and effective even in a small proportion; generally 2～6％ of the weight of composition will do according to the size of the star to avoid cavities(Figs.56 and 57). This means that about 19～20％ water is added to the composition for kneading.

Organic solvents, e.g., acetone, amyl acetate ($CH_3C00.C_2H_5$) or alcohol, are used with compositions which contain magnesium; naturally water cannot be used. In this case celluloid or Igner(the commercial name of powdered celluloid), which possibly contains a small amount of talc, is popularly used as a binder. When a better star ignition is required, high viscosity nitrocellulose should be used, this is industrially made and sold commercially.

The nitrocellulose solution is prepared as follows:

NC Paste

Nitrocellulose H5O(contains 15% alcohol)	10
Diphenylamine $(C_6H_5)_2NH$	0.15
Amyl acetate(or Acetone)	100

in weight ratio. Solid nitrocellulose should be put into a glass bottle and then the amyl acetate in which the diphenylamine is previously dissolved. Stir it well. Undissolved powder lumps will however appear in the liquid. The bottle should be corked and left for a day, to obtain a perfect uniform and transparent solution.

Amyl acetate has a high boiling point(over 130°C) and is not so volatile which makes it useful for cutting stars. Sometimes acetone which has a lower boiling point (56.3° C) is used, especially if the paste is required to dry quickly, e.g., when pasting some round stars or pasting an igniting composition on to pressed stars. The cohesive power of the solution is not too large, but the dried stars become quite hard.

It may be thought that synthetic resins, which consolidate by the action of some catalizer, might be used for cut stars. It is not very useful however due to the slow burning rate and the poor ignition which occurs with these stars.

To manufacture the cut stars, add an amount of water or binder solution to the composition and knead it well. The quantity of the solution is best determined previously for each kind of composition. The kneaded plastic cake must not be too soft to be cut into cubes. When an organic solvent is used, we can decrease the quantity of the binding agent if one of the components dissolves into the solvent. Place a part of the kneaded mass onto a thick wooden plate which has rulers of a definite thickness(e.g., 3mm, 6mm, 9mm etc.) fixed to the edges. Spread the mass on the plate pressing with the fingers and then tap the mass with a wooden hammer to produce a hard plate of the composition. The height of the mass must slightly exceed that of the rulers. Lay a long thin straight-edged tool on the mass and cut away the residual mass sliding the tool along the rulers to form a uniformly thick plate of composition. The residual mass is returned to the next operation. Remove the rulers to obtain the plate of composition. Cut the plate into parallel strips at equal intervals which are the same thickness of the plate, and then at right angles in parallel at the same intervals. The cutting is sometimes more easily done by sprinkling powder of the same composition on to the surface. The cut pieces are then sieved to separate them from each other into perfect cubic stars. Dry them correctly. It is then possible to paste ignition composition on to the stars by the same process which is described later. During the operation the prepared kneaded mass must be covered with wet cloth or a lid to prevent it from drying.

When organic solvent is used, the plate of composition is brittle, and rather difficult to cut. The wet cut stars must therefore be carefully handled to avoid damage. But when they are well dried, they become quite hard and easily handled. (See also 14.2.)

The number of cut stars which can be manufactured in a day amounts to something like 30,000 pieces for 3 mm stars and 15,000 pieces for 6 mm stars using soluble glutinous rice starch as the binder.

The manufacturing process in the USA and Europe is set out below (Fig.60).

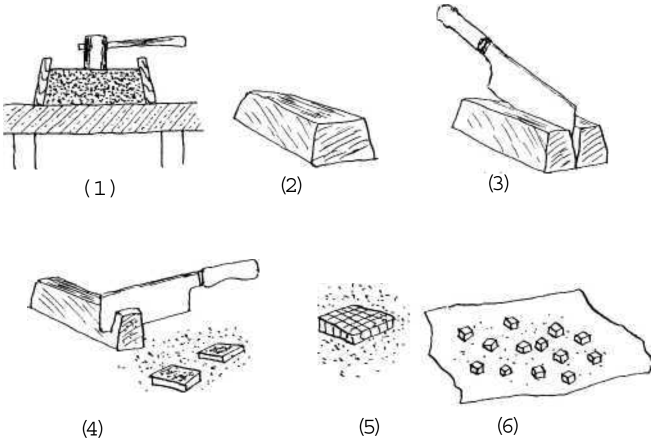


Fig.60. Manufacturing cut stars by the American method

First a kneaded mass of composition is placed in a mould on a table made of marble or synthetic material. The mass is tapped with a wooden hammer. Then the mould is removed upwards. The mould has a slope at the four sides and this taper means that it is easily removed from the mass. The mass left on the table is cut into small cubic pieces by guesswork using a long straight edged tool, sprinkling it with powder of the same composition,

(2) Pasted stars

Pasting is peculiar to Japanese firework manufacture. Stars are allowed to grow into a spherical shape by sprinkling the powder of a composition on to core grains. This process is popularly applied for the manufacture of colour changing stars used for the Warimono shells; Chrysanthemum. In Japan maximum effort is made in the production of stars of this kind.

The manufacture of good round stars is the first condition of the manufacture of good shells. What is a good star? The star which burns out quickly, shows quite strong end brightness, has a heavy core, produces a straight trajectory and which has small deviation in grain size, is best.

Cut stars are best for the core ecause they can produce a high end brightness, moreover the burning rate of cut stars is generally large. However the manufacture of cut stars is considerably troublesome and for the sake of efficiency in operation, other kind of cores; e.g., rape-seeds, sand grains, immature ears, corn, rice corns etc. are used. When the cores are too small, the star do not give a high enough light intensity at the end and they are enlarged with plaster if necessary. To increase the weight of a core a case shot is used by some manufacturers.

Here is a description of the method of pasting stars, using water, and commencing with cubic cut stars. First prepare a slurry with water from the same composition as the cut stars of the core. The slurry is called "Toro". The viscosity of the Toro is important; at first the viscosity must not be too high, because the cores are light and apt to stick to each other. Add water to the Toro to adjust the viscosity so that the cores do not stick to each other during the operation. As each star grows and becomes heavy, the grains do not stick to each other as much.The next operation increases the viscosity so that the water in the slurry does not soak into each grain quite so much or so deeply during the operation. Place well dried cubic stars in a bowl which has a round base. Pour the Toro on to the stars in small amounts pasting the surface of each cubic star with it by shaking the bowl constantly. Sprinkle powder of the same composition on to the stars and shake the bowl again. The powder adheres on each grain. If the grains stick together separate them by hand or sieving. Repeat the operation; adding Toro and then powder two or three times and then place the grains in the sunshine. If they are left in the shade, the water soaks into the grains, and the grains crumble. When the grains are perfectly dried, repeat the same operation once more, and all the grains will become spherical. Next the grains are coated with a new composition by the same operation according to a colour change plan. The grains thus grow step by step by the repetition of the coating process. If the Toro remains at the bottom of the bowl during shaking, the amount of Toro is too much; if the powder remains at the bottom, then the amount of the powder is too great. Under ideal conditions the bottom of the bowl glistens.

The thickness of the layer pasted at a time varies according to the kind of composition. Blackpowder-type compositions and compositions which contain flake aluminium powder affect the grains as a kind of lubricant and the grains slip across each other and catch quite a small amount of the composition. In this case the grains grow quite slowly. On the other hand other compositions generally allow the grains to grow quite rapidly. The thickness that can be placed on the surface of the grains in the latter case, depends upon the degree to which the water has soaked into the grains and weather conditions. In strong sunshine, if the wet pasted layer is too thick, the surface of the grains dries before the inner moisture has been driven out. Under these conditions the moisture remains in the grains for a long time. This is called "Driven in". On the other hand in weak sunshine it is possible to increase the thickness of the layer in the one operation. Thus the growth of the grains at a given time may be about 0,5~1.0 mm in the case of blackpowder-type compositions or the compositions which contain flake aluminium and 1~2 mm for other compositions.

Generally the pasting can be done 2 times on a fine day in March, 2~3 times in May, 3~4 times on hot days in July and August. It is necessary to stop the pasting at about 2~3 o'clock and to dry the grains well before they are stored.

The completed stars vary in grain size, and for good display effects we must select the grains passing through particular sieve sizes.

When the Toro is left for a long time, it generally loses its viscosity due to the degeneration of the glutinous rice starch and by the action of the other component materials(Table 15). It must be renewed as far as possible.

In the manufacture of elaborate colour changing stars, we put a layer called "Changing Relay" between two colour layers in order to create the illusion that all the stars change their colour clearly and simultaneously in spite of the deviation in burning. The composition of the changing relay must produce a weak light of neutral colour and is set out as follows:

Changing Relay I	
Potassium perchlorate	35%
Potassium nitrate	35%
Hemp coal(or Paulownia coal)	24%
Soluble glutinous rice starch	6%

Changing Relay II	
Potassium perchlorate	81%
Accroides resin	13%
soluble glutinous rice starch	6%

When round stars are manufactured from rape-seeds, sand grains or other small grains as the cores, it is convenient to use a spray which contains 20 g of alcohol solution in 80 g water for the pasting, in place of the Toro, because the spray of the alcohol solution prevents the grains from coagulation. When the grains grow to 3~3.5 mm in diameter, it is better to use water only to produce hard grains.

When the composition is not suitable for using water in the pasting, we use a nitrocellulose solution in acetone or another suitable solvent which is easily vaporized in place of the Toro. Amyl acetate needs a rather longer time to dry than acetone. (See (1).) During the operation inflammable gas generates, and it is not wise to use a closed drier; drying in the sun is safest in this case. The other operations are the same as for Toro.

The processes above are hand processes which have been popular in Japan, recently however they are being gradually exchanged by machine processes. The mechanical operation gives harder grains than the hand operation, and the ignitability of stars must be duly considered when using the mechanical operation. A revolving drum with a round base in used for this purpose.

During drying the grains are at a somewhat elevated temperature. Well dried grains are generally sensitive to shock and friction. The shaking, removing and transference into another container must be done with the greatest care. The dried grains must be cooled to room temperature, leaving them in the shade before the next pasting; otherwise it is not only dangerous, but also difficult to apply the next layer because the water of the Toro rapidly soaks into the grains when the temperature of the grains is high. Destructive or burning inspections are forbidden near the coating place.

The shape of the container during the pasting has an influence on the growth of the core stars, especially with cut stars (Fig.61). When the

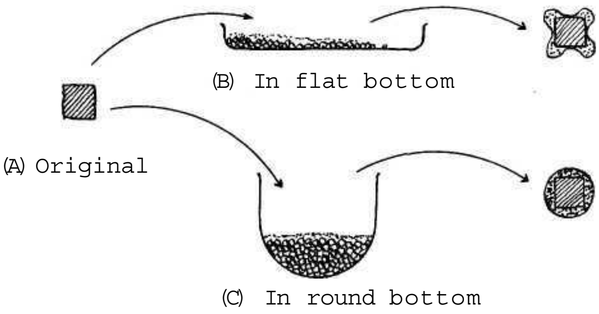


Fig. 61. Ihe influence of the shape of pasting container.

bottom is flat and the stars are light, each of the original stars(A) grows like (B) due to the low pressure on the surface. This is avoided by pressing the stars by hand during the operation, or by using a container which has a round bottom like (C).

(3) Tapped stars

Tapped stars are manufactured by using a cylinder and plunger(Fig.62), A small amount of composition is put in one end of the cylinder and tapped into a cylindrical star.

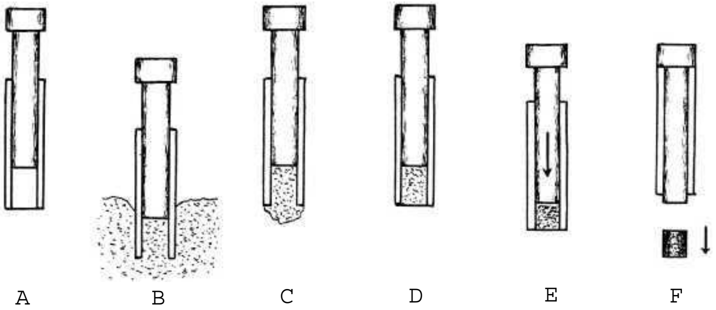


Fig.62. Manufacturing tapped stars.

Add a quantity of water or solvent to the composition and stir it well until the hands feel damp. When the composition contains shellac , rosin or other materials which dissolve in alcohol, it is better to moisten it with alcohol. Prepare a cylinder and plunger which are made of brass(a). Hold them in one hand and push them downward into the composition(B). An amount of the composition is thus forced into the bottom of the cylinder (C). The excess of the composition at the bottom is removed by the fingers (D). Place the bottom of the cylinder on a heavy stump made of hard wood and tap the head of the plunger several times with a wooden hammer(E). Remove the formed composition from the cylinder pushing it out with the plunger(F).

The efficiency of the operation is not as great as that of cut stars,but generally higher than that of the round stars. Tapped stars can be manufactured with quite a small amount of binding agent or water, and require a shorter drying time. The size of the stars is usually about 10~15 mm in diameter and length.

(4) Pressed stars

Larger stars are generally manufactured with a press. Using a hand press, the composition is kneaded softly as in the case of cut stars (the water content is about 20%). A quantity of the composition is weighed out and put in the bottom of a cylindrical form. It is pressed by hand using a driving screw or dead load press. This process is used generally to manufacture stars of about 20~40 mm in diameter, but often larger stars of about 100 mm in diameter are also produced by the same process. These stars are dried in the shade for 10~30 days and lastly in the sun.

When a hydraulic press is used, only a very small amount of water, solvent or binding material(2~3%) is enough to consolidate a composition and only a short drying time is required. The shrinking is negligible; this is the great difference between this process and the one described above. When the value for the pressure rises to more than 1500 kg/cm^2, the composition generally consolidates without water, solvent or binding material, and of course the drying process is unnecessary. It must be remembered however that stars manufactured under high pressure generally have low ignitability except in the case of blackpowder-type compositions.

When a composition which contains too much water or solvent is pressed under a high pressure, the water or solvent is squeezed out, and the pressed composition cracks perpendicularly to its axis. Therefore the amount of the water or solvent must be suited to the pressure.

Firework compositions generally contain a large proportion of crystallizing substances. The consolidation under high pressure is caused by the cohesion(bridging) power in the crystals. The surface activating agent which is often found in potassium chlorate or nitrate is not good for consolidating.

In the USA mixture of linseed oil and castor oil in ratio 1:1 is often used as a binding agent using 3~4% of a composition. When we use polyester as the binding agent at high pressure an amount as small as 2~4 does well. At low pressure the amount may be increased in place of other fuel in the composition, but too much causes shrinking and heat generation in a star of large diameter. Many substances disturb the catalytic action of the catalyzer and consequently the consolidation (Table 16).

As a mould for high pressure we generally use a cylinder and plunger for rather short stars, but for longer stars a split mould, which is described in 14.3.

14.3. Loading with compositions

This is a process for loading paper, tin or metallic cases with a composition and one of the processes of shaping. There are two ways; to load the composition as powder and to load it as a dough.

(1) Loading with powder

a) Continuous process. This is to change a composition in the powdered state into a cylindrical case, continuously moving a plunger up and down at a fairly high speed, tapping the composition to an apparent specific gravity of about 1.0~1.4. It is also possible to charge and press the composition with a metallic screw, but this is dangerous and is not used at present.

Loading lances for frameworks is mentioned as a simple example. The composition is loaded into a thin paper tube of about 10 mm in diameter, which is inserted into a copper plate mould with a funnel (Fig.63). The plunger is 4~5 mm in diameter, which is a little smaller than the mould. Fill the funnel with the composition and tap the bottom of the tube, moving the plunger up and down, and the composition falls bit by bit through the gap between the tube and plunger, to the bottom, and is tapped by the plunger. The tapped surface rises gradually and at last reaches the upper end of the tube. Then pull out the tube from the mould. The plunger can be operated by hand or machine. The composition is more uniformly loaded by revolving the tube slowly round its vertical axis by some device.

This is used for an item of relatively small diameter and low density. The manufacturing efficiency is higher than that of the step by step method described as follows.

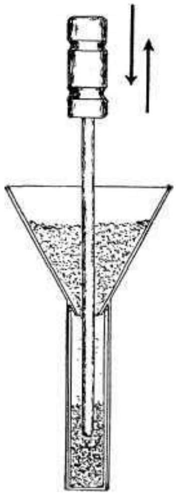


Fig.63. Continuous loading

b) Step by step process. This is to load an amount of composition into a tube by tapping or pressing with a plunger not continuously, but step by step to a high density of more than about 1.4. The operation efficiency is low, but it is popularly used in the manufacture of firework items like flares of large diameter.

The composition is loaded by hand or a press. The hand operation is applied only to small diameters of less than about 20 mm, because in large diameters chipping of the composition or inclined burning often occurs and accelerates the burning rate abnormally.

The principle of loading with a press is shown in Fig. 64. Place a tublar mould B on a base C, insert a paper tube(or other material) T in the mould, add an amount of composition W as powder and press it downwards with a plunger A at a pressure P_0. The composition is pressed and the air among the particles of the composition is driven out through the gap between the tube wall and the plunger. This is one step of the loading. The pressure in the composition decreases along the length of the composition from the plunger to the base like P_s , and the bottom pressure P_b is always smaller than the plunger pressure P_0 . Therefore the upper part of the composition becomes hard, but the bottom part remains soft. Accordingly the length of the pressed composition must not be too long. In practice we take the ratio H/D less than 0.8, where H is the length of the pressed composition and D the diameter. To avoid such an inclined distribution of the density another mould like in Fig.65 may be used. The mould has two plungers, A and C, and a spacer D. On pressing D is removed and the composition is pressed from both sides, A and C, but this type of mould is not so popular, because it is somewhat inconvenient for

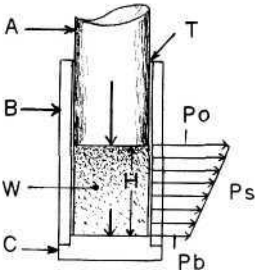


Fig.64. Pressing composition in powder state.

practical use.

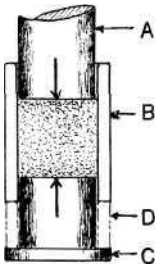
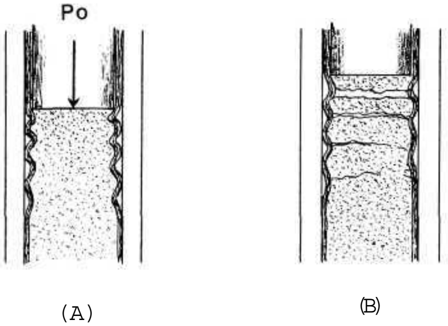


Fig.65. Pressing from both sides

When the composition is pressed, the composition is pushed downward along with the paper tube and the tube shrinks(Fig.66.A). When the plunger is removed, the paper tube stretches and the composition cracks (B). This causes abnormal burning or chipping of the composition.

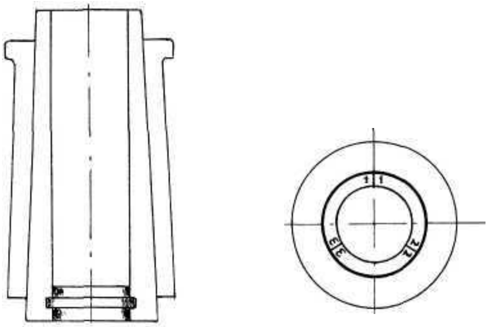


(A) (B)

Fig.66 Trouble when loading composition

Accordingly attempts must be made to minimize the shrinkage of the tube or not to allow the tube to recover by its elastic force.

To minimize the shrinkage of the paper tube we use a rather thick kraft paper tube. Sometimes an iron plate tube is used, but it hides the base of the flame during burning and decreases the candle power. Plastic tubes are also used but they also disturb the light by generating a large amount of soot. The following method is the most effective. Prepare a kraft paper tube with **a** thick wall, the outside diameter of which is somewhat larger than the inside diameter of the mould; the inside of the mould is rugged. Insert the tube into the mould. This is done very easily with a split mould(Fig.67) which consists of two metal tubes contacting each other with tapered surfaces and a metal base, (When the outer tube is removed the inner tube separates into three segments.) On loading the paper tube is fastened to the wall of the mould and prevents shrinkage. This is shown in principle in Fig.68.



Cross section Upper view

Fig. 67. Split mould.

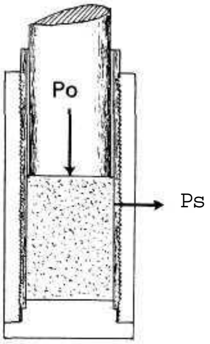


Fig.68. The principle of avoiding shrinkage of the paper tube in loading.

In this case it is more effective to minimize the friction between the inside surface of the tube and the composition by painting a lubricant like paraffin on the surface or by adding about 1% of a flow agent, e.g. calcium orthophosphate(s. R.Lancaster: Fireworks p.32(1972)), to the composition.

Another method to avoid the trouble shown in Fig.66 is to suppress the recovery of the shrunk tube after pressing. A non elastic tube may be used for this purpose, and the product becomes completely wrinkled on the outside. Products of this kind normally use a thin aluminium tube in place of the paper tube.

As it was stated earlier, one loading length of the composition is limited in a small value of H/D. Thus in the case of a long tube, the composition must be loaded in several steps. Joints occur at the boundaries of the composition for each step and this presents a new problem. In order to prevent the composition from chipping during burning, sometimes a wave, convex or concave plunger head is used and boundaries are presented like A,B or C in Abb.69. In practice this is not as effective as we think because the plunger pulls up the parts which fasten to the plunger head causing cracks denoted by c, when the plunger is removed upward. Accordingly a flat plunger head is generally used(Fig.69.D).

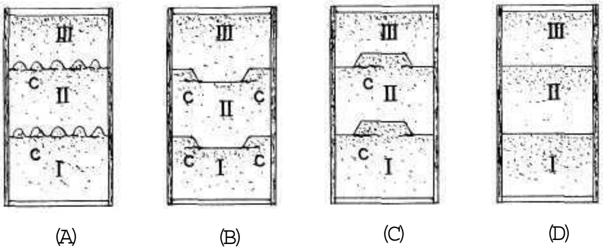


Fig. 69. Boundaries of the charges during step by step loading.

2~3% polyester in the composition is quite effective for strengthening the cohesion of the composition at the boundary to avoid chipping during burning. In this case the composition must not contain any substance which disturbs the action of the catalyzer.

When the composition contains air which is not perfectly driven out during pressing, many cracks occur in the pressed composition perpendicular to the axis(Fig.70). A proper clearance between the tube and plunger is important.

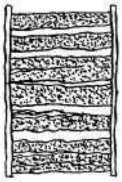


Fig.70. A trouble caused by air contained in the composition.

(2) Loading with dough

A pump is used to charge a soft dough into a tube. Other methods, e.g. by hand, often makes blowholes in the composition. Fig.71 shows the principle. For a hard dough a hydraulic press is used. The hard dough is pressed out of the bottom of a cylinder, with a plungex, through holes to form a cylinder, cords or tubes. These are left in a room for a while and cut into pieces of a desired length.

Some compositions which contain nitrocellulose and solvent or polyester can be treated by these methods. The loaded or formed composition shrinks during drying or consolidation, and these methods can only be applied to smaller pieces of less than about 20~25 mm.

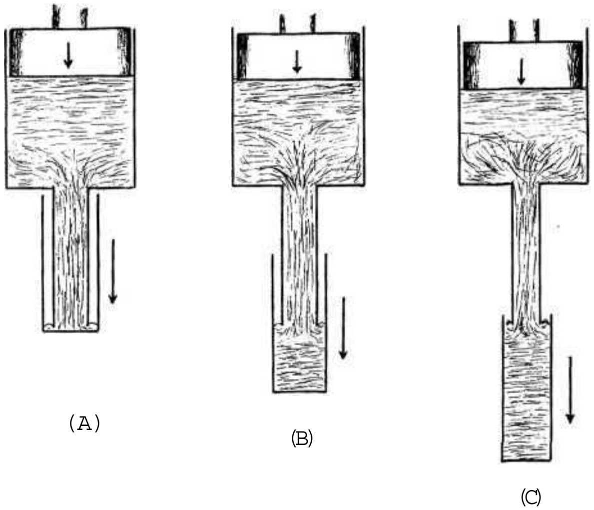


Fig.71. Loading soft dough with a pump.

14.4. Degeneration of the charged compositions

Generally the charged compositions slowly change their density and volume as they proceed to a more stable state. Sometimes the loaded tube breaks due to the swelling of the composition, or on the contrary a gap is created between the tube and composition due to shrinkage and this causes abnormal burning or deflagration. The period of instability depends upon the kind of composition; from a few minutes to a few years. The causes of instability may be set out as follows: the **vaporization** of the solvent; binding inorganic crystals; the progress of the polymerization of **a** synthetic resin used as the binder; the solution of one component in another; chemical reaction among the component materials etc.

The vapourization of the solvent(including water). A dough which contains glutinous rice starch and is charged into a tube, shrinks slowly as it dries and creates a gap especially if it is in a metal tube, even when the tube is less than 3 mm in internal diameter. During the manufacture of small pieces like igniters this is important. It is a common rule to decrease the amount of solvent in a composition as far as possible. When the composition feels to be rather wet, it contains 2~3% solvent **or** water. A composition like this is most unlikely to shrink, when it is formed into a mass under high pressure.

Binding inorganic crystals. Powdered crystals of inorganic materials generally cohere to each other by a bridging phenomenon due to the action of moisture. Many kinds of compositions therefore which are loaded into a tube as powder under a low pressure, shrink very slowly and create a gap between the tube and the composition. It often causes quick burning or deflagration. Hand loaded pieces like lances are often damaged by this phenomenon. Composition which is pressed under high pressure does not degenerate in this manner.

Polymerization of the binder also causes shrinking of the composition. The amount of catalyst must be decreased and the composition should be allowed to consolidate over many hours to minimize the shrinkage. It is better to limit the amount of the synthetic resin binder to less than 3～5% if possible, otherwise the diameter of the composition should be decreased as far as possible. This type of degeneration generally ceases after several days and this is confirmed by the stabilization of the burning rate.

The solution of certain components sometimes occurs due to contact between organic substances(e.g. shellac, rosin etc.) and oily materials (e.g. paraffin, linseed oil etc.). The consolidated composition as powder partly changes to a kind of solid of solid solution and shrinks. This degeneration proceeds quite slowly, i.e. it takes from a few weeks to one or two years. To avoid this phenomenon the composition is warmed to a suitable temperature before loading to promote the solid dissolution; this process is called "aging". This assumes that the composition will not degenerate any further after loading if it is allowed to degenerate sufficiently before loading. This process is not always effective and it is always best to select component materials which avoid such a degeneration.

When a composition contains a large amount of flake aluminium and is pressed into a paper tube, the paper tube sometimes cracks due to the swelling of the composition after the mould is removed. In this case it is better to moisten the tube as this is quite effective to prevent the tube breaking.

14.5. Pasting

After making a slurry from a composition with water or solvent it is pasted on to paper, cloth, cotton strands, small sticks or surfaces of stars etc. A large quantity of the liquid is necessary to manufacture the slurry and it is only evaporated away when the pasting is complete. Water is naturally popular for economic reasons. However, when we paste the slurry of an ignition composition on to the surface of a star which contains magnesium, water cannot be used, and an organic solvent is necessary. Some examples are mentioned in the Lancaster's book on pages 245-247.

(1) Powder pasted paper or cloth

Generally we manufacture two kinds of pasted paper or cloth; those with black powder and others with red thermit. The former is used for ordinary ignition and the latter for high temperature ignition. For the manufacturing process see the Lancaster's book on pages 245~246.

(2) Quick match

This black thread is manufactured by pasting a composition in the form of a slurry on to cotton strands. It burns slowly in the open air, but quite, quickly in a long tube with a small diameter. Unpiped quick match is often used for fire transfer in place of industrial fuse(Bickford fuse) and the paper covered fuse is used for frame-work. Various other materials are used in place of the cotton strands for cheapness. Black powder is popularly used, but chlorate composition is also used in Japan to obtain quicker fire transfer, but this is not to be recommended.

There are also other items for special use, which are made with other compositions which contain various binders and wire.

The manufacturing process for quick match is as follows: Dissolve 3 parts by weight of gum arabic in 40 parts by weight of hot water. The reason why gum arabic is used as binder, lies in the fact that the match dries relatively quickly and becomes quite stiff and easily handled, i.e. easily inserted into a paper tube. Nitrocellulose with an organic solvent can also be used as the binder, but in this case the fuse is too soft and too flexible to be handled. Prepare a double bottomed water bath made of copper. Fill the outer vessel with hot water and heat it with a safe heater which generates neither flame nor sparks. The inner vessel of the bath gives the space for pasting the slurry on to the strands. Pass the strands through a small hole at one side of the vessel, round two reels which are situated at the bottom of the inner vessel and then through a funnel-like outlet which is placed on the opposite side(Fig.72).

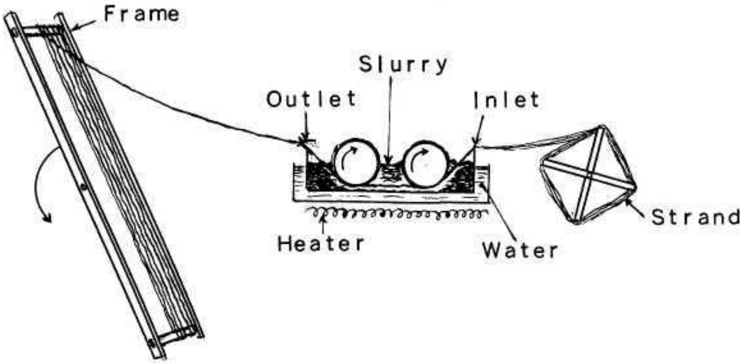


Fig.72. Manufacturing quick match.

Lastly the end of the cotton is fixed to a wooden frame. Pour a quantity of the gum arabic solution into the inner vessel and add black powder to the solution, stirring it until it produces a good slurry. Revolve the frame round its axis slowly, and the strands will be pasted with the slurry as they are pulled through it. Excess slurry pasted on the strands is removed by the funnel-like outlet which returns it to the inner vessel again.

The number of strands per length of quick match and the amount of pasted composition per unit length depends on the use, but the most popular one has about 0.8 g strands and 8.0 g composition per 1m to form a length of 4 mm diameter with a burning rate of about 30 mm/sec in the case of a black powder composition.

The paper tube which is used for the match cover is made of brown paper, with about two turns of paper and a diameter of about 8 mm. There are some devices which wrap the match with paper mechanically. A polyethylene tube is not good, because it easily melts and does not allow the fire to run quickly. A long metal tube is sometimes used to obtain very quick fire transfer.

The pasted lengths which are wound around the frame are dried in the sun. Black powder composition often appears to dry quickly due to the black colour. Contrary to expectation however, it takes a long time in practice; in a long spell of fine weather, it takes about a week in winter and about three days in summer.

Quick match made with black powder is a little hygroscopic, and should be stored in a well dried room or in a moistureproof container.

The cotton strands are sometimes boiled in potassium nitrate solution in water so that the fire is not extinguished where there are creases in the match.

(3) Pasting a prime composition on the end of an industrial fuse

In Japan industrial fuse(Bickford) has recently been used in place of the hand made fuse; the manufacture of the latter is quite labour intensive. In order to catch fire from some other heat source or to transfer the fire to other pieces the two ends of a cut fuse are pasted with a slurry of a prime composition. Sometimes a match composition which contains chlorate is pasted on one end so that it is ignited when it is rubbed with a red phosphorus striker. In general the slurry is a mixture of black powder and 10% nitrocellulose solution in acetone. In place of the nitrocellulose, celluloid solution can also be used. The ratio of the black powder to the solution is determined for ease of working. The amount of liquid however should be kept as low as possible to prevent the solvent from soaking deeply into the core of the fuse. This is quite important to avoid misfire. Moreover, the pasted fuses must be dried as quickly as possible in a drier or in the sun. When they are left undried for long time, a thin incombustible layer forms between the pasted composition and the core of each fuse, and the fire stops at the layer without being transferred causing misfire. Sather precise work is needed in this type of operation.

The slurry must be stirred often to prevent the component substances form settling out during the pasting. The solvent should clearly be a substance which is easily vapourized; acetone is good, but amyl acetate is not so good.

For the preparation of nitrocellulose solution see chapter 14.2(1).

14.6. Fuse manufacture

As described above, industrial fuses, mainly Bickford, which are modified for firework use have become popular recently in Japan. But a few manufacturers produce fuses by hand by the old method or for special use as in dark fuses.

The processes were described in Lancaster's book on page 247~249.

14.7. Drying

By this process the moisture or solvent contained in raw materials, compositions and half finished pieces is driven out. The most important problem is the drying of compositions which have been shaped into stars, particularly those pasted in more than one layer.

Generally there are two ways for drying; one is to warm things with a heat source such as sunshine, electric heaters or steam. Another is to leave the things at room temperature. "We must not heat explosives." This is an important principle in handling explosives. In some ways the former is opposed to it, and so the latter may be the best. However the former is generally inevitable to achieve good efficiency and so it must be quite clear in our mind that the use of heat with explosives is against the rule. Air conditioning is another special method; however it is not yet used on a large scale for firework manufacture due to the high cost of equipment.

(1) Drying in the sun

The advantage of this method lies in that equipments are unnecessary due to natural heat and ventilation; a wide drying area is also easily obtained where various kinds af compositions - even those which cannot normally be mixed due to manufacturing regulations - can be safely set out in an uncovered state, with the maximum efficiency of labour; that even when the compositions are scattered on the ground, they lose their ignitability because of weathering and there is less irregularity and smaller strain compared with the process of drying in a drier. Looking at it in this way, it is impossible to find any other method at present which is better. Thus drying in the sun is even now the most popular method in firework manufacture.

Nevertheless drying in the sun is often disturbed by the weather, i.e. by cloud, showers, wind and dust etc. Sometimes an accident can even occur from sparks or other high temperature sources which are invisible in the daylight, for they can be brought from some heat source at a distance. Clearly therefore in or near the factory the firing of shells, toyfireworks or rockets even for experiment must be forbidden. The drying places are often located near or between workrooms, but this is quite dangerous, because an accident in one room can propagate fire instantaneously to another room as it passes along the drying area.

The ultraviolet rays in sunshine generally cause chemical degeneration of materials. Dr.Osada studied this problem in firework materials(see.13.1). However in practice there is no chance of such long exposure of these materials in the sun as there was in Dr.Osada's experiment, and perhaps it is not necessary to worry unduly about this kind of degeneration in ultraviolet light. The fact remains however that direct sunshine is not good chemically for various materials.

The degree of rise in the temperature during drying in the sunshine depends mainly on the sun's intensity, but it is affected also by the colour or the nature of the surface of the dried pieces. Fig.73 shows examples on a clear day in midsummer in Tokyo. According to the curves the available maximum temperature is 66°C for the black stars and 59°C with the silver stars. The temperature of the stars rises to the maximum at noon. This time is earlier than that of the maximum room temperature which occurs at 1~3 o'clock. (On some days the maximum temperature of the stars occurred at 11 o'clock.) Until about 2 o'clock the temperature of the black stars is higher than that of the silver stars, but after that time the position reverses so that the silver stars are higher.

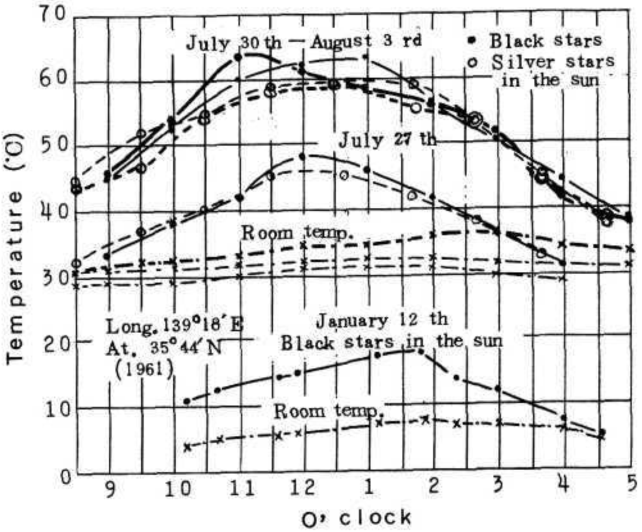


Fig.73. Temperature of stars drying in the sunshine.

For drying in the sun a rack and containers are prepared. The rack is most conveniently set up on the ground at a height of about 60 cm. A wooden rack is the safest, but it is easily damaged by the weather; a well painted iron rack is commonly used. A shallow wooden tray is popularly used as a container but those made of plastic resin should be avoided due to possible trouble with static electricity. Metallic parts like the nails which are used for the container must be of nonferrous materials, copper, bronze etc. The drying containers for potassium chlorate compositions or other sensitive compositions must be so constructed that the bottom of the upper case does not rub the composition in the lower case when they are piled up. The author heard of an accident which occurred because of trays sliding across each other.

When drying a wet composition in the form of powder, grains, pasted stars etc, place the container on the rack, spread a sheet of kraft paper on the container and place the wet composition on the paper and spread the material uniformly. In the sun stir the composition gently at intervals. When the composition is perfectly dried, pack the composition with the kraft paper, making a note on it of the name of the composition, the date, the name of the worker etc. and store it. For kraft paper we sometimes use paper from unbound waste cement bags which is quite cheap and strong. Plastic bags are not recommended, because they create droplets of moisture inside and they are easily charged with static electricity.

Grains of composition which contain water-soluble paste and have been shaped in the wet state; e.g. cylindrical stars under low pressure or cut stars; contain about 20%' water. These crack when they are exposed to direct sunlight, except in the case of the smallest grains, i.e. less than about 5 mm in thickness. The cracking sometimes causes spontaneous ignition due to internal friction when the compositions are sensitive. Larger wet grains should therefore be dried in the shade for several days to gradually remove most of the water and lastly they are exposed to the sun. For avoiding cavity formation see Table 15 in 13.7.

Pasted stars must be quickly placed in the sunshine to prevent the water from soaking into the stars. Accordingly in many firework factories the drying area is placed near the pasting room. It is not a very safe thing to do, but it cannot be avoided.

Care must be taken with the organic solvents which are used for shaping compositions observing the above precautions. The solvent makes the grains porous causing swelling and deformation when the grains are suddenly exposed to sunlight.

It is generally quite safe to dry covered compositions such as pasted shells, packed compositions etc.

The dried materials should be cooled in the shade before the next process.

(2) Drying by infra-red light

The principle of the drying by infra-red light is almost the same as that in the sun; the only difference is that an artifical heat source is required. Accordingly for fireworkers who have been accustomed to using the open air this method has a wider adaptability, assuming that the electric power conditions are favourable.

The pieces are put in a shallow container on a rack and heated by infra-red lamps placed above them. The drier has no walls, and we can see from the outside that the pieces are quite brightly lit. It is very easy to look after them during drying and of course the manufacturing plan can be better worked out than it can using sunlight. There is no need to preheat the drier, which is generally necessary for other kinds of driers. On cooling the pieces can be quickly removed from the drier, because they are rapidly cooled without being disturbed by the remaining heat in the drier. The drying effect is best on the surface of pieces as it is in sunshine and therefore the temperature of the pieces differs according to the state of the surface as it is when drying in the sun. It is necessary to know the maximum temperature for each piece in order to control the drying conditions, particularly when we dry various kinds of compositions.

The driers are equipped with 250 KW infra-red lamps of the reflector type and they are arranged about 20 cm apart facing downwards. The rack for the drying vessels is arranged so that the distance between the lamps and the articles to be dried can be adjusted easily to produce any required distance between the two. A glass plate is inserted horizontally between the lamps and the drying pieces to avoid the possible contact of inflammable dust from the fireworks with the lamps. A sheet of wire-netting is also spread under the glass plate to protect it. It is best to use an aluminium plate as a reflector at the level of the lamp head so that the lamps shine through it. The sides of the lamps are guarded with a fireproof wall. The electric wire which is used in the equipment must covered with some heatproof material, otherwise it degenerates gradually and crumbles into decay over a long period of use. In order to dry 10 kg of wet composition an apparatus with 18, 250 KW lamps and 1m x 2m drying space should be adequate. Such an apparatus should produce a drying temperature of about 50°C at a distance 60 cm below the lamps.

The common industrial method which carries material to be dried along a conveyor belt through a tunnel of infra-red lamps, is too dangerous for fireworks and is not used.

Drying with infra-red rays must be done under open conditions so that it may be observed from the outside. In this way the temperature does not rise too high. Workers are also apt to close the apparatus with some kind of curtain, but this is abnormal and dangerous.

(3) Drying by warm air

This drier was originally used for manufacturing confectionery and has recently been adapted for firework manufacture. For the heat source an oil burner or an electric heater is used. The air which is introduced through a filter into the heater, is heated indirectly by an iron plate wall(heated by the burner) or directly by heated wires. As the air passes through the drying room it catches the moisture from the drying material and is led out of the drier. Temperature changes take place quickly and the drying efficiency is quite good. For example, shells pasted with one layer of kraft paper are perfectly dried in two hours at 60°C, but the temperature of the heat source is too high to dry bare compositions, mainly because there is a danger that over heated matter can fly into the drying room, even when the temperature of the air is low. A snag with oil burning heaters is that it can be difficult to discover the small perforations which can occur in the wall of the burning chamber caused by old age. The author has heard of many accidents which have occurred by drying compositions in a drier of this type. Naturally it is therefore not recommended for bare compositions, but only for packed ones, e.g. for shells covered with paper.

There are other types of drier which use steam as the heat source. This is safer than those above, but it is necessary to have a steam boiler and other attached facilities and it is not too simple for firework factories.

(4) Drying by hot water

The air is warmed by a heater through which hot water is circulated, it is introduced from the bottom of the drying room. It passes among the drying racks in an upward zigzag path, naturally removing the moisture from the articles in shallow containers on the racks. This is very suitable for drying the most sensitive compositions in small amounts. However it is not yet too widely used because such sensitive compositions are generally manufactured by the wet process and are dried naturally without heat. Drying in this way is quite slow, and is not suitable for drying material which contains a large amount of water, for drying large pieces or for drying when the door needs to be frequently opened; e.g. pasted shell or pasted stars. However it is suitable for compositions which contain small amounts of moisture and for pieces which do not have to be completed rapidly.

(5) Drying by vacuum or by removing moisture in the air

The heating of firework composition is a generally forbidden principle. Therefore the safest way is to dry the compositions by vacuum or with air which contains very little moisture. But it needs a vacuum room and a vacuum pump. The time for the drying itself is not very long, but the operation before and after the drying takes longer. Recently drying by high vacuum and freezing has become popular in other industries. An alternative method of blowing dried air by air conditioning may be useful, but all these methods are a little slow in their implementation due to the high cost of the equipment.

The best application of the drying methods described above may be summarized as follows(Table 18).

Table 18. Applications of drying methods

		Natural	Sunshine	Infra-red	Warm air blast	Hot water
Composition as powder		X	0	X	X	O
Shaped composition	Large water content	0	X	X	X	X
	Small water content	X	0	0	0	0
Pasted stars		X	0	0	A	x
Pasted shells		X	0	0	0	X
Sensitive compositions		0	X	X	X	X

Symbols: 0: the most suitable,
A: suitable with care.
X: not suitable.

Accidents have occurred with almost every method in the past; drying in the sunshine, with infra-red rays, in warm air and even with hot water. To minimize accident it is quite important to select the drying method so that it is suitable for the articles to be dried. It is also important to always keep the drier clean. The dried compositions or pieces must be treated with great care, especially when they are removed from the drier. In general they must be removed after they have completely cooled to room temperature and it sometimes takes a long time, at least one day. Naturally this does not fit the busy work pattern in an ordinary firework factory, but it is quite dangerous if it is not observed in practice. Shaped compositions which contain an inflammable solvent must be thoroughly exposed to the air in a large room to vaporize the solvent as much as possible before transferring it to the drier.

15. Firework compositions and parts

Compositions which are used for fireworks are mixtures of various components and all the oxidizers dissolve in water. These compositions therefore are easily damaged by moisture. Sometimes this is useful for temporarily keeping a composition in a safe state, as in the wet process for example,sometimes however this can lead to a misfire.

So many kinds of composition are used for fireworks that a particular kind of operation may be required for each type. This is quite complicated and troublesome, but important.

15.1. Bursting charge

The description here particularly refers to the bursting charge of the chrysanthemum shell which are called "Warimono" in Japan. A different bursting charge is used for the other kind of shell called "Poka" which simply uses black powder grains.

There are three requirements for the bursting charge of Warimono; to break the shell into pieces, to ignite the stars and to project the stars with an uniform trajectory with the least curvature. Indeed the bursting charge is the motive power of the shell, and it is essential to concentrate our energy on this research just as much as on the stars. The bursting charge is, like a cannon, both the explosive of the shell and at the same time the propellant for the stars. It must produce an explosive force which can be adjusted by the strength(thickness) of the shell. This phenomenon is not detonation, but quick burning. A high explosive which detonates destroys the stars and is difficult to use as a bursting charge.

There are several representative compositions for the bursting charge as follows:

Potassium chlorate bursting charge, H3

Potassium chlorate	75%
Hemp coal(or Pawlownia coal)	25%
Glutinous rice starch	2%(Additional percent)

Or a ratio of chlorate to hemp coal of 10:3 is also popular. After many sensitive tests it is known that this is quite unexpectedly insensitive to shock and friction; perhaps a little more sensitive than black powder.

On the other hand it becomes highly sensitive, when it is mixed with sulphur, sulphur compounds or red phosphorus. In these circumstances it especially increases in friction sensitivity; this is a fatal defect. It is important therefore to pay close attention when loading of shells, where great friction often occurs, to prevent the composition H3 from contacting the black powder which covers stars or with the fuse composition which often contains realgar. When a shell containing H3 misfires high up in the air and falls down to the ground, it often explodes if the ground is hard. This may be caused by strong friction between the charge H3 and the stars which contain sulphur or realgar.

The H3 bursting charge has the largest burning rate of all the bursting charge in use at present; three times larger than that of a potassium perchlorate charge and half as much as that of black powder in the open air. The burning rate of H3 does not particularly depends on the pressure and when a pile of this composition burns, it looks like a detonation.

The H3 charge has two great advantages; the first is to project the stars quite a distance even when the wall of the shell is not very thick, and the other is to give an exact round shape to the flower even in small shells, e.g., of 2.5 inches or 3 inches diameter. Any other kind of charge will not be effective for such small shells. The H3 charge is therefore still essential.

Potassium perchlorate bursting charge, KP

Potassium perchlorate	70%
Hemp coal (or Paulownia coal)	3.8%
Sulphur	12%
Glutinous rice starch	2% (Additional percent)

This bursting charge was produced and first used practically in 1955 to avoid the danger of the chlorate charge H3. The author has not heard of any accident produced by this charge from the beginning. In 1966 the another witnessed an accident with a 2k inch shell which contained this KP charge. The shell exploded when it was fired. Photographically it was clear that it did not explode in the mortar, but at a small distance from the muzzle. It was concluded that the accident was caused by some other source other than the bursting charge, because it did not explode in the mortar. In any case for such a large shell a black powder bursting charge is much safer than either H3 or KP.

The KP charge is unsuitable for small shells of less than 3 inches in diameter as it gives an irregular shape to the flower. It contains the sulphur as a sensitizing agent in order to improve the smaller shells as far as possible. It shows a relatively high sensitivity to mechanical action, but the degree of sensitivity is little lower than that of black carlit in industrial use.

The great advantage of this KP charge is that it causes less trouble in the manufacturing operation than that of the chlorate charge H3; i.e. the friction sensitivity of the KP charge in contact with black powder or other compositions which contain sulphur or it's compound is not so high as that of the chlorate charge H3. Therefore it can be said that the KP charge is safer than H3 during the loading of shells or to the shock on the ground in the event of a misfire.

The KP charge has almost the same explosive force as that of H3, but the burning rate of the former is about one third smaller than that of the latter and a half of the rate of the black powder bursting charge as described above. But when the burning pressure increases, the burning rate is very much increased; it is possible to bring the burning rate to the same degree as that of H3 by pasting an extra number of layers of paper on the shell. When the thickness of the shell wall is inadequate, the KP bursting charge burns even after the explosion of the shell with consequent loss of efficiency.

Black powder bursting charge, BP

Potassium nitrate	75%
Hemp coal(or Paulownia coal)	15%
Sulphur	10%
Soluble glutinous rice starch	2%(Additional percent)

This charge is quite insensitive to shock and friction, but of course it increases friction sensitivity in contact with chlorate. This has only half the explosive force of H3 or KP, but it is recommended for big shells more than 8 inches in diameter. There are two reasons; one lies in the safety problem of course and the another is that this charge easily allows us to obtain the optimum diameter of the flower in a big shell. The flower which develops in the sky from a big shell is especially attractive not only because of the large diameter, but also because of the high density of the stars. When the flower is too large in diameter, the beauty suddenly decreases if there is a decrease in the density of the stars. The intensive charge of H3 or KP often causes this failure.

Potassium perchlorate bursting charge,
No.5, No.44 and No.46

	No.5	No.44	No.46
Potassium perchlorate	70%	70%	75%
Hemp coal(or Paulownia coal)	30%	30%	-
Lampblack	-	-	25%
Potassium bichromate	-	5%	5%
Soluble glutinous rice starch	2%	2%	2%
Burning rate ratio in the open air based on No.5=1.0	1.0	1.5	4.8

These charges were produced in 1967 by K.Takada and Y.Kinsei(Hosoya Firework Co.: Studies with firework shells, especially chrysanthemums, which contain no chlorate, p.2(1967)). These compositions were selected from 47 samples after various tests. They contain no sulphur or sulphur compounds, but in No.44 and No.46 potassium bichromate is present playing a role as a catalyzer for decomposing potassium perchlorate. The sensitivity is rather low, but rather higher than that of BP. No.5 and No.44 are used in practice, but they are weaker than the KP charge. No.46 is impractical due to the high cost of the lampblack, but the force is rather larger than that of KP. If the particle size of carbon is small, the force is much larger.

The No.5 or No.44 charge is most popular for shells of the middle and large size, i.e. 6~10 inch shells.

Take care not to inhale the dust when using potassium bichromate because it is toxic.

The characteristic values of the above bursting charge are shown in table 19. As we see in the table, the starting velocity of stars propelled by KP can be increased to the same value as H3 by increasing the number of pasted layers of paper to 1.2 times more than is required for H3.

Table 20 shows the sensitivity values measured by the author. Other data on friction sensitivity measured by the BAM machine have been reported(N.Ishikawa, M.Kusakabe, H.Sudo and T.Sakuma: Friction sensitivity of firework compositions, J.Ind.Explosive society, Japan Vol.35,No.3 p.138(1974)).

Table 19. Characteristic values of bursting charges for chrysanthemums

	Chlorate comp.	Perchlorate comp.		Black powder comp.	Perchlorate comp.		
	H3	KP		BP	No.5	No.44	No.46
Burning rate in solid state **at 1 at.**(mm/sec)	3.0	1.0		2.0	-	-	-
Temperature of explosion (°C)*	3100	3600		1800	-	-	-
The volume of explosion gas at 0°C and 1 at. (ℓ/kg)*	570	480		370	-	-	-
Heat of explosion (kcal/kg)*	640	690		400	-	-	-
Force of explosives (kg.dm/kg)*	$0.74\mathrm{x}10^{6}$	$0.71\mathrm{x}10^{6}$		$0.31\mathrm{x}10^{6}$	-	-	-
Experimental data of 6 inch shells, where the stars are arranged in ring form							
Weight of bursting charge (g)	234	256	200	232	-	200	200
Weight ratio of bursting charge to cotton seeds	13/14	13/10	10/9	13/10	-	10/9	10/9
Diameter of a star(mm)	12.2	12.2	13.8	12.2	-	13.8	13.8
Weight of a star (g)	1.5	1.5	2.2	1.5	-	2.2	2.2
Burning time of a star (sec)	2.0	2.0	2.6	2.0	-	2.6	2.6
Number of pasted layers of kraftpaper(Japanese Kozo-paper) on a shell	(40)	(40)	20	(40)	-	20	20
Starting velocity of a star (m/sec)	71.4	63.5	-	56.7	-	-	-
Flying distance of a star in a horizontal direction (m)	55	50	70	45	-	67	80

Note: The symbol (*) denotes calculated data.

Table 20. Sensitivity of bursting charges

I. Drop hammer test with a 2kg hammer

	Chlorate comp.		Per-chlorate comp.		Black powder comp.		Perchlorate comp.					
	H3		KP		BP		No.5		No.44		No.46	
	H	N	H	N	H	N	H	N	H	N	H	N
Not mixed with any other material	79cm 50cm	50 10	62cm 60cm 37cm 25cm	10 10 30 10	85cm	10	>130cm	50	60cm	30	79cm	30
5% As_2S_2 is added	50cm 25cm 20cm	10 10 10	50cm	10	-		-		-		-	
10% S is added	25cm	10	-		-		-		-		-	
10% black powder is added	38cm	10	-		-		-		-		-	

Data of picric acid for comparison:

H	N	H	N	H	N
32cm	10	30cm	50	28cm	10
30cm	50	29cm	50	26cm	30
30cm	50	28cm	50	23cm	10

II. Friction test by Yamada's machine

	H3		KP		BP		No.5		No.44		No.46	
	W	N	W	N	W	N	W	N	W	N	W	N
Not mixed with any other material	75kg	10	87.5kg 75kg 75kg 62.5kg	10 10 20 10	*	50	*	50	*	20	50kg	20
5% As_2S_2 is added	3.7kg	10	50kg	10	-		-		-		-	
5% S is added	12.5kg	10	-		-		-		-		-	
10% S is added	7.5kg	10	-		-		-		-		-	
5% Sb_2S_3 is added	37.5kg	10	-		-		-		-		-	

Data of picric acid for comparison:

W	N
over 100kg	7
75kg	10

Note: The symbol (*) means that no explosion occurred. The symbol H means the maximum height without explosion, N the number of trials at H or W, W the maximum weight without explosion. The temperature for the tests were between 0° and 20*C.

Each bursting charge is manufactured into grains by pasting it on to some cores in order to obtain good fire transfer. Sometimes however it is made into grains without cores for a shell such as a multi-petalled flower, which has an internal space which is too narrow to permit large grains. The time taken for the fire transfer from the centre to the outer main stars in a 12 inch Warimono is supposed to be about 0.0004sec on experiment, provided that the bursting charge is well grained.

Cotton seeds are most popular as cores because the surface of the grain is downy so that it holds the composition very well. Rice chaff is also popularly used for smaller class shells. For larger shells seeds of Japanese cypress are used in mountainous districts and pieces of cork are also used for the largest shells. In any case core material must be roughly spherical, must hold the composition well, and should not allow the fire to remain in it after the explosion and if possible it should be ultimately biologically degradable.

The thickness of the composition pasted on each core is quite important. When the thickness is too great, the efficiency is low, because the composition continues to burn, even after the shell has burst. Ideally it should burn out before the shell breaks. The optimum thickness depends upon the kind of bursting charge. Chlorate or black powder composition, which has a large burning rate, can have a slightly larger thickness. On the contrary, perchlorate composition which has a small burning rate can not have such a large thickness. The optimum thickness however depends also upon the strength of the shell case. Generally the burning rate increases as the strength of the shell case increases, especially with perchlorate composition. Therefore, as the number of pasted layers of paper on the shell increases, the thickness of the composition on the bursting charge can be increased.

In view of this theory all that remains to be asked is what should be the ratio of the composition to the cores. The grain surface of the cores varies considerably with the material, and the composition which is fixed on the surface of the cores also varies in thickness on the cores. In practice it is best to determine the ratio by experiment, and in ordinary cases in view of the author's experiments the optimum ratio may be as follows(Table 21).

Table 21. The optimum weight ratio for the composition of the bursting charges in relation to the materials of cores.

Diameter of shell	Bursting charge	Composition:Material of core		
		Rice chaff	Cotton seeds	Cork pieces
Less than 3.5 inches	H3	4:1	-	-
"	No. 46	6:1	-	-
5 inches	KP,No.5,No.44	5:1	1.4:1	-
6 inches	No.44,No.5	-	1.4:1	7:1
More than 7 inches	No.44,No.5	-	1.0-1.3:1	8:1
"	BP	-	1:1	8:1

Note: Concerning the composition ratio of the bursting charge, H3,KP, BP,No.5,No.44 or No.46 see the tables which are beforementioned in this chapter.

The manufacture of the bursting charge grains. Prepare the cores in uniform size and remove foreign matter by sieving them with suitable sieves. Cores in groups sometimes cause fire to remain after the explosion. Dry them in the sun. Weigh out a quantity of the cores and then the composition according to the ratio in Table 17. Add a suitable amount of water to the composition in a tub and stir until it becomes a slurry. Add the cores to it and stir them well by hand until the composition sticks well on to the surface of the cores. Lastly dry the pasted grains well in the sun.

The thickness of the composition which is fixed on the surface is quite irregular for chaff and about 0.47~0.49 mm on average cotton seeds. The apparent specific gravity in both cases is about 0.48~0.50.

As described above, the bursting charge is manufactured quite roughly at present, but clearly it ought to be done most carefully as one would with cannon propellant.

15.2. Compositions for stars

Compositions for chrysanthemum shells(Warimono) must be selected with special care, but for Poka the selection is not as serious as for Warimono.

The conditions required for Warimono are set out as follows: The stars must have a large burning rate to give a straight trajectory; they must have a large critical wind velocity so that they are not extinguished by the air flow when they move at high speed; they must be easily ignited or one composition must ignite another easily. All of these requirements cannot always be satisfied at the same time however, and the stars are manufactured by a good arrangement of compositions in the various layers of a star(especially in the case of round stars).

Round stars are generally used for Warimono, but this shape is most unstable during burning compared with other shapes, e.g. a cylinder or tube, and quite extinguishable when moving at high speed in the air. This is the point where fireworks have to make the greatest effort, especially in the case of perchlorate compositions.

When we manufacture colour changing stars, we must choose the compositions so that the ingredients of one layer and those of another layer do not react with each other.

As there are many kinds of stars for Warimono and Poka, the following are only representative examples.

(1) Coloured flame compositions

The purpose of these compositions is to produce a flower in coloured lights or flames. There are two kinds generally used; one is the low temperature class(a flame temperature: 1700-2200°C) and the other is the high temperature class(a flame temperature: 2500-3000°C), where the compositions contain magnesium.

a) Low temperature class compositions

These are perchlorate compositions which contain no sulphur. The perchlorate can be replaced by chlorate without changing the colour. It is necessary to plan the composition so that the flame temperature is as high as possible to obtain a good colour. These are consolidated adding water.

Red Star:

Potassium perchlorate	66%
Accroides resin	13
Lampblack(or Paulownia coal)	2
Strontium carbonate	12
Polyvinyl chloride	2
Soluble glutinous rice starch	5

Specific gravity=1.30 g/cc
Burning rate =1.7 mm/sec

The purpose of the lampblack or paulownia coal is to allow the composition to burn quickly.

Yellow star:

Potassium perchlorate	68%
Accroides resin	18
Sodium nitrate	7
Lampblack(or Paulownia coal)	2
Soluble glutinous rice starch	5

Specific gravity=1.10 g/cc
Burning rate =3.2 mm/sec

The yellow colour is the easiest to obtain.

Green star:	
Potassium perchlorate	47.2%
Barium nitrate	28.3
Accroides resin	14.2
Chlorinated isoprene rubber(Parlon)	4.7
Soluble glutinous rice starch	5.6

Specific gravity=1.49 g/cc
Burning rate =1.4 mm/sec

With barium nitrate alone as the oxidizer the composition does not burn quickly and creates a large amount of ash. To avoid this, potassium perchlorate is added to the composition. The chlorinated isoprene rubber intensifies the green colour of the flame.

Blue star:	I	II
Potassium perchlorate	60.8%	66.5%
Accroides resin	9.0	9.9
Basic copper carbonate	12.3	-
Cupric oxide	-	13.4
Chlorinated isoprene rubber(Parlon)	13.1	5.4
Soluble glutinous rice starch	4.8	4.8
Specific gravity=	1.54 g/cc	1.60 g/cc
Burning rate =	2.0mm/sec	1.4mm/sec

Violet star:	I	II
Potassium perchlorate	61.3%	64.0%
Accroides resin	9.1	9.5
Basic copper carbonate	5.0	-
Cupric oxide	-	5-2
Strontium carbonate	7.4	7.8
Chlorinated isoprene rubber(Parlon)	12.4	8.7
Soluble glutinous rice starch	4.8	4.8
Specific gravity=	1.66 g/cc	1.64 g/cc
Burning rate =	1.8mm/sec	1.4mm/sec

b) High temperature class compositions

Generally the compositions which contain magnesium burn at high temperatures, which excite the emitters(molecules or atoms) in the flame quite well. They therefore give a far more brightly coloured flame than the low temperature class compositions. The burning rate is also larger. Accordingly we can obtain quite superior stars even when using perchlorate as the oxidizer.

Nevertheless some allowance must be made for ignition technique and for storage. It is necessary to ignite them correctly by using the techniques described in Part 3. The compositions have to be sealed also to protect them from moisture. In practice however simpler dampf-proofing methods can be used for firework pieces which are used up in a short time.

At low temperatures in winter or in small quantities it may be possible to consolidate the compositions into stars with water and soluble glutinous rice starch except few compositions when we use a magnesium powder which is coated with linseed oil. It is an important rule however to use a binder solution in an organic solvent for this consolidation in place of the water and glutinous rice starch, this is to avoid the danger of generating heat and hydrogen gas. Nitrocellulose solution in amyl acetate or in acetone is very convenient to use for this(s.14.2 (1)).

Red star brilliant:

Potassium perchlorate	30%
Strontium nitrate(anhydride)	20
Magnesium(60 mesh, coated with linseed oil)	30
Polyvinyl chloride	18
Lampblack or paulownia coal	2

Specific gravity=1.4-1.5 g/cc
Burning rate =1.5 mm/sec

This composition is somewhat hygroscopic because it contains strontium nitrate. When moistureproof stars are manufactured with this composition using nitrocellulose paste, they can be used in practice. The burning rate is adjusted by changing the ratio of magnesium to oxidizers. Potassium perchlorate decreases the ash.

Yellow star brilliant:

Potassium perchlorate	
Ultramarine	13
Magnesium(60 mesh, coated with linseed oil)	30
Polyvinyl chloride	10
Lampblack(or paulownia coal)	2

Specific gravity =1.4 g/cc
Burning rate = 3.8 mm/sec

For yellow flame there is no problem, because it is always obtained easily. The polyvinyl chloride has no relation to the flame spectrum, but it has a role in making the flame transparent and for obtaining a clear yellow.

Green star brilliant:

Barium nitrate	42%
Magnesium(60 mesh, coated with linseed oil)	25
Polyvinyl chloride	15
Larapblack(or paulownia coal)	2
Potassium perchlorate	16

Specific gravity = 1.6 g/cc

Burning rate = 2.2 mm/sec

c) High temperature class compositions which contain ammonium perchlorate

When ammonium perchlorate is used as a component for the compositions of stars, the flower may be quite beautiful due to the clear colours, but at present it is not popularly used, because the stars gradually become unignitable after manufacture. This is caused by a moistened layer formed by a reaction between the ammonium perchlorate in the composition and the potassium nitrate in the black powder pasted on the surface of the star as the igniter. When a composition which contains ammonium perchlorate is coated with a layer of some composition which contains no potassium nitrate and no ammonium perchlorate, e.g. a potassium perchlorate composition, and which is then coated with a layer of black powder as the igniter, the same reaction occurs between the ammonium perchlorate and potassium nitrate, by osmosis through the interlayered composition; the whole of the star becomes wet and unignitable. The author found a solution to this problem using the following igniter composition when the humidity is less than about 60%.

Igniter B

Sodium nitrate	80%
Paulovmia coal	15
Sulphur	5

This is a kind of "B"-black blasting powder which contains sodium nitrate in place of potassium nitrate and does not cause such a reaction with ammonium perchlorate as described above.

In high temperature class compositions which contain magnesium there is another problem; that is the reaction between ammonium perchlorate and magnesium to create magnesium perchlorate, which is quite hygroscopic. This problem is thus settled by using potassium bichromate as a stabilizer which perfectly stops the reaction. The magnesium powder is also coated with potassium bichromate before mixing. In this case the compositions can be consolidated using glutinous rice starch and water. For ignition of the stars they are coated with a slurry of Igniter B in which 2-5 additional % potassium bichromate and some quantity of nitrocellulose paste are added. Take note that the bichromate is an irritant to the skin and mucous membranes. When the stars must be stored rather long in high humidities, they should be manufactured for ignition by the same way as it is described for twinklers(pp.224,225).

Ammon red star brilliant;

Ammonium perchlorate	41.0%
Magnesiura(60 mesh, coated with potassium bichromate)	33.3
Accroides resin	9.5
Strontium carbonate	9.5
Potassium bichromate	1.9
Soluble glutinous rice starch	4.8

Specific gravity=1.03 g/cc

Burning rate =4.6 mm/sec

Ammon yellow star brilliant:

This is obtained from the above formula of "Ammon red star brilliant" replacing strontium carbonate with ultramarine,$Na_2S_2.3NaAlSiO_4$ (?).

Specific gravity=1.08 g/cc

Burning rate =5.5 mm/sec

Ammon green star brilliant:

This is obtained also from the formula of "Ammon red star brilliant" replacing strontium carbonate with barium carbonate.

Specific gravity=1.30 g/cc

Burning rate =4.3 mm/sec

These compositions are used for special artistic effect. The shells which contain these stars are not necessary to be of moistureproof construction.

Barium nitrate cannot be used for the compositions of this type because the stabilizer, potassium bichromate, is spent reacting with the barium nitrate to produce barium chromate which is insoluble in water.

(2) Silver compositions

Aluminium is a substance which is not very easily vapourized, but when it is burnt with an oxidizer, it is partially vapourized and forms a flame.

Brilliant core:

Barium nitrate	66%
Aluminium(fine flake)	27
Boric acid	1
Soluble glutinous rice starch	6

The Doric acid is to suppress the reaction of the aluminium with the barium nitrate in a wet state(R. Lancaster: Fireworks, principles and practice, p.31(1972)). This is used for the cores of round stars and it gives a strong flash-light at the end of the stars of a chrysanthemum. The burning rate is quite large, even when it is consolidated. The core is shaped as a 3mm cut star. Larger cut stars decrease their power of ignition.

The stars burn so quickly that they move, as if they were swimming round by rocket action when the core is ignited in an unbalanced way. We call the phenomenon "Swimming", and to avoid this it is better to coat the cut stars with the following composition until the cut stars become rounded.

Core coating composition:

Potassium perchlorate	33%
Barium nitrate	34
Aluminium (fine flake)	10
Rosin(BL combustion agent)	8
Antimony trisulphide(or sulphur)	9
Boric acid	1
Soluble glutinous rice starch	5

The following composition does not burn as quickly as the brilliant core, producing a silver flame.

Silver star:

Potassium perchlorate	56%
Rosin(BL combustion agent)	5
Aluminium(fine flake)	32
Lamp black	2
Soluble glutinous rice starch	5

(3) Fire dust compositions

a) Metallic fire dust compositions

Metallic fire dust compositions are generally difficult to ignite, but they become easily ignitable by means of the process described in 7.2.

Silver wave:

Potassium perchlorate	x %
Aluminium(somewhat coarse flake)	y % (x + y = 100)
Soluble glutinous rice starch	5 additional %

This is mentioned also in 7.2. This produces a pretty silver fire dust. When we change the weight ratio x/y, the fire dust is obtained in various forms with slight changes of colour. If the proportion is 50/50 there is a large silver fire dust flame of short duration; where the proportion is 35/65 we get a small flame with yellowish fire dust of long duration.

Golden wave:	No.1	No.2	No.3
Potassium nitrate	37%	37%	37%
Aluminium(somewhat coarse flake)	47	47	47
Antimony trisulphide	9	-	-
Sulphur	-	9	-
Realgar	-	-	9
Boric acid	1	1	1
Soluble glutinous rice starch	6	6	6

The boric acid prevents the potassium nitrate and aluminium from reacting with each other(R.Lancaster: Fireworks, p.31(1972)). No.1 and No.2 produce a pretty golden fire dust. No.3 produces a somewhat reddish gold effect, and looks more elegant than No.1 and No.2. When we use antimony trisulphide, sulphur and realgar, as components in one composition with various ratios between them, various colour tones of gold can be obtained.

Golden chrysanthemum:	
Potassium nitrate	40%
Aluminium(somewhat coarse flake)	30
Sulphur	10
Realgar	10
Hemp coal(or paulownia coal)	2
Boric acid	1
Soluble glutinous rice starch	7

This produces brilliant yellow fire dust.

The display effect of metallic fire dust has to be tested in a star shell; a burning test on the ground does not give a correct valuation.

b) Charcoal fire dust compositions

	Chrysanthemum 6.	Chrysanthemum 8.	Chrysanthemum of mystery	Tiger tail	Willow
Potassium nitrate	55%	49%	45%	44%	35%
Sulphur	7	6	-	6	12
Pine charcoal	33	40	50	44	45
Soluble glutinous rice starch	5	5	5	6	8

When we change the weight ratio of the three components, potassium nitrate, sulphur and charcoal, in steps, we have reddish fire dust sparks with correspondingly varied lives. Chrysanthemum 6 and 8 are of relatively short life and fit stars for the chrysanthemum(Warimono). To obtain a pretty remaining fire, it is not enough merely to mix the three components, but the potassium nitrate must be allowed to soak into the charcoal particles. For this purpose a wet process can be effective to mix the three components. (The name "Chrysanthemum 6 or 8 means that the weight ratio of the charcoal to the potassium nitrate is 6:10 or 8:10.) Willow produces a fire dust with a long life and is used for willow shells, but the fire dust often falls to the ground without being extinguished and the wind direction must be considered when displaying willow shells. The chrysanthemum of mystery contains no sulphur and the fire dust looks quite weak. It creates a rather different and lonely fantasy(s.3)• The same care must be taken with effect as with the willow stars, because the fire remains in the embers for long time.

c) Black powder-metal fire dust compositions (s.also p.127)

When a metal powder is contained in a black powder type composition, it creates fire dust or sparks of special beautiful effect. It may come from the "Senko Hanabi" effect.

Silver wave chrysanthemum:

Potassium nitrate	50.0%
Sulphur	17.5
Pine charcoal	7.5
(These three are previously mixed densely as in the manufacture of black powder,if possible)	
Aluminium(somewhat coarse flake)	7.5
Magnalium	1.5
Antimony trisulphide	2.5
Realgar	7.5
Soluble glutinous rice starch	6.0

It produces a strange fire dust which looks as if red, yellow and green twinkling fire particles were mixed together.

Dr. Winokur proposed many formulae which produce superior effects as follows(Robert M. Winokur: The pyrotechnic phenomenon of glitter, Pyrotechnica, No.2, February, 1978):

Winokur's compositions:	No.32	No.33	No.34	No.35	No.38
Potassium nitrate	38%	43%	40%	36%	40%
Sulphur	13	10	10	13	12
Charcoal	10	10	10	10	12
Barium nitrate	14	13	16	16	13
Atomized aluminium	12	13	12	12	12
Red iron oxide	8	7	7	8	7
Dextrin	5	4	5	5	4

(4) Twinklers

It is known that magnalium burns vibrationally under certain conditions. In 1955 the author studied the burning of compositions which contained magnalium, barium nitrate and sulphur in various weight ratios in order to use magnalium as an illuminant in place of magnesium. However the compositions burned vibrationally and could not be used. Later in 1961 twinklers appeared in some firework displays in Japan. These were stars which displayed this oscillatory burning in a different way to ordinary illuminants. As far as the author remembers, the Ikebun Firework Co. in Shizuoka-ken manufactured quite pretty green twinklers. In 1967 Y.Kinsei in the Hosoya Firework Co. discovered that ammonium perchlorate also produces this oscillatory burning phenomenon in the same way as barium nitrate. He produced compositions which contain magnalium, ammonium perchlorate and sulphur, but there was a fear that these compositions were rather sensitive to shock and friction, possibly caused by the sulphur. Later the author studied various materials, and found that the essential substance which causes the oscillatory burning is a sulphate, and it is far more effective than sulphur. To obtain good colours the author used magnesium in place of magnalium. These compositions will be described below.

According to R.6.Hall in Sngland there was a formula noted in a old mixing book called "Orion" Flashing Guns, dated 1898 as follows:

Composition No.1:

Sulphur	24	(51%)
Fine magnesium powder	8	(17)
Fine aluminium pyroflake	3	(6)
Barium nitrate	12	(26)

Composition No.2:

Sulphur	6	(55%)
Fine magnesium powder	2	(18)
Barium nitrate	3	(27)

In Germany U.Krone and F.-W.Wasmann suggested that a twinkler composition consists of two kinds of compositions mixed with each other, i.e. a smoulder composition and a flash composition(F.-W. Wasmann: Festtreibstoffe mit pulsierenden Abbrand, Explosivestoffe, page 1, Heft 1, Januar/Februar (1973); U.KronerStrahlungsemission in intervallen-oscillierende Verbrennung pyrotechnischer Satze,Jahrestagung 1975 in Karlsrue, Institut für Chemie der Treib- und Explosivestoffe; F.-W.Wasmann:Pulsierend abbrennende pyrotechnische Systeme, ditto). In 1979 Robert G. Cardwell wrote a review of twinklers(Strobe light pyrotechnic compositions: A review of their development and use, Pyrotechnica No.5, page 6(Austin, U.S.A., 1979)),

Ammonium perchlorate smoulders when it is mixed with a small quantity of magnesium. This can be used for the smoulder composition. A mixture of magnesium and a sulphate flashes when it is heated to a high temperature. This can be used as the flash composition. When the two compositions are mixed with each other and ignited, it begins to smoulder. Firstly during the smoulder the flash composition does not react and remains in the smouldering zone(a semi-reacted zone) because the temperature of the zone is lower than the ignition point of the flash composition. As the smoulder proceeds a heat accumulation occurs in the zone to raise the temperature which finally reaches the ignition point of the flash composition, when a flash suddenly occurs. Thus smoulder and flash repeat producing a oscillatory burning. Examples of ammonium perchlorate base compositions are set out as follows:

Table 22. Twinklers of the ammonium perchlorate base

	Red	Orange	Yellow	Green	White
Magnesium(60 mesh, coated with potassium bichromate)	30%	30%	40%	23%	-
Magnalium(80 mesh, ditto)	-	-	-	-	25%
Ammonium perchlorate	50	60	50	60	60
Strontium sulphate	20	-	-	-	-
Calcium sulphate	-	10	-	-	-
Sodium sulphate	-	-	10	-	-
Barium sulphate	-	-	-	17	15
Potassium bichromate as a stabilizer, add.%)	5	5	5	5	5
Specific gravity(g/cc)	1.22	1.15	1.20	1.31	1.38
Frequency(hertz)	3.5	6.9	3.5	3.1	9.7
Burning rate(mm/sec)	4.4	6.9	9.7	1.7	11.4

These compositions are manufactured into stars as follows: One of the compositions is kneaded by adding 25 parts of 10% nitrocellulose solution in acetone to 100 parts of the composition by weight and it is then cut into cubes, e.g., in 9 mm cubes by the method described in 14.2-(1). They are then coated with an ignition composition (s. p.225) using the same nitrocellulose paste until the shape of the cut star becomes round. The stars are further coated with ordinary black powder style compositions using the same paste to ensure the ignition. In this case the nitrocellulose paste is effective to suppress the osmosis which produces hygroscopic ammonium nitrate in the layer of the ignition composition when the minimum thickness of the layer is not less than 1-2 mm.

Ignition composition for twinklers:

Potassium perchlorate	74%
Rosin(BL combustion agent) or Accroides Resin	12
Hemp coal or paulownia coal	6
Aluminium(fine flake)	3
Potassium bichromate	5

The following nitrate base compositions were proposed by Y.Kinsei. The process of manufacturing the stars is almost the same as that of the ammonium perchlorate base.

Twinklers of the nitrate base:

	Green	Yellow
Magnalium(coated with linseed oil)	18%	12%
Barium nitrate	40	33
Potassium nitrate	-	7
BHC	5	11
Sulphur	30	27
Antimony trisulphide	7	5
Sodium oxalate	-	5
Burning duration of a 12mm round star	6.4 sec	4.8 sec

The same ignition composition described above can be used also for the nitrate base twinklers. In this case the potassium bichromate is unnecessary and the nitrocellulose paste should be used for the ignition coating with the ignition composition.

(5) Flare stars

These are used as illuminant and they hang from a parachute. Increasing population density and urbanization mean that parachute flares are going to be gradually phased out for safety. They can still however be used at sea, on lakes, in the desert or in a district where there is no danger of fire.

Flares:	Barium light	Sodium light I	Sodium light II
Barium nitrate	50%	-%	-%
Sodium nitrate	-	50	40
Magnesium(40 mesh, coated with linseed oil)	50	50	60
Consolidating agent (polyester etc.,addi.%)	3-5	3-5	3-5
Specific gravity (g/cc)	1.80	1.45	1.30
Burning rate (mm/sec)	4.0	5.0	6.4
Light intensity (cd/cm)	8,000	14,000	28,000
Light energy per gram (cd.sec/g)	11,000	18,000	24,000

The barium light uses the BaO spectrum and the sodium lights, I and II, use the strong spectrum spreading on both sides of the NaD lines. The burning data are shown as a summarized standard in the case of flares loaded at a high pressure. The barium light produces a white flame. The optimum burning range with few sparks or cinders is limited from 45 to 55% magnesium. The sodium light is larger than that of the barium light.

Sodium nitrate has not been used in Japan up to now due to its hygroscopic nature, but material which is well purified is hardly hygroscopic, and is extensively used in Europe.

(6) Smoke stars

a) Stars of smoke dye compositions

These are used for parachute smokes, smoke willows or smoke chrysanthemums.

Smoke dye compositions for stars:

	Red	Yellow	Green	Blue	Violet
Potassium chlorate	28%	32%	33%	33%	29%
Milk sugar	20	28	27	27	25
Rhodamine B cone	30	-	-	-	13
Oil orange	22	-	-	-	16
Oil yellow(Butter yellow)	-	40	20	-	-
Phthalocyanine blue	_	_	20	40	17

The potassium chlorate and milk sugar play a role as heat and gas producing agents. Wheat flour can be used in place of milk sugar. The compositions above are suited for smokes of short duration, of less than 10-20 sec. Longer burning times make the compositions lose their beautiful colour, but it can be extended to some extent by increasing the weight ratio of the dyes to potassium chlorate.

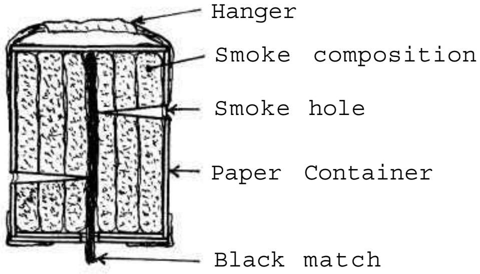


Fig.76. Smoke flare for dye compositions
(Parachute smoke).

Fig.76 shows a smoke star which is hung by a parachute. The composition is packed with a piece of thin paper (Japanese Gampi) and rolled into an eddy-cylinder(Fig.77). Then it is pressed into a paper container. This process was produced to make the work cleaner. Two or three smoke holes are bored in it with an awl from the outside.

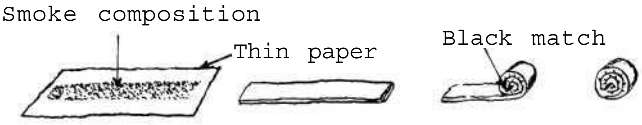


Fig.77. Packing a smoke composition before loading.

Smoke willow stars which display a group of fine coloured lines streaming through the sky, are manufactured as follows: Add *3%* soluble glutinous rice starch to one of above compositions and knead it into a mass after adding an amount of water to it. Manufacture cut stars of 10mm cube from the mass. Dry them indoors and then in the sun and then finally paste on the grains the igniting composition(black powder). This process produces quite a beautiful willow, but it stains both the room and the worker; it is especially dirty with soluble dyes like rhodamine.

Another type of willow smoke star which gives large streamers of colour is manufactured by loading one of above compositions into a small cardboard shell 2-3 cm in diameter(Fig.78) or in a kraft-paper tube of the same diameter. The stars are bulky, and not many stars can be placed in a shell. The paper shell or tube should be thin and strong.

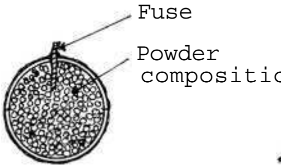


Fig.78. Smoke willow star.

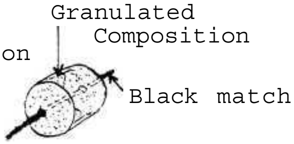


Fig.79. Smoke chrysanthemum star.

To manufacture smoke chrysanthemum stars which produce a large smoke stream in only 4-6 sec, compositions should be granulated because the compositions must be burnt up quicker than the willow. Add 2% soluble glutinous rice starch to one of above compositions and knead it adding some water to gain a wet mass. Granulate it by passing it through a sieve and dry it in the sun producing 1.5-2.0 mm grains. The grains are loaded into a small tube through which a piece of black match is threaded (Fig.79).

b) Stars of non-dye smoke compositions

White chrysanthemum or willow:

	White chrysanthemum I	White chrysanthemum II	White willow
Potassiura nitrate			48.5%
Sulphur	7	-	48.5
Realgar	-	13	3.0
Charcoal(or Hemp coal)	32	5	2.0*
Lampblack	8	5	-
Soluble glutinous rice starch	6*	11	6.0*

Note: The symbol(*) denotes an additional percent.

I and II use a white smoke generated from the flame. White willow uses the smoke formed by the condensation of sulphur vapour without flame. The realgar allows the composition to burn smoothly. The stars of I and II are coated by an ignition composition. The white willow is manufactured as follows: Form the composition into cut stars. Dry them well. Place them in a coating tub. Add to it slurry paste of soluble glutinous rice starch and shake the tub so that all the surfaces of the stars are covered with the paste. Remove them out of the tub and place them on to gypsum powder. Roll them in it until all the stars are coated with the gypsum. Dry them in the sun. Repeat these operations until the layer of gypsum becomes not less than 1.5mm minimum thickness. In order to obtain such a thickness it is necessary to do the operation six times. The gypsum gradually consolidates. Bore a hole in each star to introduce the fire in it. This is one of the most unpleasant operations in firework manufacture for the star is often ignited by the overheating of the drill(but there would be no explosion). No explosives or combustible materials must be near this operation. The bored stars must be removed at once to a safer place. Keep the speed of the drill as low as possible. The hole in each star is primed with black powder paste and dried well in the sun. Place the stars in an aluminium tub and pour soluble glutinous rice starch solution on to them. Shake the tub until the stars are thoroughly covered with the solution and then remove the stars from the tub on to a sheet of kraft paper on which black powder has been spread. Roll the stars by hand until the surface are entirely coated with the powder.

<u>Realgar yellow smoke</u>:	Yellow dragon	Yellow willow
Potassium nitrate	25%	43%
Sulphur	16	10
Realgar	59	37
Hemp coal(or paulownia coal)	-	4
Soluble glutinous rice starch	-	6

The colour of this smoke is more dense than that of dye smoke, but it looks dark yellow against the light of the sun. The smoke may contain arsenic trioxide, and may be poisonous and therefore it must not be used indoors. In the open air there is no trouble of course, and it is most popularly used at present in Japan.

The yellow dragon is manufactured by pressing the composition into a paper tube. When it is not pressed, it smokes quite quickly and this is used for stars of the daylight yellow chrysanthemum(Fig.79). In this case the composition can be used without consolidation or granulation. The yellow willow composition is formed into pumped stars and is coated with gypsum as it is with the white willow described above,

<u>Black smoke stars</u>:	Black dragon	Black willow
Potassium perchlorate	56%	57%
Anthracene	33	40
Sulphur	11	-
Hemp coal(or paulownia coal)	-	3
Soluble glutinou rice starch	-	7(Additional percent)

The black dragon composition is pressed into a tin tube and primed with a small igniting star and a piece of black match. The black willow is used in the form of cut stars. The anthracene is somewhat expensive, and half the quantity can be replaced by naphthalene with the same effect. There are three requirements for black smoke stars: producing pretty smoke; no remaining fire and safety in manufacturing and handling. The above compositions nearly satisfy all the three, but it is quite difficult to ignite them. Therefore in this case of the dragon it is necessary to use an ignition star as a first fire composition and in the case of the black willow stars to coat them first with the silver wave composition(15.2(3)c) and then with the chrysanthemum 8, 6 and black powder one after another.

15.3 Thunder(Flash report)

Thunder is the noise caused by the explosion of a composition and which emotionally increases the activity of the firework display. The composition which also produces a flash effect is called "Flash thunder".

Flash thunder:	No.1 Flash thunder	No.2 Flash thunder	No.3 Thunder	No.4 Thunder
Potassium chlorate	43%	-%	-%	-%
Potassium perchlorate	-	50	64	72
Sulphur	26	27	13	-
Aluminium(fine flake)	31	23	23	28

Note: The detonation velocities of these compositions are shown in Table 4 (p.44).

The flash thunder No.1 is a chlorate composition. This is easily ignited and it explodes perfectly even in a relatively small turn of kraft paper without glue or any container, and there is no need for a strong capsule. This kind of composition is therefore most popularly used at present in Japan from the economical standpoint, but it is sensitive to shock and friction, and recently the chlorate has been gradually replaced by perchlorate.

The noise zone of the perchlorate composition is shown in Fig.80.

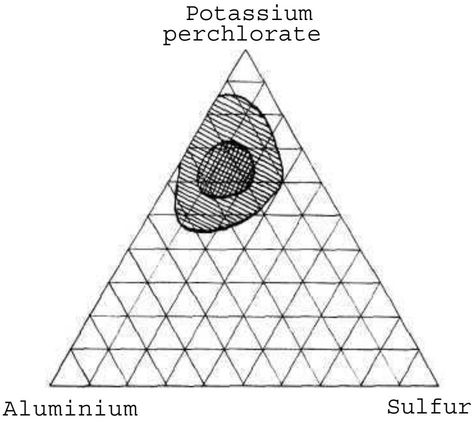
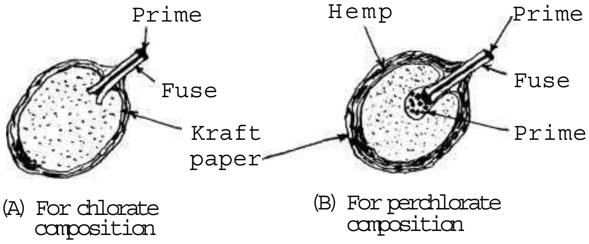


Fig.80. The noise zone of potassium perchlorate composition

The single shadowed area shows the medium intensity noise zone and the double shadowed area shows the loudest. With this composition the capsule must be strong enough to explode completely and moreover some device must be made to ignite the composition easily. No.2 is relatively well ignited and most popularly used. No.3 gives the loudest noise. No.4 contains neither sulphur nor sulphide and this produces a slightly smaller noise than the first three, but it is the safest of all to handle.



(A) For chlorate composition

(B) For perchlorate composition

Fig.81. Constructions of noise units.

The constructions of the noise units are shown in Fig.81. During the manufacture of the units, the composition must only be lightly compressed, otherwise it only burns like a toy fountain without explosion, especially with perchlorate compositions. It is best to keep the composition lightly in a capsule to obtain the loudest noise, but this type of noise unit cannot be used as a filler for shells lest it causes an accident.(The

author has experienced such an accident.) The construction of the unit cannot withstand the action of the bursting charge. To avoid this trouble, it is the best to manufacture the noise unit in a scallion form, which was produced in earlier times, although it looks rather primitive.
The surface of the scallion capsule must be carefully pasted with kraft paper to prevent the composition from the direct fire of the bursting charge. The manufacture of the noise units is unexpectedly difficult, it must be carefully supervised.

15.4. Whistles

Gallic whistle:

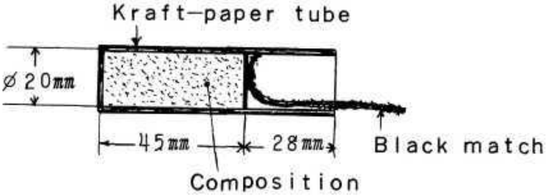
Gallic acid	25%
Potassium chlorate	75

Picrate whistle

Potassium picrate	63
Potassium nitrate	37

Benzoate whistle

Potassium benzoate	30
Potassium perchlorate	70



Another composition; a **mixture** of 25% sodium salicylate and 75% potassium perchlorate is sometimes used also, but it is too hygroscopic to keep the whisling nature even for a few weeks, and it is not yet popular in Japan.

The gallic and picrate whistles mentioned above are sensitive to mechanical action.The gallic whistle composition has almost the same sensitivity to shock as the picrate whistle. To friction the gallic whistle composition is far more sensitive than the picrate whistle, almost the same as red thermit, a mixture of red lead and ferro-silicon, but less sensitive than red explosive, a mixture of realgar and potassium chlorate. Potassium benzoate can be manufactured with benzoic acid and potassium carbonate. The whistle is weaker than gallic or picrate whistles but the safest of the three.

15.5. Hummers

Hachi (Firework hummer):

Black powder in powder (74% potassium nitrate, 13% sulphur, 13% charcoal)	70%
Black powder in small grain	10
Aluminium (middle flakes)	20

In Japan the firework hummer is called "Hachi" which means a bee.

Prepare kraft-paper tubes of 15mm inside diameter, 30mm long and a wall thickness of about 2mm. Close up one end of each tube with gypsum. Charge the composition solidly into the tubes, using a press or wooden hammer. Next close up each of the charged tubes with gypsum. Carefully bore a hole in the side of each tube in the centre using a hand drill. Lancaster maintains that it is better to place the direction of the hole at a tangent to the internal diameter of the tube. Insert a piece of twisted paper pasted with black powder into the hole of each tube as the igniter and secure it by winding a piece of hemp round it.

These hummer are loaded into a shell, and when ignited they fly around irregularly sending flame and fire dust sparks out of the hole with humming sound.

Larger hummers are called "Mad Lion". These are shot directly from mortars.

15.6. Comets, Flower comets

Comets are manufactured as follows: Prepare a strong paper tube. Place a star at each end of the tube, charging a quantity of blackpowder grains between them. Close up both ends with pasted paper. Bore a hole into the tube at the side and insert a piece of fuse into it and secure it with a piece of hemp or epoxy resin(Fig.83).

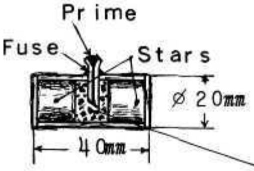


Fig.83. Comet.

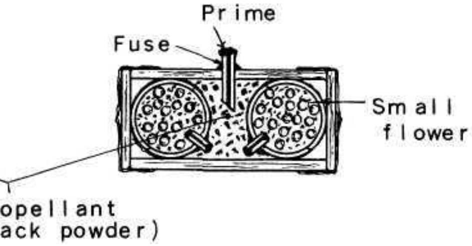


Fig.84. Flower comet.

When the fuse is ignited, the propellant is ignited after a short time projecting the stars in opposite directions. Small flowers(described later), thunders, smoke stars etc. are often used in place of stars. In this case the tube needs to be enlarged. Fig.84 shows a "flower comet which produces two small flowers.

15.7. Small flowers

3~5 mm round or cut stars are mixed with an amount of bursting charge. A quantity of the mixture is charged into a small shell and pasted with kraft paper on the outside. There are two ways to fit it with a fuse. One is to put a piece of fuse into the shell before charging the stars. The other is to bore a hole into the charged shell which has been pasted with the kraft paper and to insert a piece of the fuse into it. The latter is easy to operate, but quite hazardous. The latter method must be therefore limited only to stars made of insensitive composition.

The small flowers are used inside shells, for trajectory display (Kyoku), starmines etc.

15.8. Falling leaves

Prepare a coloured flame composition. Sandwich it with several sheets of Japanese paper by pasting one over the other as in Fig.86(B). Cut it in cards and bind four or five of them into a bundle with a piece of powder pasted paper. Paste one end with an igniting composition. Fig.86(A) shows the construction of the piece.

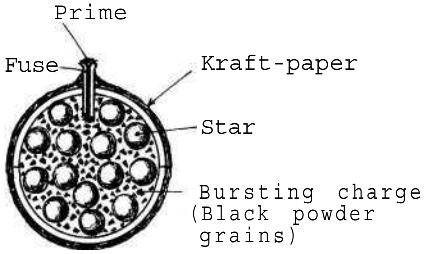
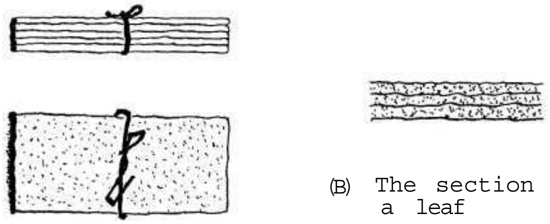


Fig.85. Small flower.


(A) A bundle of falling leaves

(B) The section of a leaf

Fig.86. Falling leaves.

When the bundles are charged into a shell and displayed in the sky, the leaves fall burning, like the leaves of trees falling down in autumn. Japanese falling leaves are not as good as the name suggests due to the short duration and poor colour of the fire. An improvement is required.

15.9. Kyoku

This ie a special name in Japanese and difficult to translate into English or other languages. It is thought that it came from the word, Kyoku-Gei, in which Kyoku means stunt and Gei means art. Kyoku then is nearly translated as "A stunt display", or "A firework piece for a stunt display". The word, Kyoku, is used in both the singular and the plural.

There are two kinds of Kyoku, one is used as a shell effect and the other is fixed to the outside of the shell as an accessory. These pieces display various effects at timed intervals by a combination of several units with fuses.

Examples of Kyoku found in shells are shown in Fig.87(A) and (B).

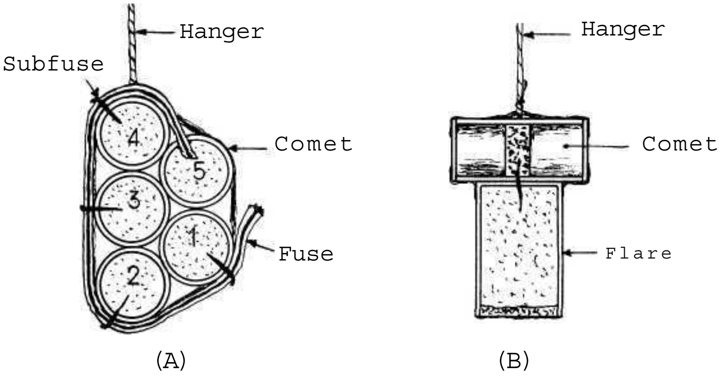


Fig.87. KYOKU with separating stars.

These are suspended by a parachute after they have been projected from the shell in the air. With (A) the fuse is first ignited and then the pieces are ignited step by step in the order 1, 2, 3, 4, 5 at regular time intervals. Bach piece is a comet and at each ignition two stars are projected from this at the same time in opposite directions. In (B) the flare is first ignited and the comets are projected when the flare has burnt out. These are called "Kyoku with separating stars".

The Kyoku effect fixed to the outside of a shell is described in 19.

15.10 Waterfalls

Waterfall:	Potassium nitrate	40%
	Aluminium(mixed large size flakes)	49
	Sulphur	4
	Boric acid	1
	Glutinous rice starch	6

This is insensitive to shock or friction. The boric acid suppresses the reaction of the aluminium with the potassium nitrate in the wet state avoiding the generation of heat(R.Lancaster: Fireworks, Principles and Practice, page 31(1972)).

Add as little water as possible to the composition and knead it well. Generally it is said that good kneading allows it to produce many long burning fire dust sparks, but this is not always true. This is charged solidly in strong paper tubes. Further description is in Lancaster's book on page 223.

R.Lancaster recommends the following composition which is lightly pressed in a dry state. The composition reqires a very hot igniter.

Waterfall of Europe:		
	Barium nitrate	52%
	Potassium nitrate	8
	Aluminium(Dark pyro or Silver)	22
	Aluminium 5~30 mesh flakes	14
	30~80 mesh flakes	5
	Boric acid	0.5

16. Warimono (Chrysanthemum)

Warimono is a shell which displays a flower like a chrysanthemum in the sky. The stars stretch out to form a round flower. The **duration** of the flower is **generally** 2～4 seconds.

16.1. General constructions for Warimono

The most popular construction of a Warimono shell is shown in Fig.88 For a precise description see Lancaster's book on page 258.

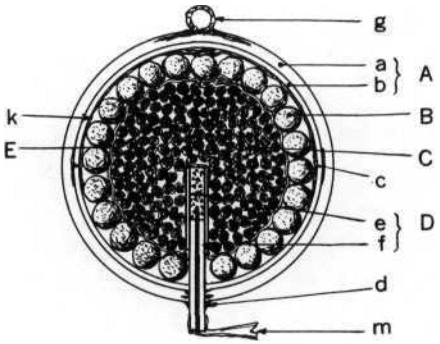


Fig.88. A representative construction of the Warimono shell.

16.2. Preparations

When hand made fuse is used,trim the two ends of a length **rejecting** the end pieces. Cut the fuse in a prescribed length(Fig.89).

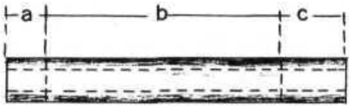


Fig.89. Preparation of a hand made fuse.

<u>a</u> is the end piece about 6 mm long and is called the "Split length". This is split just before loading the shell in a mortar to avoid misfire. <u>b</u> is the part which effects the delay from the shot to the explosion of the shell.

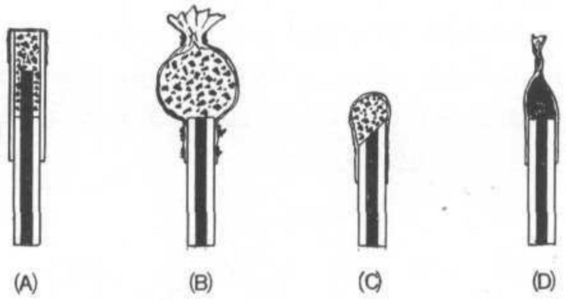


Fig.90. Preparation of fuses.

The part c is the "Core exposure", where the cover is removed with a knife to expose the core composition of the fuse to ensure ignition(Fig.90.(A)). Further devices are made in various ways to ensure the ignition from the fuse to the bursting charge(Fig.90). (A), (B) and (C) are **the most** reliable methods. At (D) a piece of black powder pasted paper is bound around the end of the fuse and the upper part is twisted. This is quite simple and often used, but sometimes it causes a misfire, because the powder pasted paper often fails to catch the last fire of the fuse. Therefore (D) is not to be recommended.

Recently in Japan a kind of Bickford fuse, which is especially manufactured for firework use and called "Main cord" has been brought over here(s.13.10.(86)). Fuse which has a core composition covered by asphalt is not recommended, because the asphalt soaks into the composition during long storage prolonging the delay time; this often produces an accident and the shell falls to the ground without opening in the air. To ensure ignition the fuse is primed with a blackpowder paste made of nitrocellulose or celluloid solution in acetone(14.2.(1)). There is also a risk of misfire when a solvent like amyl acetate is used because it is not as volatile as acetone. This is because of the formation of a thin incombustible film between the core composition and the pasted priming composition. Other methods to ensure the ignition of the bursting charge with Bickford fuse are shown in Fig.91.

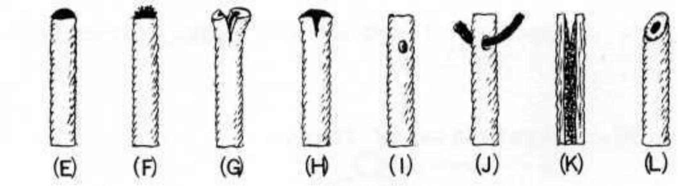
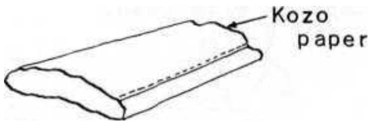


Fig.91. Preparations of Bickford fuse.

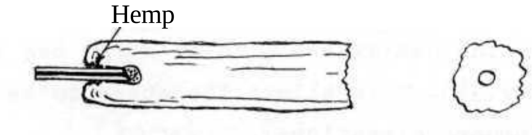
(E) is the ordinary primed fuse described above. (F) is sprinkled with blackpowder grains at the pasted end and is better than (E). (G) is split at the end, but there is the risk that the core composition at the end drops away. (H) is primed with paste on (G). Never use too much paste or the core composition may be damaged by the solvent. (I) is drilled at the side, but it is not always certain. (J) has a piece of match or twisted powder pasted paper passed through the hole, but sometimes there is a misfire due to the low quality of the match or twisted pasted paper. Moreover these additives become inert with strong compression and the fire stops at the compressed point. Therefore the match or paper must be passed through the hole quite loosely. (K) is bored cut at the end into the core composition to obtain a lot of fire at the end. But it is not always sufficient to ensure the ignition. (L) is a slanting cut for the same purpose. All these need to be reinforced by the method (A),(B) or (C) in Fig.90.

In the author's experience the construction of type (A) covered by tin foil is the most reliable. Some people use quite small diameter cores in their own handmade fuse, about 1~2 mm in diameter, but it is quite dangerous, because it often causes the fire to stop. A hard core made by a low quality powder pasted paper also often causes a fire stop. Prepared fuses must be tested adequately by sampling and inspection.

Combining the fuse and the bursting charge bag. Manufacture a bursting charge bag with Japanese Kozo paper, which should be cut to a width about three times as long as the inner diameter of the shell; crumble the bag until it is softened. The quality of the Kozo paper must be good so that it is not split during loading. Synthetic plastic sheets such as PVC should not be used due to the electric charge. Insert the outside end of the fuse into one end of the bag and paste and tie them with a piece of hemp string. Turn the bag inside out(Fig.92).



(A) Preparation of the bursting charge bag.



(B) Combination of the bursting charge bag and fuse.

Fig.92. Preparation of the bursting charge bag.

The bag serves to separate the bursting charge and the stars by standing between the two and also by keeping the positions stable. The separation of the two is most important when using a chlorate bursting charge and stars which are coated with black powder. In this case the bag must not be split nor allow the compositions to leak.

Fitting the hemispheres. In general the two hemispheres do not fit each other as a perfect couple if they are made of cardboard and they often need sanding at the edges.

Fitting a hemisphere with the fuse. Take one of the hemispheres and measure it to find the centre. Bore a small hole in the centre from the inside and carefully remove the furring on the outside caused by the drill. Insert the end of the fuse combined with the bursting charge bag from the inside of the hemisphere, securing the fuse by winding and pasting a piece of hemp around it or by using epoxy resin. Paste a piece of Kozo paper around the outside end of the fuse to protect it and dry this in the sun. The hemp winding is not easily dried when it is too thick and it is best to add the hemp in two stages, (See Fig.93.)

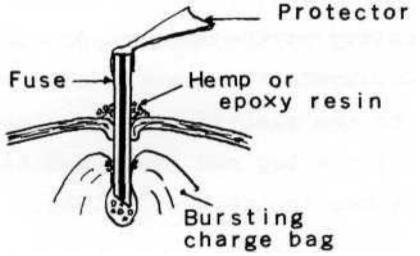


Fig.93. Fitting a hemisphere with fuse.

The operation must be quite elaborate, because a pressure of about 25 kg is exerted on the fuse when the shell is fired.

Fixing with outer bag. Paste the hemisphere with an outer bag made of Kozo paper and turn it over(Fig.94). This allows the stars to be charged in the hemisphere in an upward direction.

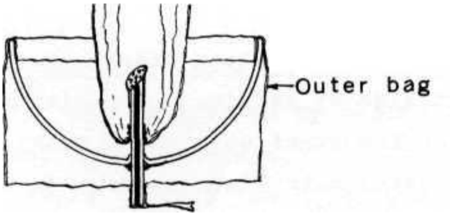


Fig.94. Fitting hemisphere with the outer bag.

16.3. The assembly of Warimono

It may well be a Japanese custom to sit on the floor to assemble shells, but it is rational, for it is possible to arrange all the components and tools around the worker and to avoid the shock caused when things fall on the floor. (But as described later, for shells which require less explosive than Warimono a working bench is often used in ordinary manufacture.) The operator must take care not to build up a mass of material around the working area. When chlorate compositions are used, have a wet cloth to hand, and wipe the hands with it immediately after handling each composition. Cutting powder pasted paper or quick match must be done in another room.

The assembly should be done by one person in one room, if possible. At the most only two people may be allowed in one room. Other operations should always be forbidden in the same room for safety. These are quite important lessons from previous accidents.

Fig.95 shows the assembling operations.

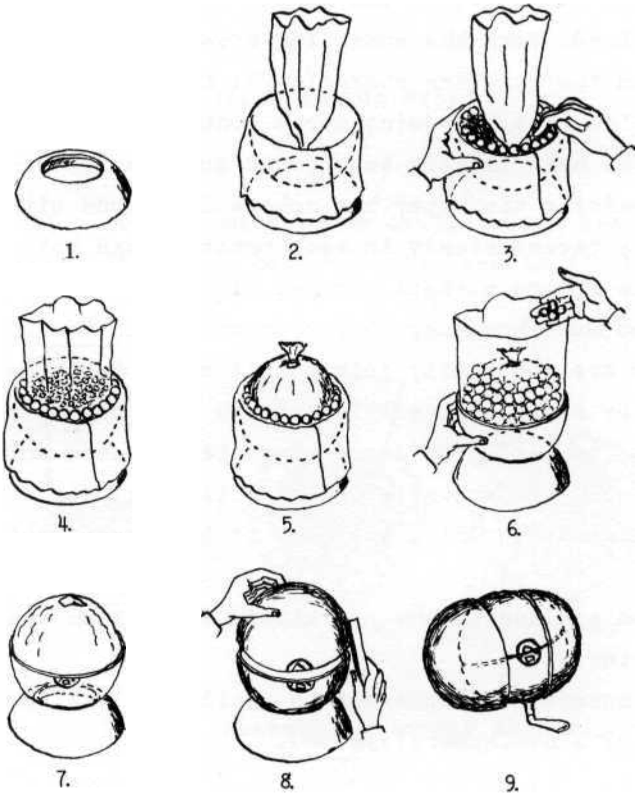


Fig.95. Assembling operations for Warimono.

Prepare a stand which is composed of one hemisphere(1). Place the prepared hemisphere which is fitted with the fuse, bursting charge bag and outside bag on the stand(2). Charge the main stars in the hemisphere and arrange them in one layer along the inside(3). Place the total amount of the bursting charge in the bursting charge bag(4). Tie the upper part of the bag with a piece of hemp string, adjusting the arrangement of the bursting charge so that the bag is round(5). The amount of bursting charge should be previously determined. Turn the outer bag upward and arrange the stars inside the bag around the bursting charge(6,7). Cover the contents with the upper hemisphere so that the joint marks come together in the right position(8). Using one hand lightly tap around both hemispheres with a small wooden bar, pressing the upper hemisphere downwards with the other hand(8). The contents become steady in each position and both the hemispheres form a single sphere without any gap. If a clearance still remains, this is caused by too much bursting charge or stars. On the contrary, if both the hertuspheres are too easily jointed, it shows that the amount of the bursting charge or stars is insufficient. In both cases try the same operation again increasing or decreasing the contents until they are correctly assembled. Fix the assembled shell efficiently by covering it with two more hemispheres(9). Write the name of the shell on the paper protecting the fuse.

This description applies to the operations for medium size shells, 5~8 inches in diameter.

Nobuyuki Koda invented an implement to facilitate the rapid arrangement of the stars inside of a hemisphere(Fig.96).

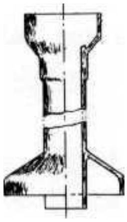


Fig.96. An implement for arranging stars.

For smaller or larger shells than those described above, the operations are suitably modified. In Fig.97 the contents are at first arranged separately in each of the two hemispheres and then the two are jointed. This is mainly applied to shells of less than 5 inches in diameter, but some fireworkers use this method up to 9.5 or 12 inch shells.

Fig.97. Coupling method.

Fig.98 shows a popular method for shells which are more than 9.5 inches in diameter. First the bottom hemisphere is filled with stars and bursting charge and then this is fitted with the upper hemisphere which contains a loading hole. Through this hole the stars and bursting charge are charged, separating them with the bursting charge bag. Lastly the hole is covered with the cut out piece of the upper hemisphere. During assembly the shell is tapped with a wooden bar on the outside as described above.

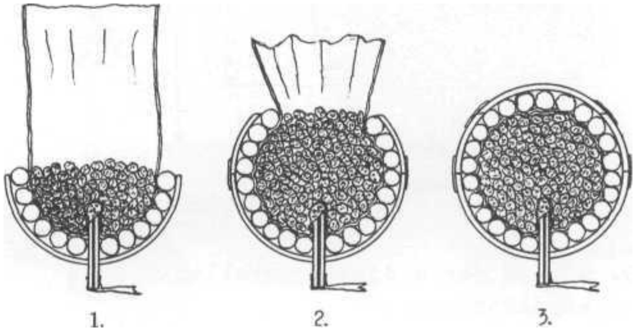


Fig.98. Assembling larger shells.

The representative method of assembly for a double petalled chrysanthemum is as follows: First plan the inside spheres. This depends upon the individual plan, but in general the diameter of the middle sphere (Dm) is equal to about a half of the internal diameter of the shell(Di), and that of the centre sphere Dc about *1/4* of Di. The size of each star in the middle sphere is equal to about half the size of the main star; the size of the centre star is about *1/4* that of the main star. There are various arrangements, but it is difficult to manufacture the shell if the parts are not in a good size ratio. In this kind of shell, the ratio of the space occupied by the stars is greater than it is in ordinary shells, and the space occupied by the bursting charge is somewhat less than normal, This causes a decrease in the diameter of the flower in the sky and to avoid this, some device must be made. Generally the grains of the bursting charge of the middle sphere are made smaller than those of the main bursting charge and those of the centre sphere are smaller than those of the middle, e.g. chaff is used for the core of the charge. (See Fig.99.)

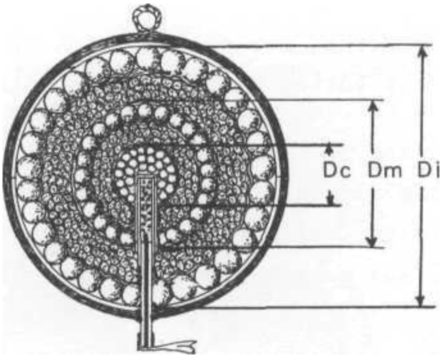


Fig.99. A plan for a double petalled chrysanthemum.

Making the centre sphere. Prepare a kraft paper tube, which is later to receive the fuse. Close the top of the tube with a piece of thin pasted Gampi paper(Fig.100-1). Then fit the paper tube with a bag made of Japanese Kozo paper for centre stars(2). The bag is the same diameter as the centre sphere. Insert the tube in the bottom hemisphere mould and put it on a stand. Next place some of the centre stars and the bursting charge consisting of smaller grains in the bag in the mould and press it down well with the fingers(3). Add the upper hemisphere mould and provisionally fix the moulds with adhesive tape. Fill the bag in the mould with the mixture and press it down well with the fingers(4). Tie the top of the bag with a piece of cotton string. Remove the adhesive tape and tie the shaped sphere, at the gap between the two hemisphere moulds, along the equator with a piece of red string, slightly separating the moulds(5). The red string is used as a mark for the next assembly. Remove the upper mould and then the bottom mould. Wind white cotton string around the sphere taking care not to spoil the shape(6). In this way the centre sphere is completed.

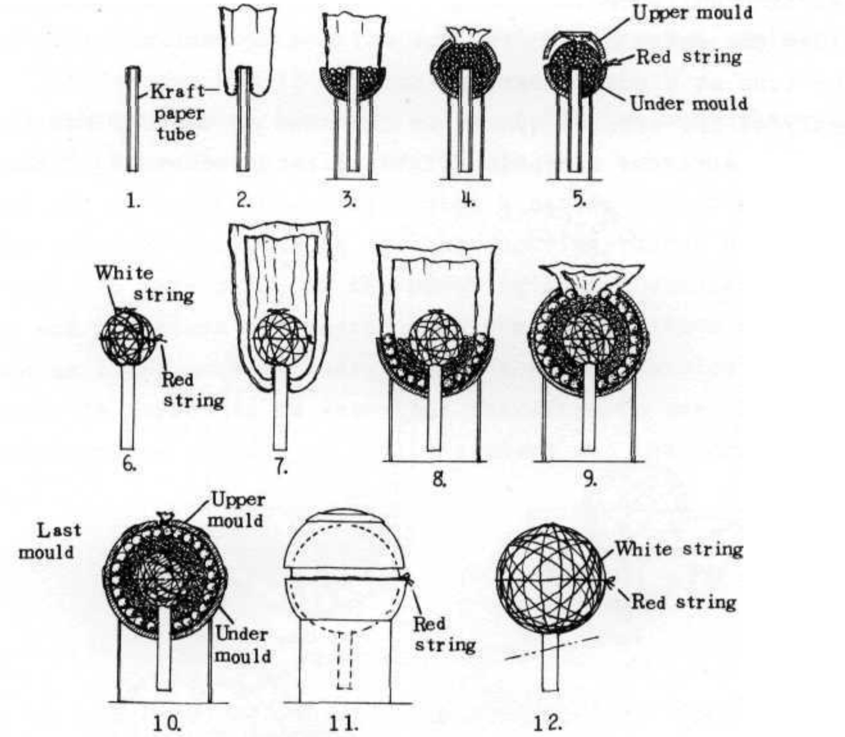


Fig.100. Assembling the internal spheres.

Next fit the centre sphere with two bags tied on the tube(Abb.100-7). The size of the outside bag is the same in diameter as that of the middle sphere and the inside bag should be little smaller than that. Fit this below with an hemispherical mould. Arrange the middle stars along the inside of the outer bag along the mould. Place a quantity of medium size bursting charge in the inside bag until the bottom hemispherical mould is filled(8). In this case it is necessary to ensure that the level of the red string corresponds to the upper edge of the mould. (This is also important when assembling the main sphere afterwards.) Fit this with an upper 1/4 sphere mould and fix it with tape. Load the middle stars and bursting charge separately(9). Then fit this with the last upper mould and complete the loading. When the mould is filled, twist the top of the inside bag. Tap the mould on the outside lightly with a wooden bar until the **contents** are settled. If a space is left in the upper part of the mould, load more stars and bursting charge and repeat the same operation until the mould is tightly filled. Bind the top of the outside bag with a piece of cotton string(1O). Remove the tape and make a small clearance between the upper and lower moulds. Tie the shaped middle sphere with a piece of red string along the equator through the clearance(11). Remove the moulds. Wind white cotton string on the middle sphere taking care not to deform the shape of sphere. Cut off the projecting kraft paper tube at a point near the surface of the sphere(12).

Assembly of the outside sphere is the same as that of the single petalled flower with the exception of the first process of fitting the internal sphere.

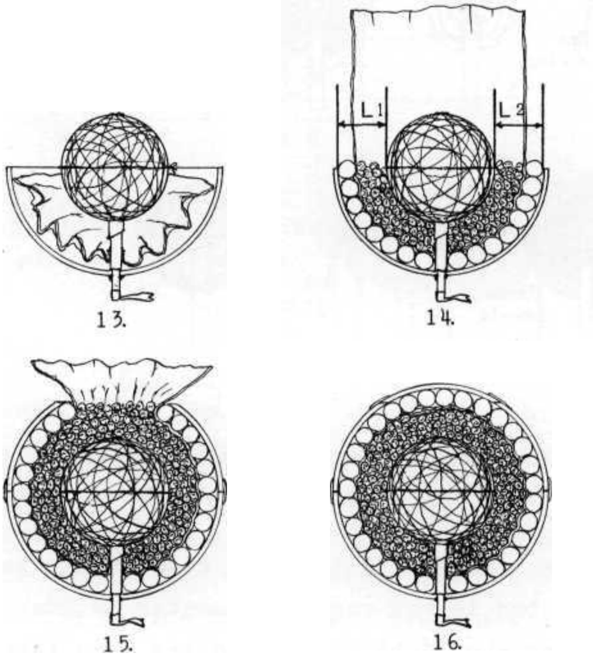


Fig.101. Assembling the outside sphere.

The type of fuse for this purpose must be (A) in Fig.90, because it is rather small in diameter and is easily inserted into the kraft paper tube of the internal sphere. When the shell is fitted with the internal spheres, the red string mark should be at the same level as the edge of the bottom hemisphere(Fig.101-13). Load the stars and bursting charge as shown for

14, 15 and 16 in Fig.101. In the case it is quite important that the internal sphere should be concentrically placed in the shell, i.e. the distance L_1 and L_2 must be equal from every side.

There is a somewhat different method of assembly; by this method the internal sphere is fixed in the middle of a length of tube, in which a small hole is bored to introduce the fire from the fuse, rather like the Greek letter ϕ (phei). This is called "Nuki-shin".

The manufacturing process described above is quite laborious, and generally firework makers prepare them out of season, i.e. mainly in winter.

Another method involves the completion of the two hemisphere first, coupling them together later as in Fig.97. In this case the centre and middle stars are elaborately arranged with a bamboo pincette.

Another simpler method is to mix the bursting charge with the pistil stars(Fig.102). In this case, if the bursting charge consists of chlorate composition and the stars are coated with some composition which contains sulphur such as black powder, there may be a risk of explosion from shock when the shell is fired. It is essential therefore to use the same kind of composition on the surface of both the stars and the bursting charge.

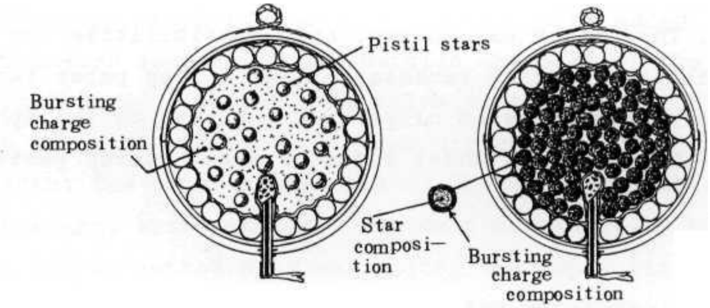


Fig.102. Mixed pistils. Fig.103. Coated pistils.

Yet another method is to coat the stars with the bursting charge (Fig.103), but this is not so often used.

16.4. Pasting shells

The loaded shell is pasted with many layers of a strong paper, Kozo or kraft-paper, especially with Warimono shells to allow the bursting charge to burn completely at the explosion point, i.e. to allow the stars to fly as quickly as possible.

There are two ways of pasting. One is to use wide pieces of the paper with the fibres arranged perpendicularly to the length(Fig.104(A)). The other method uses long strips of the paper with the fibres parallel to the length(Fig.104(B)).

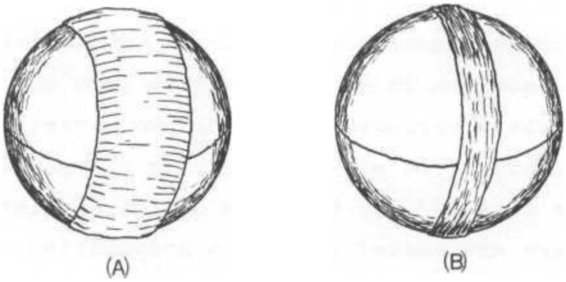


Fig.104. Pasting methods.

The former is the most popular due to labour efficiency and the latter is only used for manufacturing specially elaborate shells, because it is quite labour intensive. The latter may however have possibilities for development with a mechanical pasting technique using a long paper tape.

Using the former method the pieces of paper are placed on the sphere in the order shown in Fig.105, using wheat flour or wheat starch paste.

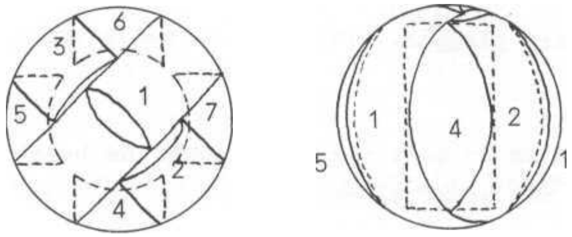


Fig.105. The order of pasting.

The paper is prepared as follows: Paste a sheet of paper on one side with a paste which does not contain too much water(Fig.106-1). Fold the paper with the paste in a kind of sandwich(2). This is to prevent the paste from drying. Cut the paper in strips of a precise width(3). The strips(4) are separated to expose the pasted surface. The pasted strips must be well stuck to the sphere as in (A) in Fig.104 by rolling the shell with a rolling board. When one layer of paper has been added, the shell must be quickly dried in a drier or in the sun. The same operations are repeated until the required number of layers have been added, this is simply obtained from the following traditional and theoretical formula:

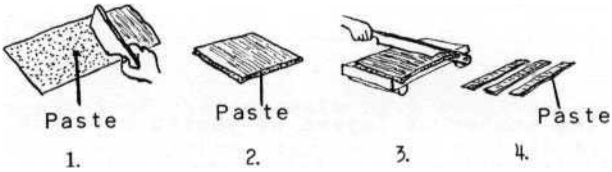


Fig.106. Preparation of pasting paper.

$$N = 5.6\ D/J\ ,$$

where N is the required number of layers to be added in ordinary cases (or a standard number), D the outside diameter of the inner shell in cm(s.Fig.88) and J is the mean value of the tensile strengths measured in both parallel and perpendicular directions to the fibres in kg per 1 cm width. The tensile strength of the paper varies considerably with the thickness, brand and type, it must therefore be measured even by quite a simple method such as pulling the paper strips with a spring balance. For example, when we obtain the strengths 6.2 kg/cm in parallel and 3,9 kg/cm in perpendicular directions to the fibres, we have the mean value (6.2+3.9)/2=5.05=J. For a 6 inch shell D=13.5cm. Therefore N=5.6X13.5/5.05=15.

The fuse must be secured during the operation with pieces of pasted hemp wound several times as shown in Fig.107 in order to avoid a premature burst when the shell is fired. The last layer is finished by method (B) in Fig.104 to improve the final appearance. The shell is generally fitted with a hanger before finishing, if it is necessary.

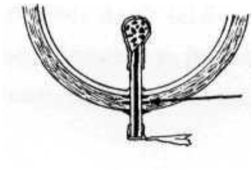


Fig.107. Fitting of fuse.

When necessary , the number of layers of pasted paper is checked by firing a shell if it is optimum to obtain a good effect. When the shell explodes with a large explosion flash and the stars do not fly very far, it means that the number of layers is insufficient. When the stars fly too far, it means that there are too many layers. In the former situation the number of layers can be increased, but in the latter case it is quite useless. It is therefore quite important to make tests during pasting when using new materials, or for newly designed shells or elaborate shells. It must be remembered that too great a number of layers of paper makes it difficult to load the shell in the mortar.

16.5. Standard values of Warimono stars

These are at present as follows(Table 23).

Table 23. The standard values of stars
for Warimono Shells

Size of shell in diameter (inch)	Size of main star in diameter (mm)	Number of main stars per shell	Amount of bursting charge per shell (K)
3	9	150	35
3.5	10	160	55
5	13	180	135
6	15	200	270
7	18	220	550
8	19	260	770
9.5	21	300	1800
12	23	340	2400

The amount of bursting charge in the table does not include the core. The values in the table are quite variable according to the design.

17. Poka

Poka is a shell which displays willows, comets, parachute, reports, whistles, flags, bills etc. rather than a round flower. Poka has less bursting charge than Warimono, and the weight of the shell is only half as large as that of Warimono for the same size.

17.1. General construction of Poka

The arrangement of the contents of a shell is quite different from one type to the next, because they vary so much in size and function. The construction of Poka is shown in principle as Fig.108. A Poka shell consists of a fire chamber only, or a fire chamber and a fire prevention chamber. The fire chamber contains the parts which must be ignited and the fire prevention chamber contains the parts which must be protected from fire.

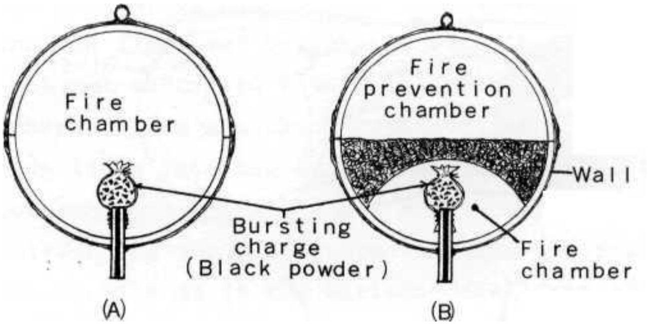


Fig.108 Poka shell construction

17.2. Assembling Poka

The preparation of the fuse is almost the same as for that of Warimono. The time of ascent to the maximum height is a little shorter than that of Warimono due to the smaller weight, but the same length of fuse as for Warimono is also applied to Poka for the sake of simplicity. (S. 16.2.)

The arrangement of the contents in a shell is determined by the way in which they are to be displayed, and they must be arranged individually, A parachute shell is set out here as a representation.

The assembly of a five parachute shell. Prepare a couple of hemispheres(the large size for Poka, s. 13.8.(83), Table 17) with bursting charge, five flares(white, red, yellow, green, blue), five parachutes, filling(cotton seeds, chaff or sawdust), pieces of fire protecting paper (pieces of brown paper for the parachutes and sheets of glossy paper for the fire chamber wall) etc. Place the bottom hemisphere, which is fitted with the fuse and bursting charge, on a stand. Arrange the flares in the hemisphere so that the primed parts face the bursting charge (Fig.109-1). Attach an identifying coloured mark to each end of the string fixed to the flares. It is only necessary to use coloured parachutes in the case of coloured smokes.

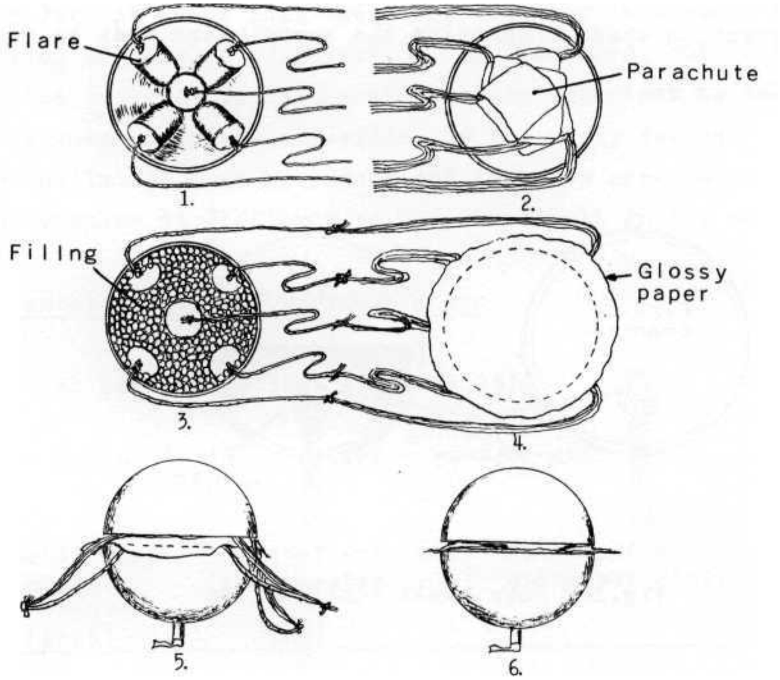


Fig.109. Assembly of a five parachute shell.

Cover the flare with a sheet of glossy paper. Place the filling on it and press it well with the fingers to prevent the flares from moving(3). Cotton seeds are the best filler. Fold the parachutes, pack them with pieces of brown paper to protect them from fire(Fig.110) and arrange them in the upper hemisphere(Fig.109-2). Cover the parachute with a piece of brown paper to prevent the filling from penetrating into the parachutes. Fill up the upper space with filling(chaff or sawdust) and cover it with a sheet of glossy paper as a separating wall(Fig.109-4). The paper plays two roles; fire prevention and to stop the movement of the contents of the sphere. Combine the flare and parachutes with their string attachments so that they do not get entangled with each other(Fig.109-3,4) and then couple the two hemispheres which are thus prepared into one sphere(Fig.109-5). Place the string lines into the sphere winding them in the form of a ring. Shake the upper hemisphere lightly and shake out the excess filling(chaff or sawdust) between the two hemispheres(Fig.109-6). Press and fix the two hemispheres temporarily as in the Warimono shell and send it to the next process, pasting. Fig.111 shows other kinds of shells. The assembly is simpler than those above, i.e. the parts are placed only in the fire chamber((A) and(B)) or in the fire prevention chamber((C)).

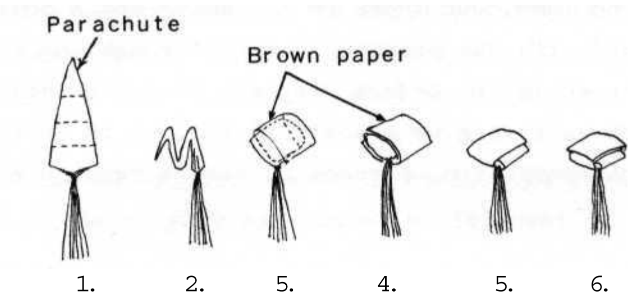
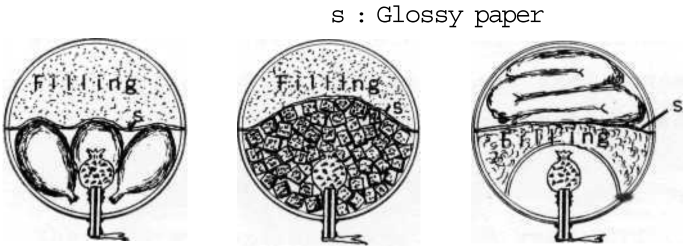


Fig.110. Preparation of parachute.



(A) Five reports (B) Fine willow (C) Comic figure

Fig. 111. Examples of Poka shells.

The combination of the fuse and bursting charge is a problem, because the bursting charge of Poka shells occupies rather a small space. There are several ways of combining them. Fig. 112 shows examples, (A) is the most reliable, but takes time. The bag must be made of a strong paper such as Kozo. (B) is often used, but it does not always function perfectly. (C) has no fuse, but there is a chamber and a hole for the charge. It is charged with the bursting charge through the hole and fitted with the fuse as in (D) before display. When the shell (C) contains a non-explosive such as a flag or a comic figure, it is quite convenient for handling and transportation, because it can be handled as paper.

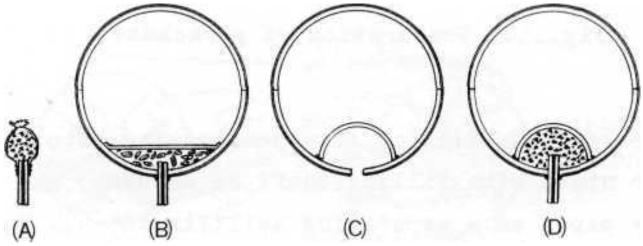


Fig.112. Combinations of bursting charge and fuse.

Accidents often occur due to an incomplete combination of the fuse and the charge. Fig.113 shows examples. (E) shows that the head of the fuse pierces the cover, and the charge does not catch the fire from the fuse. This occurs from shock when the shell is fired, especially when the fuse is cut aslant. (F) is fitted with a curved fuse, which is popular among many manufacturers due to the ease with which it can be fitted. This does not cause an accident like (E), but as in (F), which shows that the bursting charge space is moved due to the shell revolving when it is fired and the charge again does not catch the fire from the fuse. The charge cover must therefore be fixed firmly to the inside of the sphere. (G) shows that the charge bag is broken and the charge is dispersed into the filling during handling or transportation. This also causes a misfire.

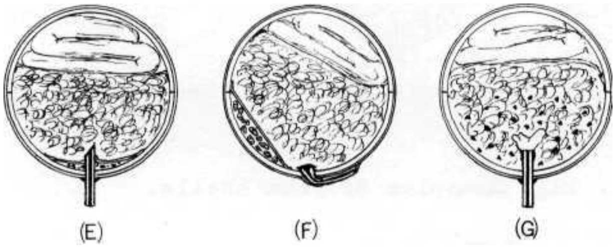


Fig.113. Examples of bursting charge misfire.

In general if there is nothing to prevent it, the contents of a Poka shell will easily change their position in the sphere due to rotation of the shell during handling, transportation or during firing. This often causes a misfire, and a device to prevent rotation is generally fixed to the joint of the two hemispheres. For example, the glossy paper(s) which separates the units and the filling in Fig.111 fulfills this role. The edge of the paper sheet projects out of the sphere and is caught firmly in the joint so that it gets pasted in during the next pasting process.

The space occupied by paper-made articles, e.g. parachute, flags, comic figures etc., is roughly calculated as follows:

$$V = k*S ,$$

where V is the space occupied by the folded article in cc, S the surface area in m^a and k the constant which is 100~200.

17.3. Pasting the shells and the bursting charges

The Poka shell sphere must be broken into two hemispheres along the joint when it explodes, otherwise all the contents will not be thrown out or they will be damaged by fire. This is quite a different requirement from Warimono. The strength of the joint therefore must be a little less than that of the hemispheres. Fig.114 shows an accident which occured, when the joint was stronger than the hemisphere.

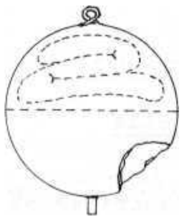


Fig.114. An abnormal break.

When the joint is too weak, another accident often occurs when the shell is fired; the contents are accelerated to break off the upper hemisphere along the joint and they spring out of the shell; this is called "Head separation". The greater the shock and the heavier the contents, the more it occurs. (it is considered that sufficient filling to support the contents might well reduce this abnormal acceleration.) The strength of the joint must be adquate.

The number of pasted layers of paper for an ordinary Poka shell is calculated by the following formula:

$$N = 1.8\ D/J\ ,$$

the symbols are the same as the formula in 16.4. The pasting process is the same as for Warimono. The joint of the two hemispheres is first pasted and then the remainder. For small shells less than 4 inch in diameter the joint is pasted two or three times and then the sphere is pasted and finished with only one layer of paper, because small spheres can take the pressure when they are fired.

The amount of the bursting charge for a Poka shell depends upon the strength of the joint, but generally it is as follows(Table 24).

Table 24. The standard values for the bursting charge of a Poka shell (using black powder)

Size of shell (inch)	Charge (g)	Size of shell (inch)	Charge (g)
3	2.0	7	6.0
3.5	3.0	8	7.0
5	4.0	9.5	8.0
6	5.0	12	10.0

18. Miscellaneous shells

The Warimono and Poka shells described above are the most representative in construction, but there are some other shells which lie between these two and some are quite different from them.

18.1. Small flower shell units

The small flowers are also called, "Flower garden" or "Thousands of flowers". It involves loading many small shells in one big shell. There are two types; Warimono(Fig.115.(A)) and Poka((B)). The corresponding styles are shown in the right side of each figure.

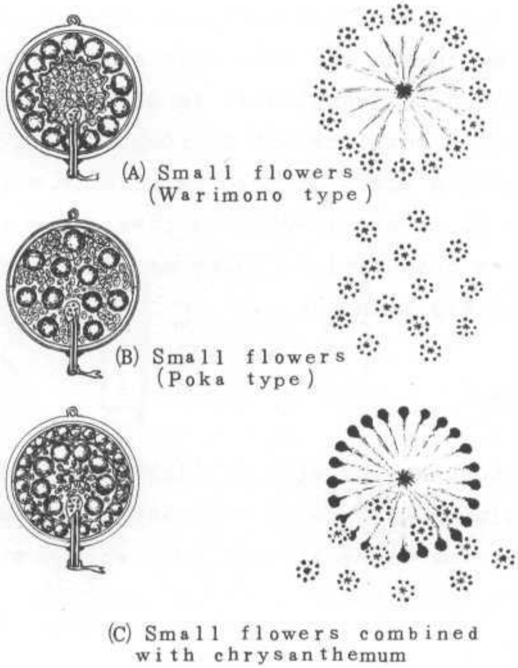


Fig.115. Arrangements of small flowers.

18.2. Small flowers combined with chrysanthemum

A large chrysanthemum developes in the sky and then small flowers appear on the chrysanthemum(Fig.115.(C)). With another type the small flowers appear only after the big chrysanthemum has been extinguished. This is achieved by using somewhat longer fuses for the small flowers. These varieties are only successful when the size of the shell is large enough to contain many small flowers, i.e. 9.5 inches or more.

18.3. Crown willow

This shell resembles Warimono in construction, but the bursting charge is somewhat weakened and the life of the stars is prolonged to about 8~10 seconds. The composition of the stars is the charcoal dust sparks,"Willow",and it is used for night shells. With smoke willow stars for daylight shells. The displaying of the willow effect is the same as that in Fig.11.

18.4. Cracker stars

This shell is also a kind of Warimono. Each of the main stars contains a cracker as the core. When the flower has been developed in the sky, the stars crack as the burning ceases and they make a great deal of noise. For the noise composition, red explosive is used because it can produce a loud noise with only a small amount of composition. The explosive in the wet state is rolled with a sheet of Kozo paper into a cord, which is cut in small pieces while it is still wet. The pieces are coated immediately with another safer composition. These are finished by pasting with composition as with ordinary main stars.

18.5. Willow in the moon

This is in principle a combination of a daylight and a night shell. This is a kind of Poka containing a flare of high intensity and smoke stars of realgar composition. The smoke streams look white rather than yellow at night when they are illuminated by the flare(s.5).

18.6. Charcoal ball

This gains its name from its appearance as a charcoal ball. This is manufactured by coating a black powder type composition many times on an ordinary and rather small shell. During the coating process pieces of hemp are wound around the sphere for reinforcement. This is quite labour intensive, but the effect is very pretty(Fig.4.8). The fuse of this shell is apt to misfire due to the absorption of moisture during coating, and some device is necessary to avoid this.

19. Assembly of Italian type shells

Shells of this type are quite popular in Europe and the USA. The shells are cylindrical and resembles Japanese Poka shells in principle. The process of assembly may be understood in the following figures (Fig.116 and 117).

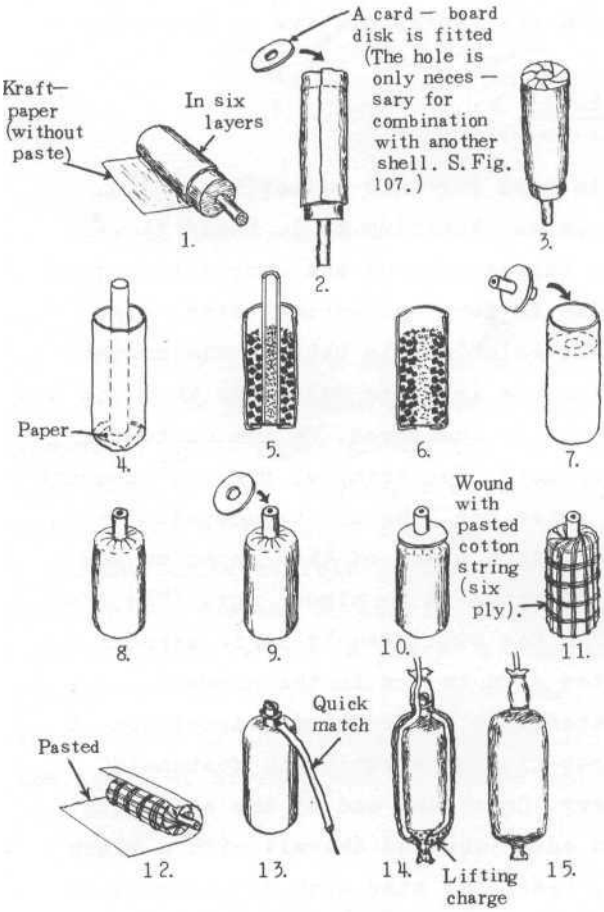


Fig.116. Single break shell of the Italian type.

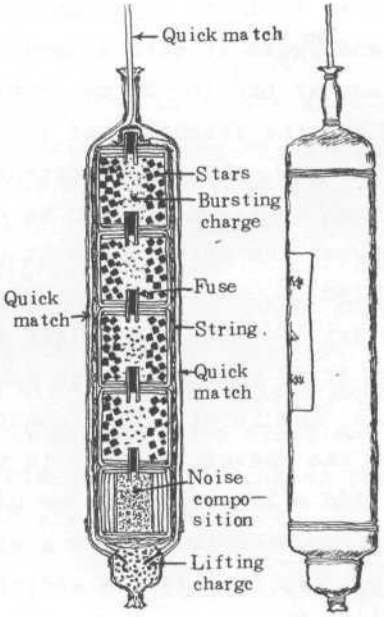


Fig.117. Five break shell of the Italian type.

20. Kyoku-do

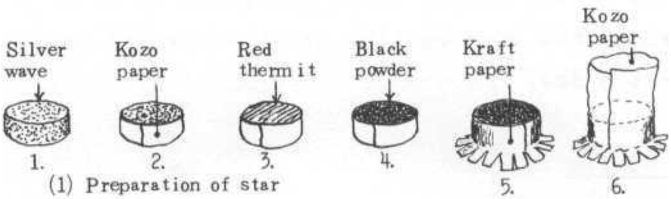
This is a kind of Kyoku attached to a shell which displays effects on the trajectory. The word "Do" means here a trajectory. A silver tail, small flowers, comets, thunder, whistles etc. are commonly used as the Kyoku-do. The prefix "Ascending" is used, e.g. "Ascending silver tail", "Ascending comets" etc.

Important manufacturing point for Kyoku-do are as follows: The pieces must be strong enough to avoid breakage during firing, they must be ignited by the flame of the lifting charge and they must not be separated from the shell by the shock from the lifting charge. When more than two pieces are fixed to a shell, each must function well without disturbing the others. The following descriptions are representative of Kyoku-do.

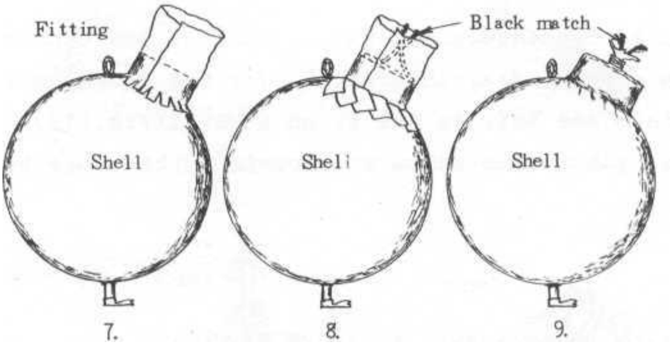
20.1. Ascending silver dragon(tail)

The composition "Silver wave" is used for this effect(15.2.(2)). Place a quantity of the composition in an aluminium bowl. Knead it well adding water to it in small amounts. Charge some of the composition into a mould and press it with a hand press to form cylindrical star, e.g. 42 mm diameter and 18~20 mm long. The relationship between the amount of water and the intensity of the pressure is quite delicate. When the pressure is low, the water content must be increased. On the contrary, under a high pressure it must be decreased. For example, under a pressure of 660 kg/cm^2 the optimum amount of water per 1 kg of the composition is about 150 cc. Next paste the star with a piece of thin paper on the side and dry it naturally in the shade until it is almost dry. (The star may crack if it is exposed too much in the sun.) Lastly it is exposed in the sun, and it will take about ten days to dry in the summer.

Then one end of the star is pasted with an ignition composition as follows: Add a 10% celluloid or nitrocellulose solution in acetone(NC paste) to red thermit to form a slurry. Cover one end of the star with the slurry. Dry it well. In addition cover the red thermit with a black powder paste for safety in handling. Paste the star with Japanese paper and then paste a piece of emarginated kraft paper on the side as shown in Fig.118 and dry it.



(1) Preparation of star



(2) Fitting shell with the star

Fig.118. Preparation of "Ascending silver tail"

In order to fit a shell with this star, place it on the shoulder of the shell and paste down the emarginated edge. Secure it by pasting pieces of kraft paper around the base of the star. The position of the star must be near the hanger so that the shell is not caught by the inside wall of the mortar when loading or firing(Fig.118(2)).

For ignition, fold in two a piece of black match which is about 6 cm long, place one end on the ignition surface of the star and secure it with the paper which is pasted around the star tying the black match into the paper with a piece of hemp string, thus exposing the other end of the black match on the outside (Fig.118(2)).This construction is to protect the ignition surface and to ensure ignition.

20.2. Ascending tiger tail

Tiger tail:	Potassium nitrate	44.2%
	Pine charcoal	44.2
	Sulphur	5.4
	Soluble glutinous rice starch	6.2

This produces a charcoal fire dust stream. The manufacturing process is almost the same as that of the silver tail, but there is no need of the red thermit for ignition. The burning time of this star 32 mm in diameter and 20 mm long is about 5 sec.

20.3. Ascending comets

This is also called "Ascending separating stars". The construction of the comet unit has already described(15.6). For the Kyoku-do several comets are combined into one unit to fix it on a shell(Fig.119). The length of each fuse is planned to allow the comets to be projected one after the other on the trajectory of the shell as it ascends in the air; about 12 mm minimum and increasing 5 mm each time. The pieces are arranged as parallel crosses around a paper tube; firstly the one which has the minimum length of fuse, following this two by two in the order of the length of the fuses. They are clearly and firmly fixed on the shell with iron wire. When the setting is over, the fuse ends are divided into two, a piece of black powder pasted paper is inserted into each of the fuse ends and this is secured with hemp string. This is to ensure ignition Fig.119.1).

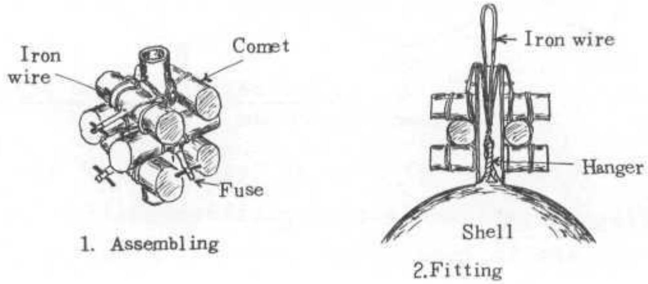


Fig.119. Preparation of ascending comets.

The Kyoku-do is fixed to the shell with a piece of iron wire which is passed through hanger and the centre tube so that the set of comet pieces can be securely tied(Fig.119.2).

20.4. Ascending small flowers

Fig.120 shows how a shell is fitted with small flowers. In this case the explosion of one flower does not cause the explosion of the others or of the main shell. Clearly the units can be quite close together.

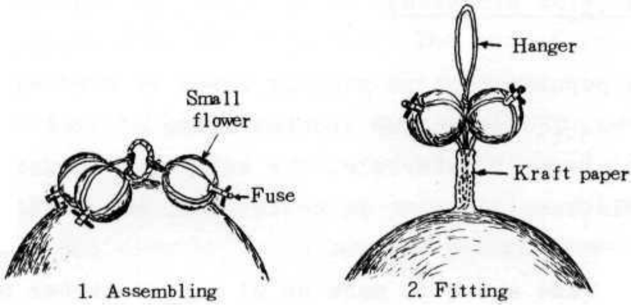


Fig.120. Preparation of ascending small flowers.

20.5. Ascending thunder

Fig.121 shows the preparation of ascending thunder. Each of the noise units can potentially destroy the others and so they are separated from each other so that the explosion of one noise unit does not affect the others or the main shell. The figures attached to the pieces show the order of explosion.

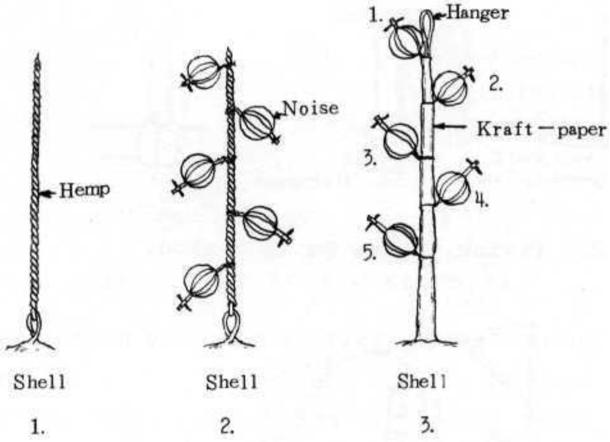


Fig.121. Preparation of ascending thunder

21. Exhibition fireworks

21.1. Lance-work (Fire pictures)

Lance-work is so popular that it readily comes to mind when we think of exhibition fireworks. The technique creates lines of fire by the linear arrangement of lances at short intervals. The technique is used to produce a portrait, a scene, letters etc.; as it comes under the heading of illuminations.

Prepare a wooden frame which is made up of square timber of about 30mm x 30mm. The size of the frame in Japan is 6 feet by 6 feet or 6 feet by 12 feet. Draw the picture with chalk on a concrete floor following the original drawing, then place the frame on the picture. Arrange long bamboo canes of 10~13 mm width on the frame and fix the canes to the frame with U-nails, following the picture lines. Next arrange and fix the lances on the bamboo canes at intervals of about 10~15 cm following the colours of the original picture. Connect each lance head with quick match. The technique for example is shown in Fig.122 and the completed frame in Fig.123.

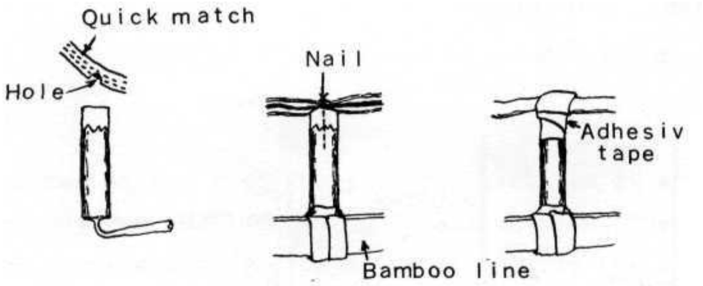


Fig.122. Fixing lances on to bamboo.

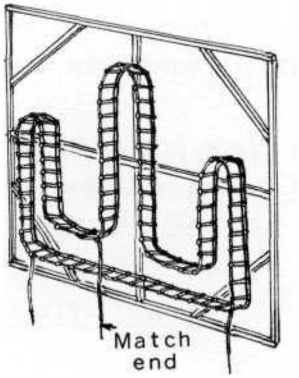


Fig.123. Completed lance-frame.

Once assembled, the lance-frame is ignited at one end of the quick match, when the fire will run through the tube igniting all the lances instantaneously. The burning time of the lances is about one minute, and the picture appears only for this time. The end of the fire picture is generally ragged due to deviations in the burning time of each lance. To avoid this effect, a star-mine of many small flowers can be fired at the same time, to attract the attention of the crowd from the fire picture. In Japan we often see a large background display which contains 12 inch shells and in these circumstances the lance-work looks like a sub-display.

21.2. Starmine

This is a traditional type of firework which simultaneously produces many small flowers, many fire streams etc. in a short time, making a very colourful effect. The setting technique varies according to the particular effect required, but in general a group of mortars are arranged in a frame to simplify firing and transport(Fig.124). A loaded mortar is shown, e.g., on the right. Shells, stars etc. are arranged in the mortar to follow some particular plan.

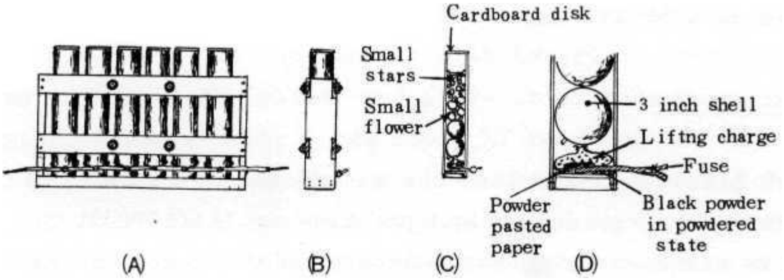


Fig.124. Assembly of 3 inch starmine.

Preparation of the fuse. Punch holes in a quick match tube at the same intervals as the mortars. Cut Bickford fuse into pieces 30~60 mm long(to give the firing time interval to each mortar). Split one end of each fuse in two. Fit the quick match into the Bickford at the points where the holes were made e.g. Fig.125 and fix them with pieces of wire.

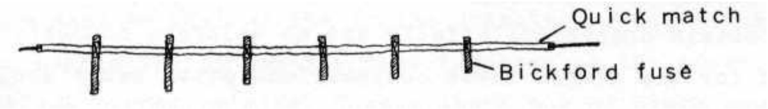


Fig.125. Preparation of the fuse for 3 inch starmine.

Assembly of the frame((A),(B)). A group of mortars are placed in a wooden frame and fixed firmly with a nut and bolt so that the mortars are not projected out of the frame by the shock of firing. Fit each mortar with the corresponding branch of the fuse and fix it to the mortar with a piece of wire. (S. Fig.124.)

Preparation of lifting charges. Weigh out 19 g of grain black powder. Pack it in a piece of Gampi-paper and tie the mouth with cotton string into a cartridge. Paste the outside of the cartridge with a slurry of black powder composition and dry it in the sun.

Loading((C),(D)). Place the cartridge in the bottom of each mortar. Sprinkle black powder in powdered state(not grain) on the cartridge and place pieces of powder pasted paper on it; these are to avoid misfire. Inspect the bottom of the mortars one by one with an electric torch to see it there was a misloading. If the loading of the lifting charge is missed even in one mortar, it causes an accident on firing; the shell explodes without leaving the tube and often breaks the frame with other shells flying in unexpected directions injuring people. Place two 3 inch shells on the cartridge in each mortar and then small flowers and stars. Press a cardboard disk in each mortar to firmly fix the contents in the mortar. Cover the mouth of each mortar with a cardboard disk and fix it well with pieces of adhesive tape. (S. Fig.124.)

21.3. Roman candle

R.Lancaster precisely describes the manufacture of this item (R.Lancaster: Fireworks, principle and practice, p.111(1972)). In Japan there is almost no difference except in the shape of the stars, which are spherical(Fig.126).

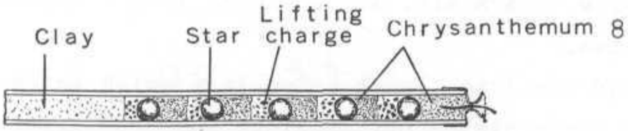


Fig.126. Roman candle.

Several stars are projected one by one at specific time intervals. Each star draws a straight trajectory or a stream of fire. Quick burning stars are used to obtain successful effects and so chlorate compositions are generally used for the stars. These compositions often cause accidents due to excessive friction when loading the stars into the tube. The cover of the ignition composition on each star is exfoliated and the exposed chlorate composition is rubbed against the inside of the paper tube with the black powder type composition. This may be the main cause of an unexpected ignition and so the layer of non-chlorate composition on the chlorate centre of each star must be thick enough to avoid such an accident.

21.4. Gold fish

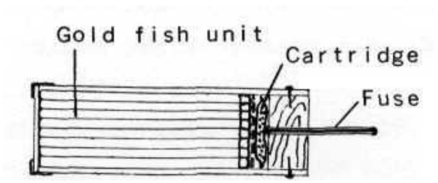
"Gold fish" consists of many pieces in which a black powder type composition is loaded into tubes like lances. The pieces are projected on to water where they move as if they are swimming in the water, producing a pretty fire dust stream. When a lot of pieces are used, they present a spectacular sight.

Preparing the composition. Use "Chrysanthemum 6" as the composition (15.2.(3)b). Mix the three components, potassium nitrate, pine charcoal and sulphur, in a ball mill if possible. Add 3% flake aluminium powder passing 150 mesh to the composition and pass it through a sieve. Weigh out 1 kg of the composition in a bowl, add water to it and knead it well to gain a suitable hardness for granulation. Rub and push the mass through a 15 mesh sieve at one side, when it will pass the sieve and come out of the other side like pieces of cord. Spread the composition on sheets of kraft paper and dry it in the sun. When it is dried, break the composition into grains with a wooden roller and sieve it if necessary.

Charging. Prepare paper tubes about 11 mm diameter, 210 mm long and with a wall thickness of about 1 mm. Plug one end of each tube with gypsum. Tie about 400 tubes in a bundle with a piece of cord, placing the mouths at one side. Place the bundle on a sheet of kraft paper on a working desk, so that the mouths are upwards. Place a quantity of the granulated composition on the bundle and shake it down into the tubes. Firmly press the charged composition in each tube with a wooden stick. The composition is thus loaded step-by-step until all of the tubes are full. The amount of composition per tube is about 15 g. Paste a piece of Kozo paper on the top of each tube to hold the composition. Paste black powder slurry on the paper and dry the tubes in the sun(Fig. 127.(B)).

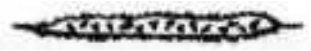
Preparation of the cartridge. Make circular pieces of black powder pasted paper(pasted on one side only) with a wad cutter. The diameter is about the same as that of the inside diameter of the mortar. Take two of them and make a bag by pasting them together at the edges, placing the pasted black powder outside. Charge about 6 g of black powder grains in it and seal it with paste(Fig.127.(C)).

Assembly. Assemble the mortar, tubes and the cartridge as shown in Fig.127.(A).



(A) Gold fish assembled

(B) A Gold fish unit



(D) Cartridge (Driving charge)

Fig.127. Gold fish.

21.5. Drivers, Saxons

These items have been precisely described by R.Lancaster(Fireworks, principles and practice, p.135(1972)).

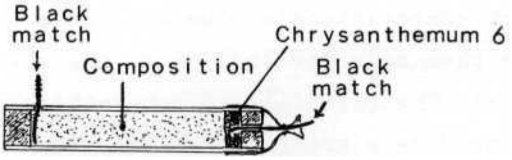
A pretty pattern of revolving fire is obtained by turning a simple wooden wheel on which some fire dust spark compositions etc. are fixed and burnt. For driving the wheel turning cases are used as shown in Fig.128.

Preparation of the driving composition. 61.5% potassium nitrate, 11% sulphur and 27.5% charcoal are mixed. If possible, this is driven in a ball mill for 24 hours, then take out the composition and add 2% aluminium powder to it and mix it well passing it through a sieve.

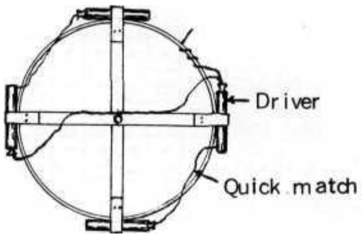
Preparation of the drivers. Prepare kraft paper tubes 28 mm inside diameter, 175 mm long and with a wall thickness of 5 mm. Plug each tube at one end with gypsum. The thickness of the gypsum should be about 15 mm. Bore a. 4 mm hole in the centre of the gypsum as the nozzle. Insert a piece of black match into the hole and secure it with a piece of paper to prevent the match escaping. Secure the paper tube on a charging nipple so that the black match fits into a hole in the nipple. First charge a small amount of Chrysanthemum 6 as the ignition composition and then the driver composition in increments, using a wooden drift and a wooden hammer to consolidate the composition until it is hard. Finally insert a piece of black match into the composition to transfer the fire to another driver.

Plug the end with gypsum(Fig.128.(A)).

Fitting the wheel with drivers. This is shown as an example in Fig.128.(B).



(A) Wheel driver

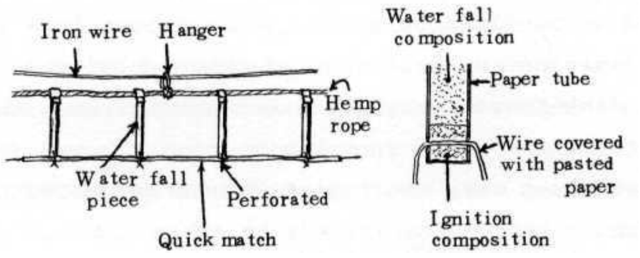


(B) Fire wheel

Fig.128. Construction of a fire wheel

21.6. Waterfalls

These items are also described in Lancaster's book on page 106. They are so named because the fire dust sparks drop to remind us of waterfalls. They are prepared as follows(Fig.129): Charge a waterfall composition which contains aluminium powder of relatively large flakes into strong paper tubes which have a thin wall which burns away. (See also 15.10.) Put a quantity of ignition composition in the end of each tube. Make holes in it from the outside and pass a piece of wire which is wound with a piece of powder pasted paper through the hole. Fix the waterfall units made in this way to a hemp rope at intervals of about 50 cm. Connect the igniting ends with a line of piped quick match.



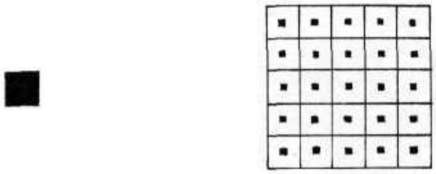
(A) Water falls hung with iron wire (B) Waterfall unit

Fig.129. Waterfalls.

22. Toy fireworks

22.1. The special conditions for toy fireworks

Toy fireworks must be safe. There must therefore be a special way to convert firework compositions(explosives) which are generally quite dangerous, to make them safe for toys; i.e. the compositions have to be divided and isolated. The principle is schematically shown in Fig.130. A composition can produce a great destructive force if it is set out in one place as in (A). But if it is divided into small amounts each being separated by a protective wall like (B), the fire which has occurred in one place cannot pass to another. A special technique may be necessary for the division and isolation, but at present scientific studies in this field are not adequate to give a clear answer.



(A) (B)

Fig.130. Division and isolation of a composition.

In general, flames, hot air, fire dust sparks, sparks or shock waves help the propagation of fire or explosion. Four of the former only promote the burning of the compositions by direct contact, but the latter causes a detonation, even when the composition is fairly distant from the source. However in toy fireworks the item which produces a shock wave is limited to crackers. It is necessary therefore to draw a clear line between crackers and other items when handling toy fireworks.

Compositions must be well covered by other material in order to protect them against flames, fire dust sparks or general kinds of sparks. In practice, the composition is wound with paper tape, twisted in pieces of paper tape or charged in small amounts into paper tubes. This plays an important role for the division and isolation of the composition. Some items like sparklers or Senk-Hanabi have exposed compositions with no cover but these compositions are quite insensitive to shock and friction and need no cover. Nevertheless they must be packed in groups with a small number in each pack.

Crackers include such items as cracker ball, Christmas cracker, Chinese cracker, pistol caps etc. On exploding these pieces produce shock waves which accompany the loud report. A shock wave is a high pressure wave which is shown in Fig.131. The shock wave causes heat generation or chemical reaction in the medium material. It may cause detonation of the adjacent composition. But this wave rapidly decreases in intensity. In order to minimise the effects of the shock wave, the amount of composition in each piece should be kept as small as possible and the shock wave should be absorbed by suitable methods, e.g. binding the composition with a piece of paper tape, twisting it in a piece of paper, surrounding it with packing material inside a paper bag or cardboard case etc. In general, crackers are dangerous in large numbers unless protected by packing. This will not be appreciated from small scale tests. For example, in the case of cracker balls, when samples packed in a paper case are shot from a small gun, they explode only along the path of the bullet. In practice, accidents often occurred,when piles of cracker balls detonated spontaneously. The author has firsthand knowledge of one such accident, when a worker removed some pull caps, used in Christmas crackers, from a wooden box containing 10,000, causing the remainder to explode. The string from each cap had been threaded through a cardboard disc and these half-finished goods had been thought to have been safely stored with sufficient space to absorb shock waves, but in practice this was not true. (Afterwards, tests were carried out to ascertain the effect of shock on large quantities of pull caps, violent detonation could not be simulated.) On June 4th 1963 an accident occured at the port of Mina Sulman in Bahrein. A worker dropped a case on a concrete floor and it exploded. It was thought that the explosion might have been caused by pistol caps, because many pistol caps were found in other cases in the same consignment. Afterwards many tests were performed in Japan in an attempt to find the cause of the explosion, but no such explosion occurred during the tests. If, in fact, the explosion had been caused by pistol caps, the caps must have been exceptionally large. The caps used in

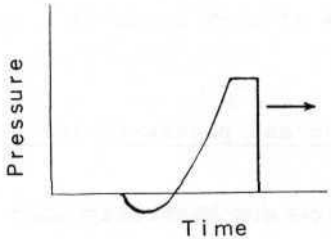


Fig.131. Example of a shock wave.

starting pistols often detonate on handling, because they contain far more composition than ordinary toy pistol caps. When in experiments, crackers packed as in the above description are thrown into a bonfire, they do not detonate, but only burn with slight noise. But what would happen to large quantities of such items in a major fire? This is not predictable.

22.2. The compositions and processes for toy fireworks

The compositions which are generally used for other fireworks are also used for toy fireworks. But there are some compositions which are used only for toy fireworks. The relationship is shown diagrammatically in Fig.132, where (A) represents the former and (B) the latter.

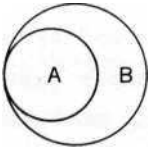


Fig.132. The relationship between compositions for ordinary fireworks and toy fireworks.

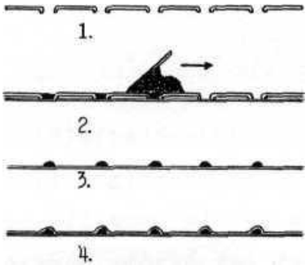
(B) includes noise compositions which are quite sensitive and snake compositions which exhibit curious phenomena, etc. It can be seen from the diagram that toy firework compositions, (A+B), are more numerous than those for ordinary fireworks (A). The reason is that, in the case of toy fireworks it is possible to increase the safety of the compositions to a high degree by complete division and isolation. Following this principle even some sensitive compositions which are never used for shells, exhibition fireworks etc. can be used for toy fireworks. For example, a composition which contains potassium chlorate and red phosphorus is used for pistol caps or another compositon which contains potassium chlorate and realgar is used for cracker balls. These compositions are generally used only for toy fireworks.

(1) Red phosphorus-chlorate compositions

This kind of composition is used for toy pistol caps(arranged on flat paper sheets or on wound tapes), starting pistol caps, pull caps etc.

Toy pistol caps(White):		
	Potassium chlorate	68 %
	Sulphur	25
	Red phosphorus	6
	Glutinous rice starch	1

For safety potassium chlorate is firstly mixed with a sufficient quantity of water and then starch, sulphur and red phosphorus are added to it into a slurry. (Some products from other countries use a black composition which contains antimony trisulphide in place of sulphur.) Prepare a metal plate which has many small holes arranged across it(Fig.133.1). Place it on a paper sheet; place an amount of the slurry composition on the plate and slide and squeeze the composition over the surface of the plate. Remove the plate, and the composition will remain only in the positions corresponding to the holes(2). Leave it to dry at room temperature. Paste a thin sheet of paper over it and dry it again(3). Cut to the required size. The dried caps must be handled with care, to avoid the risk of fire.



4.

Fig.133. Manufacturing of pistol caps.

Pull caps. These have two purposes: one is to ignite other compositions and the other to give a loud noise and to propel paper streamers etc. The composition may vary according to its use, but generally consists of red phosphorus, potassium chlorate and antimony trisulphide. Pull caps are so called because they ignite when the attached string is pulled. First, place a piece of cotton string at one end of a strip paper tape(Fig.134.1). Using a spatula place on this part a small amount of slurry composition(2). Of pourse the composition is prepared by mixing the components with water in the same way as the toy pistol caps(as the binder gelatine is popularly used). Wind the composition with the tape(3), paste the end(4) and bind the ends of the string together in a group(5). Place the groups in a cardboard case before the caps are thoroughly dry. They will not explode until they have been allowed to dry naturally. If possible it is desxrable for them to be sent to the assembly process while still wet.

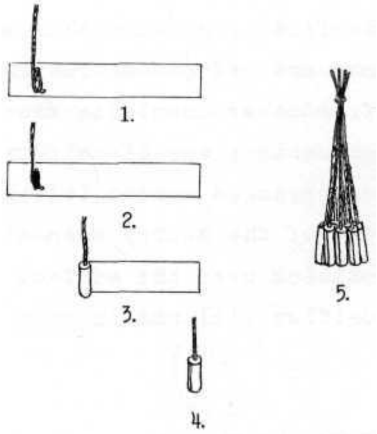
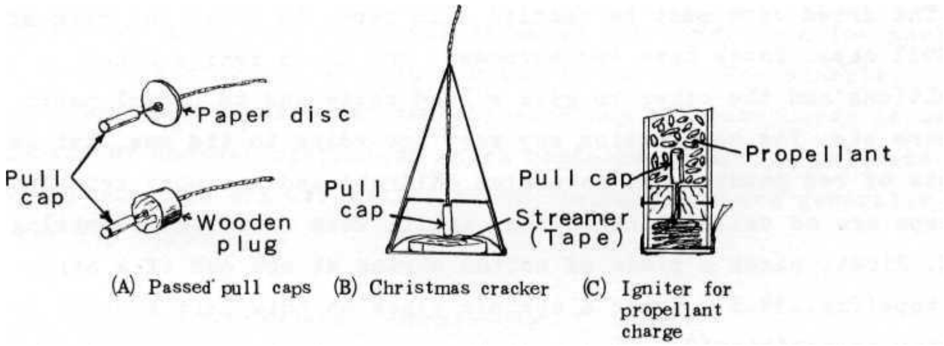


Fig.134. Manufacture of pull caps.

When one unit of the pull cap in a bundle(5) explodes, all the other units in the bundle tend to explode. Therefore it is impossible for an inexperienced person to remove a bundle from its container safely after the caps are well dried. Take out the bundle very carefully. Support each piece adequately, e.g., by passing the string through a hole in a wooden or paper disc(Fig.135.(A)). This is called "Pull cap passing". This is the only method by which the caps can be assembled as part of a toy. (B) and (C) show examples.



(A) Passed pull caps (B) Christmas cracker (C) Igniter for propellant charge

Fig.135. Applications of pull caps.

(2) Realgar-chlorate composition

This is not as sensitive as the red phosphorus-chlorate composition but is one of the most dreadful firework compositions. It is used for cracker balls, the last noise of smoke bombs, small rockets etc., under the name, "Red explosive". The wet process is recommended for the manufacture of these items, but the dry process is commonly used except for cracker balls.

Cracker ball. Each of these is spherical and about 10 mm in diameter. When it is thrown on the ground or other hard surfaces it explodes. The construction is shown in Fig.136. A quantity of sand grains coated with a paper or pulp case. The process is as follows: weigh out an amount of sand grains 2~5 mm in diameter and place it in a porcelain bowl; add a suitable amount of water and stir it into a wet state. Then weigh out the required amount of potassium chlorate and add it to the sand. Mix them together to coat the sand grains uniformly with potassium chlorate. Weigh out an amount of realgar, add it to the mixture of sand and potassium chlorate and gently and carefully mix them together by hand so that the sand grains are covered with the mixture of chlorate and realgar. The weight ratio of the realgar to the potassium chlorate is 1:2 and the sand to the composition is 10:1. Take a small amount of the mixture out of the bowl, place it on a piece of paper and pack it by twisting the edge of the paper. Make a ball shape by binding another strip of paper round it and pasting the end. Dry in the sun. The above operations are all performed by hand, but recently a mechanical process was invented. This involves freezing small portions of the wet composition and enclosing each of them in a capsule. Once the wet composition is frozen, it is quite insensitive to shock and friction.

Fig.136. Cracker ball.

For example, some cracker balls on the market contained 0.5 grams of sand and 0.05 grams of the composition per piece. This ignited at about 290° C. The shape of the sand grains influences the sensitivity of the cracker ball. River sand gives greater sensitivity than sea sand because the grains of the former are sharp-edged, while those of the latter are rounded.

(3) Snake composition

B.Lancaster described this item in detail, but a supplementary account is given here.

Weigh out 1000 g of pitch and place it in a thick aluminium bowl. Add 200 g of linseed oil and mix well. Add.1400 g of 98% nitric acid, drop by drop, slowly stirring the mixture with an aluminium rod. A violent reaction will occur with red nitrogen dioxide fumes, heat being generated. Cool from the outside with water. Stir the mixture continuously, and it will become a hot molten mass as the reaction proceeds. The temperature of the mass rises to about 200°C and the time of operation is about 15~20 minutes. If a fire occurs at a point on the surface, stir the mixture to submerge the fire and extinguish it. If the whole surface is on fire, pour water on it, but in this case the mixture will become useless. Continue stirring after all the nitric acid is charged until the reaction ceases. Take the mixture out of the bowl, spread it on an aluminium plate and leave it to cool naturally.

Pulverization. The nitrated pitch becomes brittle on cooling. Crush it with a wooden mallet and pulverize it in a ball mill.

Washing and drying. According to R.Lancaster this washing is unnecessary. But in Japan it is washed in water, because the nitrated pitch contains a small amount of acid, about 0.15% nitric acid, and it is thought that the remaining acid is a common cause of fire. Add the pulverized nitrated pitch to hot water at less than 70°C. If the temperature exceeds 70°C, the nitrated pitch often melts into a mass. Filter it with a vacuum filter. Wash the residue with 10 g sodium carbonate solution in 7000 cc water, pouring it into the filter. Then wash the residue with water again. Dry it in the sun. Take care that spontaneous ignition does not occur during the drying process described above. The yield is about 1300 g of nitrated pitch from 1000 g of the raw pitch.

Composition. The well dried nitrated pitch powder is mixed with an oxidizer which is necessary for burning. An example is shown as follows:

Black snake:	For hand press	For machine press
Nitrated pitch	75 %	72 %
Ammonium perchlorate	25	28
Soluble glutinous rice starch	-	2(Additional percent)

The composition for the hand press is damped with gum arabic solution in water when it is shaped. The content of the nitrated pitch for the machine press is smaller than that for hand press so that it is easily burnt, even when it is shaped into pellets under high pressure. For use in a machine the composition must be previously granulated.

Shaping. The compositions are shaped into pellets with a hand press or a rotary machine.

According to Weingart and Lancaster it is important to obtain a good pitch as the raw material e.g. the residue from the distillation of beta-naphthol, but the author does not find it easy to get this material at present. In Japan ordinary coal pitch is used but it has a defect for it produces much soot and smoke. There is another kind of snake named Pharaoh's Serpent. The composition contains a mercury compound and may be poisonous. At present this item is not made in Japan.

(4) Other compositions for toy fireworks

In general many compositions resemble the ones used for shells i.e. the ones for flames, fire dust sparks, fire branching sparks, noise, smokes etc. These phenomena however are seen close at hand and so the compositions are somewhat different from those for shells.

22.3. Toy firework devices(Matrix method)

The toy firework manufacturer is always required to devise a new type of toy and the matrix method described here shows something of the fundamental principles for manufacturers.

The phenomena may be classified as follows based on the compositions for toy firework which are available at present:

A: Flame(oscillating or not)
B: Fire dust sparks
C: Sparks
D: Report
E: Whistle
F: Coloured smoke
G: White smoke of sulphur
H: Yellow smoke of realgar
I: Ash
J: Flag or tape
K: Bag
L: Parachute

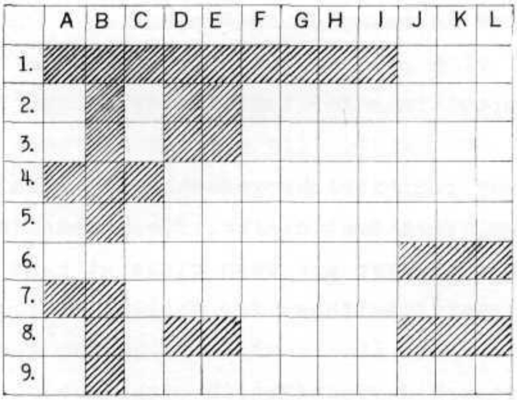
or combination of above phenomena.

On the other hand, there are various types of movement in firework phenomena. The classification may be set out as follows:

1. No movement(hand held or laid on the ground)
2. Moving(on the ground, in the water, on rails, on cable ways etc.)

3. Random or zigzag movement(on the ground or in the air)
4. Rotation, fixed at the centre(to a pile head, to a wall or hand held)
5. Rotation without central fixing(on the ground, in the water or in the air)
6. Single shot(hand held or set on the ground)
7. Successive shots(hand held or set on the ground)
8. Movement by rocket effect(hand held or from the ground)
9. Movement by propeller(hand held or from the ground)

Taking the phenomena for the abscissa and the type of movement for the ordinate we can make a matrix as shown in Fig.137.



	A	B	C	D	E	F	G	H	I	J	K	L
1.	▨	▨	▨	▨	▨	▨	▨	▨	▨			
2.		▨		▨	▨							
3.		▨		▨	▨							
4.	▨	▨	▨									
5.		▨										
6.										▨	▨	▨
7.	▨	▨										
8.		▨		▨	▨					▨	▨	▨
9.		▨										

Fig.137. A matrix for the classification of toy fireworks.

In this matrix the shadowed spaces show that these combinations are already on the market, the empty spaces are not practical or may only be practical in the future.

Generally the development of the phenomena of a single firework piece with the passage of time is shown in Fig.138.

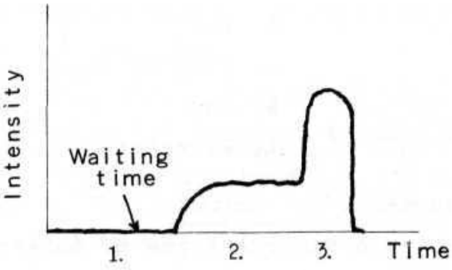
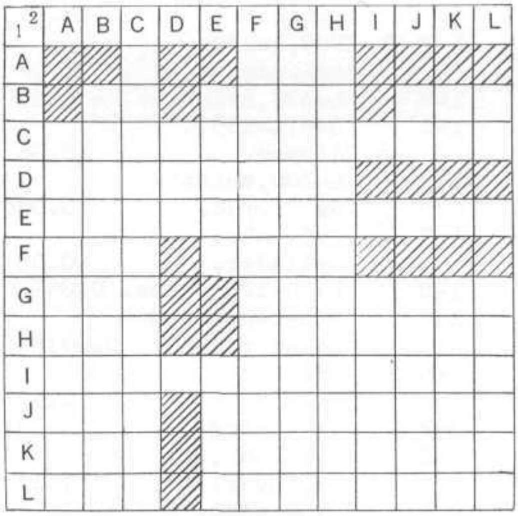


Fig.138. The development of the phenomena of toy fireworks.

The waiting time is necessary to stimulate a high feeling of expectation; when it is too short, interest decreases, but on the contrary, when it is too long, the excitement cannot be maintained, and it is often wrongly thought that there is a misfire. The best waiting time is possibly 5~6 sec. The main effect should last a little time, but the duration is also limited to the amount of composition in the toy firework effect. An accent is placed at the end, i.e. in the form of a strong but short effect. It is not good to have a weak and prolonged effect exept in special cases. A parachute would be such an example, because it must stay in the air as long as possible, The accent is constructed the good timing of two or more different phenomena. The arrangements are set out in Fig.139, where 2 means the first phenomenon and 3 the second.



1 2	A	B	C	D	E	F	G	H	I	J	K	L
A	▨	▨		▨	▨				▨	▨	▨	▨
B	▨			▨					▨			
C												
D									▨	▨	▨	▨
E												
F				▨					▨	▨	▨	▨
G				▨	▨							
H				▨	▨							
I												
J				▨								
K				▨								
L				▨								

Fig.139. Accentuation arrangements of toy firework effects.

From above descriptions we know that there are four problems in toy fireworks:

1. Discovery of new phenomena,
2. Discovery of new movement,
3. New combinations of phenomena and movements,
4. New arrangements to give an unusual accent.

What possibilities can there be except the phenomena, A~L, and the movements, 1~9 ? This may be the most difficult problem for us. But the 3. and 4. are not always difficult, because the matrix in Fig.137 and also the matrix in Fig.139 still have many empty spaces. For example, a device, 6-F-L, may be taken. This item displays a smoke stream on shooting and then has a parachute as an accent. No residual fire must be present, but this may be interesting. However once such an idea is proposed, then there is only the problem of technique and price to consider. The most important point in toy fireworks is the creation of interesting phenomena or mechanics with the least amount of composition.

Examples of toy fireworks on the market are shown in Table 25.

Table 25. Examples of toyfireworks on the market

Name	Type	Dimension (mm) and shape	Weight of composition per piece (g)	Weight of composition per volume (g/cc)
(1) Morning-glory	1-A	L=280,twisted.	0.25	0.071
(2) Glittering flowers	1-A.B	D=20,L=120, cylinder.	18.00	1.91
(3) Silver rain	1-B	D=9,L=150, cylinder.	1.06	0.111
(4) Pampas grass	1-B	L=390,twisted.	0.25	0.051
(5) Sparkler	1-C	D=4,L=185, dipped.	0.96	0.041
(6) Senko-Hanabi (Japanese sparkler)	1-C	L=200,twisted or dipped.	0.088	0.090
(7) Chinese cracker	1-D	D=5,L=40, cylinder.	0.05	0.063
(8) Cracker ball	1-D	D=10-12,sphere.	0.049-0.055	0.088
(9) Pistol cap	1-D	Paper-covered round pellet.	0.0018-0.002	0.053
(10) Smoke bomb	1-H-D	D=6,L=85, cylinder.	0.17	0.071
(11) Rat	3-B-D	D=40,ring.	0.54	0.107
(12) Chaser(Whistle)	3-E	D=8,L=80, cylinder.	1.13	0.281
(13) Pin wheel	4-B	D=50,disc.	1.61	0.164
(14) Christmas cracker	6-J.D	L=90,cone.	0.03-0.035	0.0004
(15) Parachute	6-L	D=22,L=120, cylinder with stand.	1.5	0.033
(16) Roman candle	7-A	D=15,L=300, cylinder.	10.00	0.189
(17) Comet(Rocket)	8-D	L=340,with bamboo tail, D=6.2.	1.00	0.150
(18) Flying disc	9-C	D=50,propeller	1.10	0.056

Note: D is the diameter and L the length in the third column.
The symbols of the type are the same as those in Fig.137 and 139.

As shown in above table, many toy fireworks are accentuated by a noise, D, because this is most effective but their prices are generally higher than the others. In this case,however,there are safety problems in manufacture due to the use of the red explosive. The weight of composition per volume is generally less than 0.2 g per cc; This is important in the safe handling of toy fireworks.

Part 5. Firework management

23. Principles of safety control

Here the word "Principle" refers to practice which has come through experience and to which most people would have to consent. When handling explosives we can avoid accidents if we observe these doctrines, but knowledge is different from practice. It takes many years for a person to master these doctrines.

Conservation. The first point is "Be careful!" This is obvious, but in practice great care is needed and however much experience and knowledge has been gathered, it falls short of perfection. The point really is that even if we are ignorant of the circumstances, we can maintain safety by following this doctrine. For example, at a level crossing the traffic signalboard orders us to "Stop!", and everyone must immediately stop and walk carefully. It is the same with fireworks. "Don't warm compositions!" is an obvious order, and so the operation must be stopped at once. The next order would be: "Do it below 60°C, when it is necessary!". Thus, the double approach of both prohibition and relief is the specific character of the doctrine of conservation.

Maintenance. This requires the maintenance of the same conditions over a period of time. If it was safe yesterday and all the conditions are maintained from yesterday to today, then safety will be maintained. On the contrary, if an accident has occurred the conditions must have changed.

Clearness. People must be able to follow instructions easily and without misunderstanding. For example, red is used for "Stop" and green for "Go" in traffic signals. The directions for use, or an arrow indicating the firing direction printed on fireworks are based on this doctrine. The essential point of this doctrine is that people must be able to perceive the circumstances with the minimum attention.

Simplicity. The emphasis here is on simplicity and uniformity. Here we are seriously considering the spacial arrangement of things or affairs, while in the doctrine of maintenance described above, the time arrangement was important. For example, if the traffic rule is "Keep to the right!" in one district and "Keep to the left!" in other district, people may be very much confused and there would be accidents. The workrooms for manufacturing fireworks are generally similar in type, which is rather like a box in which small instruments and tools are placed so that they can be used **for** some kind of process. This may well match the doctrine of simplicity.

True view. This emphasizes the true perspective of things or affairs in order to avoid errors of judgement. For example, when an accident has occurred, things must be left in an unaltered state. This is a requirement based on this doctrine.

Separation and isolation. The doctrines described above can be applied not only to be the handling of explosives, but to other areas also for the avoidance of accidents. However the doctrine of separation is technically only applied to explosives. Separation involves arranging explosives in small amounts as far as possible. Explosives in small amounts are not hazardous, even if they are quite sensitive. Nevertheless we must cover each of the separated explosives so that they do not affect each other. This is isolation. Moreover, isolation must be done to avoid various actions which cause ignition, explosion or detonation; e.g. mechanical actions like shock or friction, physical actions like an electric charge or temperature rise or chemical actions such as moisture or sunshine etc.

The management of fireworks is practised under the six doctrines in planning, manufacture, transportation, display etc. as described in following paragraphs.

24. Planning of fireworks

24.1. Under the principle of conservation

When we design a firework we must clearly foresee the conditions of manufacture, transportation, use etc. and take the necessary steps so that an accident does not occur.

Compositions. Red phosphorus, sulphur, realgar, antimony trisulphide or other sulphides should possibly be rejected from the compositions. It is the same to chlorates also. These materials increase the sensitivity of almost all compositions. However in practice, the requirement is not always satisfied sufficiently, and each one must be considered individually. The sensitivities in Table 28, 29 and 30(Chapter 27) may be used for planning compositions correctly. On the other hand, select each of the components so that no chemical reaction can occur among the materials. Generally a mixture of metal powder and oxidizer or chloride will cause a chemical reaction to evolve heat in presence of water. Metal powder is sometimes damaged by corrosion, and generally the grains must be coated by some protective material. A mixture of a nitrate and an ammonium salt sometimes causes double decomposition. A mixture of an ammonium salt and a chlorate generally creates ammonium chlorate which decomposes easily. When we plan a new composition, it is quite important to subject it to a sensitivity test. We can roughly know the sensitivity by rubbing or striking small amount of the composition with a hammer on an anvil. The amount of compositions used for firework pieces must be as small as possible for the purpose. When a firework feels heavy when we hold it, it shows that a large amount of composition has been used and it is not good for safety.

Other materials. Shells which explode in the sky are so planned that they turn into light fragments with no residual fire after the explosion. If a fragment is heavy, it is often fitted with a parachute, but this does not always work, because the parachute often does not function. Wooden parts stand heat relatively well, are easily nailed, bored and pasted, and therefore wooden parts are often indispensable. However they are affected by humidity and their dimensions are apt to fluctuate over a rather wide range, and they do not fit a precise design. Wooden parts allow the high pressure explosive gas to pass through them and therefore a wooden part must be covered with a tin plate when it is used, e.g., as the base of a mortar. Today plastic materials are in fashion. These are easily charged with electricity, do not withstand heat and their fragments are often sharply edged and dangerous. They are however good for waterproof construction. When a firework composition is packed with a plastic sheet, condensation often appears on the inside due to the moisture in the composition. This can cause fuses to misfire. Organic binders are also popular in place of nails or other binding materials, but the binding is not always easily inspected and is more labourious than one may think, especially a joint that has to stand force, e.g. the joint of mortar base. The binders generally contains organic solvents which is not good for health, and are not always recommended. Paints, lacquers, varnishes or binders must be used so that they do not damage the function of firework pieces. In particular they are not good for fuses, because their vapour permeates the fuses as time passes and damages them. The pieces must be assembled after the vapour is thoroughly dried out.

Igniters and ignition parts. The ignition of fuses, quick-match, powder pasted paper or even the grains of black powder with an instantaneous flame, e.g. a flame from a bursting charge or of a propellant charge, is more difficult than one may think. Arrange these pieces if possible stretched along the path of the flame. Do not hold them too firmly, but rather loosely to avoid fire stop. These pieces must often be tested by sampling. The igniters and ignition parts must be planned so that they function completely; don't abridge the process, even when it is rather time consuming in manufacture. If possible, plan the igniter of a shell so that it functions to break the shell into pieces only by the force of its own charge,even when the bursting charge is damaged by moisture etc. A specially important shell should be fitted with more than two igniters, but take care that they are not all damaged by moisture etc. The author experienced the malfunction of a 24 inch shell which was fitted,with two main fuses but which failed to explode in the sky and fell down to the ground.

Other important parts. In round Poka-shells a stopper is necessary to avoid a misfire due to the revolving of the contents. A safety device is important to avoid unexpected ignition, but in ordinary cases this is simply served by covering or packing each ignitable part with a piece of paper or paper tube which is difficult to burn.

Protection of parts or shells against shock or gas pressure. Compositions which are projected must be hard enough to avoid damage by shock of the lifting charge. The ignition composition must not be separated from the main composition by the shock. The ignition surface must not be destroyed by the strong blast of the explosive gas of the bursting or propellant charge. To meet these requirements the ignition surface is generally packed with paper or reinforced in some other way(Fig.140).

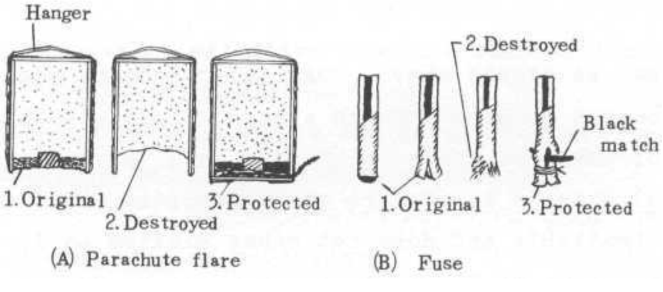
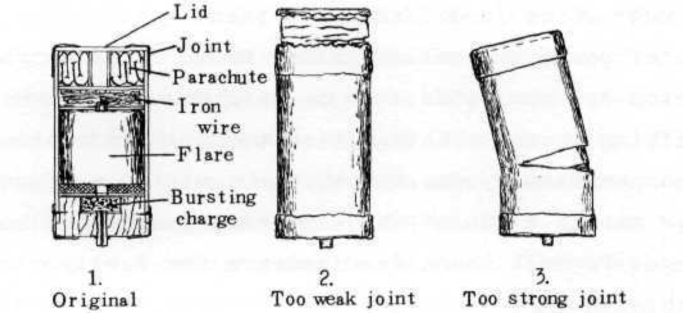


Fig.140. Method of protection of ignition surface against a strong shock or blast.

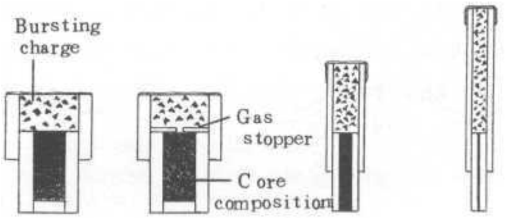
Shells can be stuffed with some buffer like sawdust or chaff in the space to protect the content from the shock. (But chaff may be forbidden in exports due to quarantine regulations.) Shells must have an outside strength which stands the shock when fired. Sometimes we have an accident because a Poka-shell is broken at the mouth of the mortar when it is fired and the contents are projected at the same time being ignited by the flame of the propellant charge. In the case of Poka-shells or some signal shells which are required to break along the joint at the explosion, the joint must have an optimum value for the breaking strength; when it is too small, the shell does not ascend on firing, but separates too early at the joint by the abnormal pressure of the shocked content; when it is too large, the shell is broken not along the joint, but at some other undesirable part causing gas to escape and the contents cannot develop well. Fig.141 shows an example of a signal flare. (See also Fig.114 (17.3)).



1. Original
2. Too weak joint
3. Too strong joint

Fig. 141. Influences of joint strength

Gas escape. As stated above, "Gas escape" means that the burnt gas of the bursting charge escapes through a gap or hole causing malfunction. The diameter of the core composition of a main fuse is one of the problems. In Fig.142, (A) shows a large core as in European shells. This type of core is quite ignitable and does not cause misfire on firing, but when it is used for a Poka shell, it causes gas escape due to the big hole after the fuse is burnt. To avoid this, it is necessary to place a gas stopper at the end of the fuse. This is troublesome, and in Japan a (B) type fuse, which has a rather small core composition, is used. Some use an even smaller type, (C), but this often causes misfire on firing and sometimes a fire stop during burning.



(A) (B) (C)

Fig.142. The various sizes of core composition of the main fuse for a shell.

The shape of firework parts. This should be designed so that it has good stability when it is put on a worktable. From this point of view unfortunately the round shape of Japanese shells is not good. The ignition composition which generally contains chlorate ought to be shaped into cubic cut stars. Otherwise they easily roll down on the floor and are invisible. This is quite dangerous, because they are too small to be discovered.

Moistureproof construction. Partial and complete protection from moisture must be considered for shells, stars and fuses. For moistureproof construction, packing with tin foil which has no pin-holes is quite convenient. This is especially effective when the composition contains magnesium.

Packing. The packing materials must not cause chemical reaction with the contents nor must they be charged with electricity.

24.2. Under the principle of maintenance

Prohibition of design change. The compositions or devices which have been used safely in practice, must not be changed without permission or unreasonably, unless they have undesirable defects. A new composition or a new device can bring new danger or new trouble. A practical composition or a practical device presently being manufactured is always more important than any imaginary one. Accidents in fireworks frequently occur owing to a breach in the doctrine of maintenance of the design. When we want to change the design, adequate and necessary tests must be done on it.

24.3. Under the principle of clearness

The following observations may help to avoid accidents, especially in the case of toy fireworks. (1) The part in which the composition is loaded, (2) the direction in which the contents project, (3) the part which is the handle, (4) the position of the fuse, (5) the directions for use etc. (Fig.143).

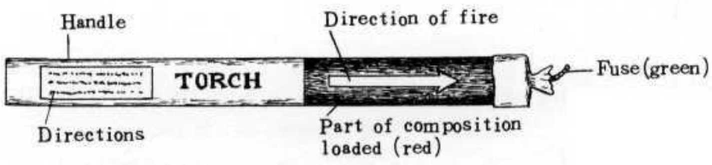
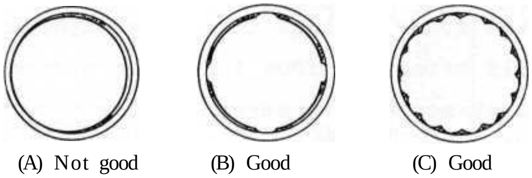


Fig.143. The labelling of a toy firework piece

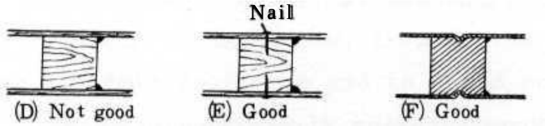
There are many kinds of composition, which cannot be distinguished from each other. To avoid errors due to this difficulty we must devise some method of separating them. For example, a white composition could be coloured by adding a small amount of dye to it; a black composition could be mixed with a small amount of aluminium flake. When this is impossible, clearly label the container with details of the composition.

Finished or half finished firework components, which resemble each other and are different in use or in concent, should be made distinguishable by painting or labelling them in a different colour or with some mark etc.

Inspection. The construction of firework pieces should be planned generally for ease of inspection. An important part should be planned so that we can see the errors in assembly from the outside. Do not use paste only, irrespective of synthetic resin or other adhesives, for jointing which must stand a large explosive force, because it is difficult to inspect whether the junktion with paste is complete or not. If the paste is used, there must be a reliable method, e.g., as shown in Fig.144(B) and (C) are reliable without any inspection; (E) and (F) are inspected from the outside.



1. Jointing a plastic tube and plug with synthetic paste.



2. Jointing a paper or metal tube and a wooden or metal plug with some paste.

Fig.144. Examples of jointing a tube and plug,

There are pyrotechnic signals on the market which are distinguished for night use by raised portions on the pieces which can be felt by the fingers in the dark. This may have an application also for fireworks.

24.4. Under the principle of simplicity

The compositions should be limited in number. In the firework world, variation is most important, and the types of compositions are apt to increase more and more. This is not good for safety control. It is best to have only a limited number of fundamental compositions, obtaining variation by changing the combinations.

The kinds of firework items manufactured in one factory should also be limited. For this reason it is best to have a guild and divide the work among the factories so that each can produce a limited items.

The kinds of firework material are then possibly limited.

24.5. Under the principle of separation and isolation

The amount of composition used for each firework piece should be as small as possible. Compositions should not be exposed on the outside of the piece which is finished so that it could catch fire.

Cover all pieces against fire. For example, toy firework pieces should be packed in bags or cases in small amounts, the quick match must be covered with a small cap on the fuse.

An igniter must be perfectly separated from the striker,i.e. the striker must be packed perfectly, e.g., with a piece of paraffin paper or placed in an isolated space so that the red phosphorus composition on the striker is perfectly separated from the prime composition. Actually about twenty years ago an accident occurred during the transportation of a packed case of toy fireworks called Bengal Match by a porter in a Yokohama warehouse. It may be that it was caused by an imperfect isolation of the striker.

25. Manufacturing fireworks

23.1. The combination of unit processes

A unit process for manufacturing fireworks is shown quite conveniently by the following simple form of account.

Unit process

Materials	Finished goods
Labour	

Materials and labour enter into the left(debit) side and come out of the right (credit) side as finished goods. Practically energies like power or heat and the loss of tools, furniture, fixtures and structures should be added to the left side, but these are quite small in firework manufacture, The operations which move the left side elements to the right are almost all physical and are seldom chemical. For example, the manufacture of potassium picrate as the material for whistles or the nitration of pitch for black snakes belong to the chemical operation.

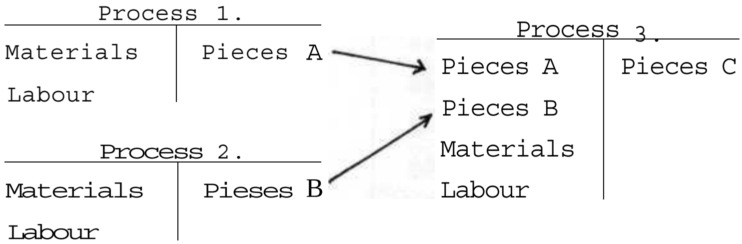
To combine unit processes there are three ways as follows:

Series combination:

Process 1.		Process 2.		Process 3.	
Materials	Pieces A->	Pieces A	Pieces B —>	Pieces B	Pieces C
Labour		Materials		Materials	
		Labour		Labour	

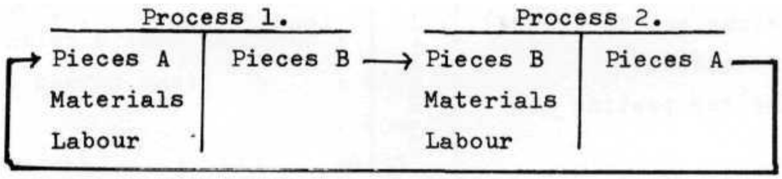
This is the simplest, the most popular and the safest combination.

Parallel combination:



In this case half finished pieces gather at the third process as in the assembly of shells. This can be dangerous. Arrange the materials and pieces in good order to avoid confusion and to avoid contact with each other.

Ring combination;



In this method half-finished pieces are circulated through several processes in ring form. They are removed out of the flow after many circulations. For example in the manufacture of round stars or paper pasting the outside of chrysanthemum shells. This may be characteristic to firework manufacture and quite laborious. The half-finished pieces are apt to be accumulated in workrooms and the stagnation of the flow of the compositions is enlarged.

Examples of unit processes are mentioned as follows:

Manufacturing parts:

Star pasting(12mm round stars)

3 mm cores(Cut stars) : 80g	12 mm round stars: 1000g
Chrysanthemum 6. :120g	(about 750 pieces)
Coloured flame composition :800g	
Persons(men) : 0.170	

Noise winding(five reports)

Noise composition	260g	Noise pieces : one set (5 pieces)
Cut fuses	5 pieces	
Packing paper	5 pieces	
Kraft paper for under winding	30g	
" over winding	56g	
Hemp	27g	
Black powder(grains)	15g	
Wheat starch paste	75g	

Note: The composition contains potassium perchlorate, aluminium and sulphur.

Comet loading

Paper tube(one end is closed)	1	Loaded comet : 1
Cardboard disc(lid)	1	
Paper piece for pasting lid	2	
Stars	2	
Black powder(grains)	0.15g	
Soft wheat starch paste	1.48g	
Persons(women)	0.0058	

Loading shells:

Preparation of hemi-sphere(6 inch Warimono)

Main fuse	1	Prepared 6 inch hemispheres: 1 set
Bursting charge bag	2.08g	
Outer bag	2.25g	
Fuse protector	0.37g	
Hemisphere(small)	1 set	
Hemp	0.37g	
Wheat starch paste	some	
Persons(women)	0.0061	

Assembly of shell(6 inch Warimono)

Prepared 6 inch hemispheres	1 set	Assembled 6 inch Warimono: 1
12 mm stars	519g	
Bursting charge	263g	
Person(men)	0.0273	

Assembly of shell(6 inch long flag(Poka))

Prepared 6 inch hemispheres for Poka(large)	1 set	Assembled 6 inch long flag: 1
Folded long flag	1	
Parachute	1	
Small noise pieces	7	
Cotton seeds	280g	
Glossy paper	6g	
Persons(men)	0.0146	

Pasting

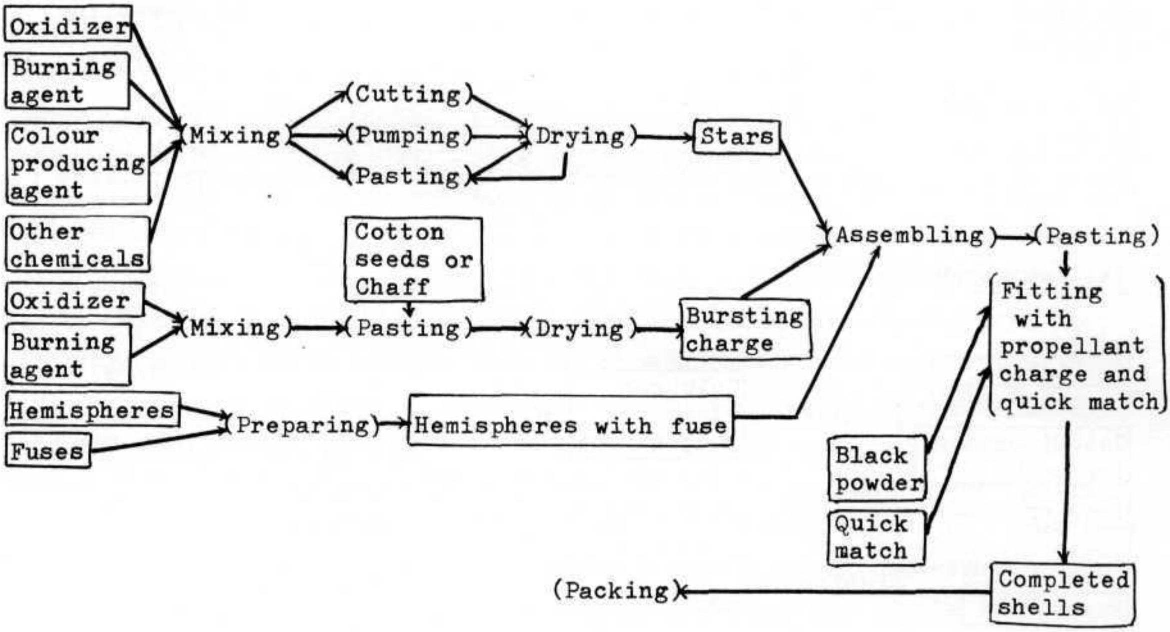
Pasting shell(6 inch Warimono)

Pastekraft-paper with Kozo (310mm x 440mm)	12	6 inch Warimono(finished): 1
Assembled 6 inch Warimono	1	
Wheat starch paste	246g	
Hemp	some	
Person(men)	0.353	

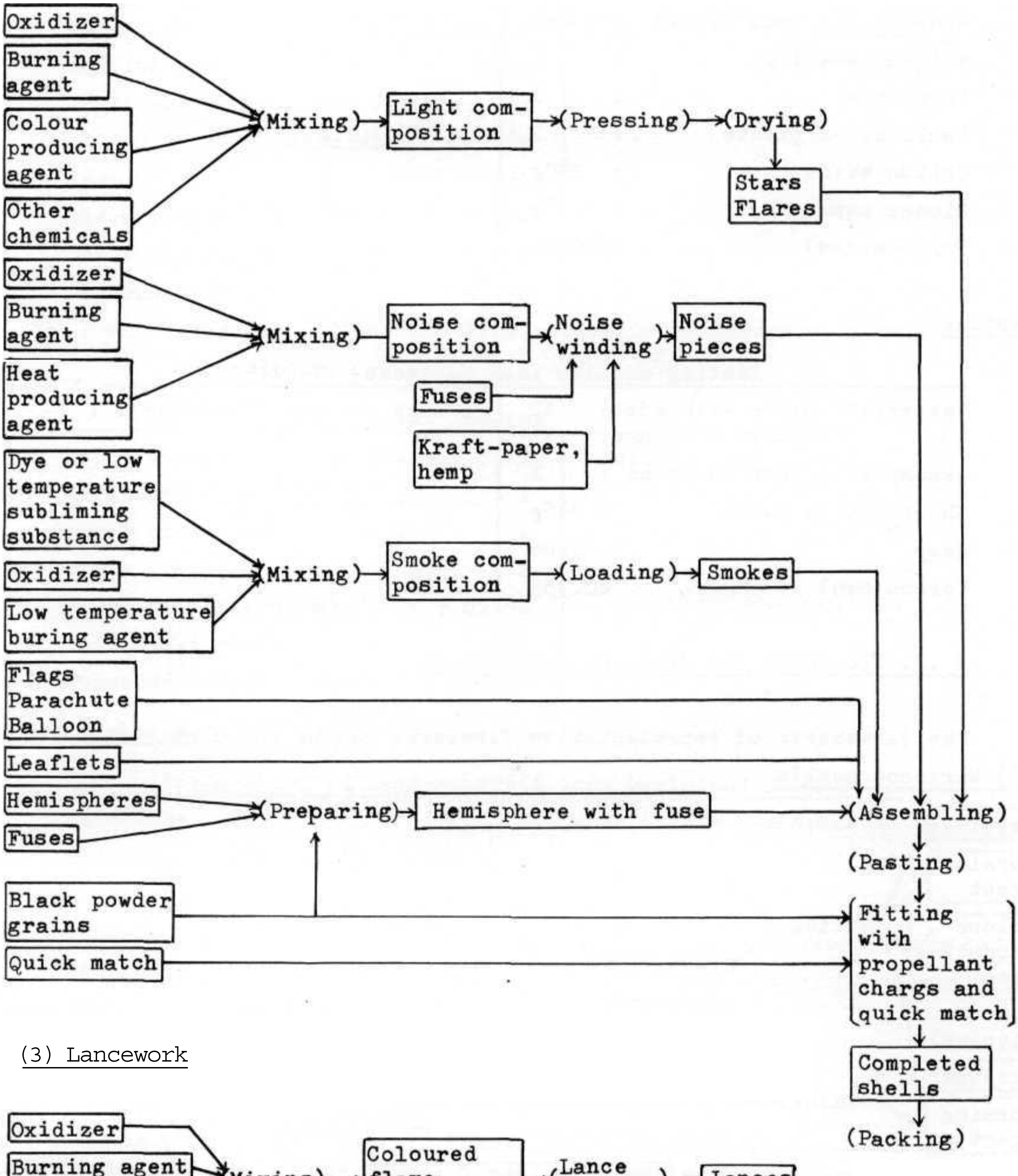
25.2. Flowsheet for firework manufacture

The flowsheets of representative fireworks may be shown as follows:

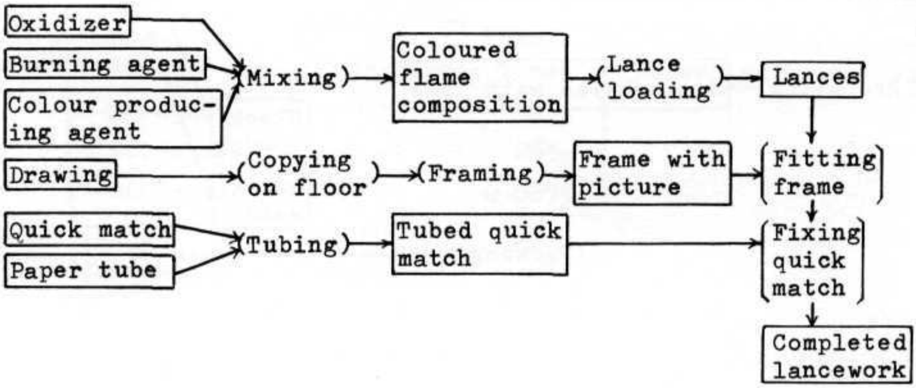
(1) Warimono shells



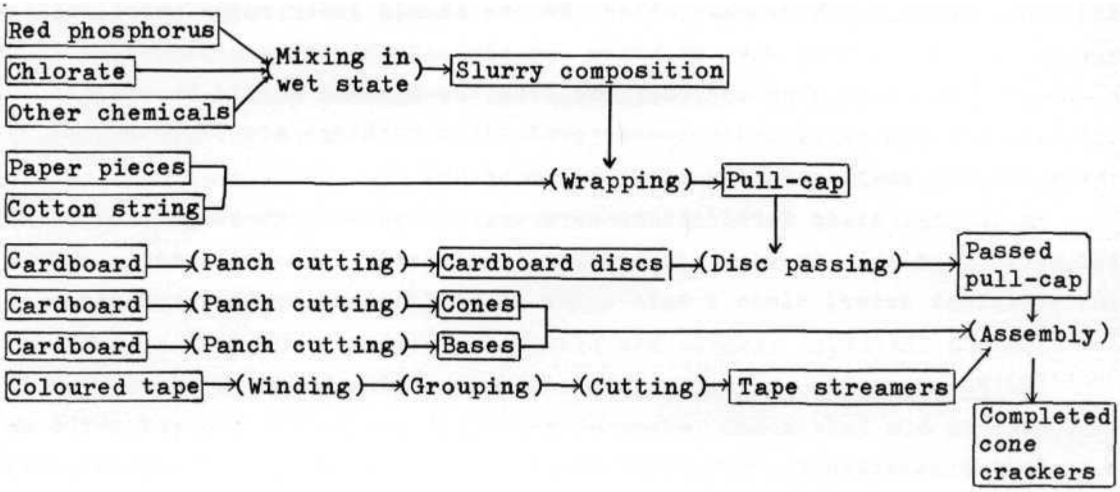
(2) Poka shells



(3) Lancework



(4) Toy fireworks : Christmas cracker(Cone cracker) as an example.



25.3. Application of the principles of safety control to manufacturing processes

(1) Personal safety

Initially the site and procedure must be organized specifically with the manufacture of fireworks in mind. This includes details on workers, workrooms, tools, furniture and fixtures, machines and containers.

Workers should put on clean clothes and socks and cut their nails short. Long trousers and long sleeved shirts must be worn. When the workers get used to such clothes, they are not uncomfortable even in summer. These clothes protect worker's skin from unexpected fire, and have saved many lives. Of course, these clothes are not fire resistant and if they do catch fire the flames must be quickly extinguished with water. Incombustible clothes of good quality for manufacturing fireworks have not been discovered yet and are not commonly used, but they may be introduced in the future. Workers should always take a towel in case unexpected injuries occur. Those working with red phosphorous should wear white coats.

Workrooms, temporary storehouses, places for drying compositions in the sun etc. should always be clean so that foreign matters cannot get mixed in to the compositions. The inside of the room, and especially the floor, should be thoroughly washed or wiped. Things which are not concerned with the process in hand should be removed from the workroom. Half-finished or other goods should not be piled so high that they may topple over. Doors or paths must not be obstructed.

Generally a new machine presents a new danger. Machines like ball mills or V-type mixers, should be checked for damage before they are used, and they should be thoroughly oiled. No one should enter rooms where machines are in operation. Even when machines are stopped, the highly dangerous operation of discharging compositions from the machine should be carried out with extreme care. Today remote controlled machines are proposed,but these are the most dangerous if problems arise.

In theory, it is forbidden to warm explosives at high temperatures, but very often this is unavoidable. But practically we cannot have a safe and efficient drier, since a safe drier is inefficient or too expensive.

(2) Maintenance

In our experience, many accidents are caused through poor maintenance. Materials, designs, processes, tools, furniture and fixtures, machines, workers cannot be changed arbitrarily. When a change is necessary, it must be made after adequate experiment, inspection and instruction, and taking the utmost precaution. Usually they shall be maintained in adequate conditions. We must pay special attention to the possibility that machines or driers are approaching breaking point without our being aware of the danger. Small cracks or small holes first appear imperceptibly in the area which is attacked by strong force or heat over a long period, and eventually cause the explosion of the contents. We must make through daily inspections and discover the signs of wear in an early stage.

Recently some firework factories have been compelled to move to a new remote place because of the rapid increase in the local population. At the new site, the water, the climate, and the people are unfamiliar, and present risks in firework manufacture.

(3) Clarity

Goods should be arranged clearly. Let us consider the process of filling large numbers of small projecting mortars with lifting charge as in the assembly of exhibition fireworks. First the mortars are arranged in a matrix. The mortars which have been loaded with the charge are moved in turn to another row to avoid missing one, which would cause the shell to explode in the mortar. If it is troublesome to move the mortars, other alternatives can be considered. One method of inspection after all the mortars are finished is by shaking them. Or all of the mortars may be inspected with an electric lamp after they are charged. Check that the amount of charge remaining corresponds to the number of mortars filled.

If a quantity of pressed stars of the same kind are stood upright on a bench,errors in the amount of composition may be seen at a glance by comparing the height of the stars.

In general many components are used for firework compositions and therefore the ingredients are often confusing to workers. Composition tables must be clearly laid out and the tare be written clearly on the outside of a vessel. When a mixing is finished, weigh the total amount of the mixture and confirm that this equals the sum of the weight of each component.

Ensure that containers of chemicals are clearly labelled. Compositions must be labelled with name, date of manufacture and composition. We often use old containers for other purposes. Check that old containers are clean, and remove the old labels. Don't use unlabelled chemicals without analysis.

(4) Simplicity

Processes should be split up into small units to reduce errors, especially with new workers. This is advisable to keep the unfinished goods moving steadily from one stage to the next to avoid the accumulation of explosives in one place.

(5) Separation and isolation

When more than one type of work is done in the same room; especially handling loose compositions; place a protective screen between the work areas.

Unfinished goods, whose composition is still uncovered, should be kept in closed containers. Large quantities of goods should be covered by protective sheets, a precaution which has saved many people when accidents have occured. The handling of loose compositions is the most dangerous of all operations.

It is important that explosives should not be subjected to shock or friction during handling. But in some operations, such as pressing, loading, assembling, cutting, boring this is unavoidable. In these circumstances only the minimum amount of composition should be allowed in the work room. The composition should be moistend if possible, according to the degree of danger, and the worker separated from the composition by some protective screen or wall.

25.4. Application of the principles of safety control to manufacturing equipment

(1) Personal safety

Equipment should be suitable for the manufacturing process, should be so arranged that accidents can be easily traced, should allow workers to escape quickly and should be combined with proper protection to save people, other equipment, other buildings etc.

Iron must not be allowed to come into contact with loose compositions, because it easily sparks; other hard and brittle metals often spark.

Electric charges cause two problems; the charge on containers and on explosives. To avoid a charge on containers, they should be made of metal which is quite easily earthed. To avoid a charge on the explosives, they should have electrical conductivity, but of course low humidity and friction promote electric charges. It is quite astonishing that a charge can occur on our fingers in the dry season, even when a well earthed copper plate is rubbed on them. Thus when grains of explosive are allowed to flow on a well earthed metal plate or wire gauze, the grains may still be charged. Table 26 shows representative data from the author's diary of electric charges in dry season. The charge does not rise however to such high values except in winter, from December to May, due to the high humidity in Japan. Generally wood cannot be charged from friction at any time. These data indicate a qualitative nature of the electric charge for each material. The more the vale increases, the more the charge.

Table 26. Electric charge of A caused by rubbing B
(Readings of a tin foil electroscope)

B\A	Soft neoprene gum	Glass	Soft polyethylene	Polystyrene	Polyvinyl chloride	Hard polyethylene	Celluloid
Copper plate	0	28	20	42	28	25	32
Red star (1)	0	2	10	2	22	25	15
Illuminant (2)	0	2	20	0	28	26	28
Black powder (mass)	1	0	28	3	24	18	24
Black powder (grains)	0	0	0	2	0	1	0
Bemberg cloth	0	2	23	12.	24	26	24
Nylon cloth	2	2	10	0	24	26	24
Fingers	0	0	6	0	25	10	22

Note : Date : Feb. 7 th. 1973.

(1) A low temperature class composition, consolidated by soluble glutinous rice starch.

(2) A high temperature class composition, consolidated by pressing.

Worktables should be made of wood and framed at the edge.

The drying room or drier for the fireworks must not be multi-purpose, but planned exclusively for firework use. Drying in the sun is unavoidable, but if it is placed near workrooms this tends to conduct fire from one room to another in an accident, i.e., this violates the principle of separation. Careful consideration should be given to the position for drying in the sun.

When we use a new machine, it must be tested first to see if it operates correctly and safely. For this purpose it is best to use an inert substance in place of the true composition if possible. Newly developed or designed machines are often out of order and this period is the most dangerous one. Repair of the machine should not be done until the composition has been completely removed from the machine.

Reservoirs are extremely important structures in firework factories. The author experienced an accident where a worker ran out of a room on fire. He ran like mad with flames all over his clothes and the author pushed him into a near-by reservoir where he was saved. It is essential to have static water tanks near to rooms where fire can occur; e.g. red phosphorus workshops.

(2) Maintenance

The position, construction or elements of manufacturing equipment must not be altered without sufficient reason.

(3) Clearity

This involves the clarification of the danger zone in the factory, fire extinguishing equipment, the number of workrooms. The maximum number of workers in a room, the limit on the maximum quantity of explosives allowed in a room, special or exclusive use of a room, equipment, instruments, e.g. for red phosphorus use, for chlorate use etc.

(4) Simplicity

The types of special workrooms in which special machines are placed, may be different from each other according to the kind of work. However ordinary workrooms are better to be constructed in the same way as far as possible. In such rooms workers can conveniently operate with the same precautions for safety.

(5) Separation and isolation

In a factory workshops are separated from each other. The factory and the village or town are also separated. The distances are determined in Japan according to the following formula:

$$D = K\sqrt[3]{W} ,$$

where D is the distance in meters, K a constant which is changeable according to the kind of explosive, e.g. K=3.0 for high explosives or K=2.4 for black powder, and other conditions and W the weight of explosive placed in a room. If the values of W in two neighbouring houses are different, the larger value is applied to the calculation. Detailed discussion is omitted, and the appropriate laws should be studied.

26. Displaying fireworks

The principles of safety control should be considered, especially the principle of separation and isolation.

26.1. Fire precautions

The firework display may also be a means of spreading fire, and needs the greatest care. Fire on the ground is often caused by residual fire in cinders or in fragments of shells, by direct fire from a low exploding shell or on the ground, or by fire remaining in burnt pieces of a parachute which is carried a long way by the wind.

Water is the best remedy for fire. When children are enjoying toy fireworks, it is best to have a bucket of water to hand. Care must be taken because modern clothes are quite inflammable. It is best if we are able to shoot shells on board a ship which has strong deck boards, on a lake or on the sea, as this is safer. Inflammable substances, e.g. dry grass, firewood, houses which are roofed with straw or dry cryptomeria bark, oil tanks etc., are the greatest obstacles for firework displays. Firing shells in places surrounded by bushes or by a forest is also quite dangerous, but very often we are obliged to fire in bad conditions. In such cases take suitable precautions to extinguish accidental fire and inform the local fire brigade.

Occasionally a bomb shell misfires in the air and falls down to the ground where it explodes and spreads a large amount of burning stars.

When there are inflammable materials near-by, the place is instantaneously filled with fire and it makes fire fighting difficult. Even just after rainfall things on the ground are not always wet particularly in sheltered spots, and there is a danger that the stars might fly into well dried inflammable matter and causes a big fire.

A source of fire which can be seen is extinguishable, if the fire fighting equipment is adequate, but much more troublesome are the sources which cannot be seen. For example, a display was finished early in the evening at 8 o'clock and everyone was fast asleep. In the night about 1 o'clock a big fire broke in the straw roof of a house. When it was discovered, it was too late. The fragment in which fire remains most easily is the fuse, for this part can sometimes hold fire activated by the "Senko-Hanabi" phenomenon for a long time. A fuse composition which contains realgar particularly has this tendency more than others. Needless to say it is important to keep watch for fire for a long time, even when the display is finished. Quick match which is made of black powder composition also has such a nature. Daylight smoke stars which contain dyes with a high vaporizing temperature sometimes have residual fire.

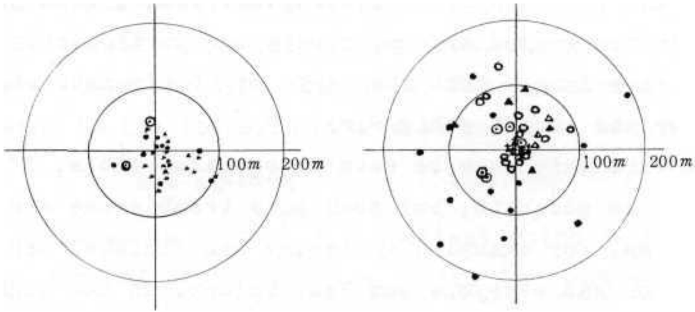
A parachute sometimes carries residual fire which cannot be seen, and as it is carried by the wind so far it can be more dangerous. Parachutes of course can be so constructed that they are fireproof and so after careful testing are useable. Commercial shells cannot be inspected by users, and so parachutes are unavoidably disliked. There is also the problem that in a daylight display there is the danger of children running after the parachute in a street of busy traffic.

26.2. Misfires

A shell which has misfired in the sky is referred to as a "Black shell". This is an accident caused usually by a malfunction of the fuse. It falls down on the ground with a strong shock; sometimes it explodes, and sometimes does not. It is said that the explosion is caused mainly by the chlorate bursting charge. Perhaps the stars which are covered by a layer of black powder are rubbed under high pressure against the bursting charge composition which contains chlorate to cause ignition. On explosion the stars are instantaneously cast over a wide area especially if it is a Warimono shell.

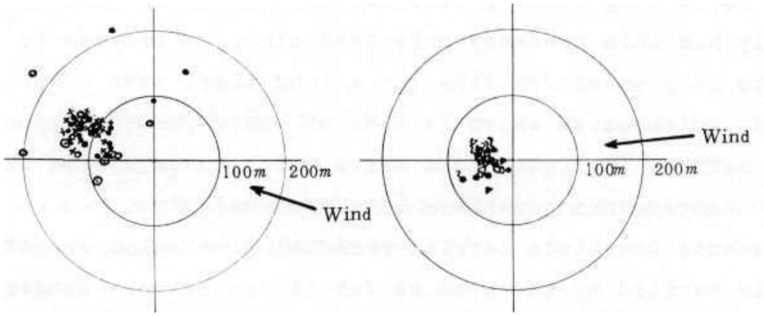
Experiments have taken place to see how far from the mortar black shells are likely to fall on the ground. Fig.145 shows four examples, (A) is an experiment by the Hosoya Firework Co. on January, 1956, (B) by Tokyo-to on February 29th and May 1st,196o, (C) by the same on May 16th .

(D) by Saitama-ken on April 4th, 1969.



(A) Windless, at River Tama, near Nagata Bridge.

(B) Windless, at the junction of River Tama and River Aki.



(C) Strong wind(6~11m/sec), at the same place as (B).

(D) Moderate wind(3.5-4.0 m/sec) at River Arakawa,near by Kumagaya.

Symbols : ▲ : 3.5 and 5 inch Warimono,
△ : Poka of the same size,
• : 6 inch Warimono,
○ : Poka of the same size,
◎ : 8.5, 10 and 12 inch Warimono,
• : 6 inch Warimono with Kyokudo.
• : 6 inch Warimono with tail coad.

Fig.145. Experimental results for black shells.

Each graph shows an oversight of the area in which the samples of the shells fell on the ground. Samples were inactive round shells, adjusted in weight with sand and they were shot at the origin of the coordinates (a small smoke was attached to each shell in order to see it easily during flight). Some of them were attached with a Kyokudo as in Fig.119 or a tail cord. In (A) the black shells fell in an area 100m diameter, but in (B) they were distributed in a wide area 250m in diameter. It is not clear where the difference came from, perhaps it was caused by turbulent air flows in the sky and the rotation of the shells. Note that

Kyokudo prevents the Shell from rotating and it allows to fly smoothly in the air. This is also observed more clearly in (C), where the shooting conditions were the same as in (B) except the date of the experiment and the strong wind; only the Shells which had Kyokudo feil in a narrow area. (D) resembles (A) very well. In this case about half of the Shells were attached with a cord tail, but all of the Shells feil in a area 100 m radius. It is supposed that the Shells in (B) and (C) might be different in construction from those in (A) and (D), especially in eccentricity. Clearly it is quite effective in any case to minimize the falling distance of black Shells by using some method to prevent the Shells from rotating, e.g., by attaching some effective Kyokudo or tail. The piece on firing must be attached to the Shell firmly so that it is not separated on firing and does not cause fire after it falls on the ground.

The falling area deviates towards the lee as seen in (C) and (D). The amount of deviation is roughly calculated as follows from these experimental results:

$$D = 10\ U_0\ ,$$

where D is the deviation from the origin in m and U_0 the wind velocity measured on the ground in m/sec (at a height of about 1.5 meters from the surface of the ground). This formula can be used for spherical Shells regardless of the size and weight in a vast field. (The wind velocity differs according to the altitude. Dr.Y.Takahashi proposed the following formula:

$$U/U_0 = (H/H_0)^{1/n},$$

where U_0 is the wind velocity at the height of H_0 and U at H. This is adapted to the altitude from 2 m to 120 m and at larger altitudes the velocity becomes constant or rather decreases. The value of n lies between 2.2 and 3.5. Over the ground n=3.0 and over the sea n=2.5. The value H_0=2m is generally used.)

26.3. Preparation for display

The men and the goods should arrive at the display site as early as possible in daylight in order to see the place and the neighbourhood, arrange the Shells, prepare the firing, inspect the prepared Shells and prepare the shooting places by installing mortars etc. The work must be finished before the evening so that the men can take their evening meal in good time. There are often situations where the display site is divided. The director must call all the workers together before they divide to make the display arrangements as clear as possible. There are some places where a two way radio is no help. It is useful to train the workers in some simple method of flag signaling or Morse code using an electric lamp.

The firing site should be flat, hard and convenient for shooting operations. Drive stakes into the ground, and fix bars them between. Arrange mortars along the bars and bind them with pieces of rope. Often we are obligied to shoot on the slope of a hill or on a projection of a rock at the seaside. In this case we make constructions on the ground to modify the place or use sand bags to securely fix the mortars. The normal working aids and drinking water etc. are indispensable.

The Shell störe is set windwords at a distance from the shooting place; the larger this distance, the safer the place is. On the other hand the Shells must be easily carried with safety and with minimum labour. A path must be simply constructed if necessary for carrying the Shells and equipped with lights for night use.

The Shells must be stored in covered boxes and when the Shells are removed from the Container they must be quickly covered with a fire protective sheet. The Shells are best placed in a tent with the entrance placed in the opposite direction to the firing site. The tent protects the Shells from sparks, moisture and rain.

26.4. Preparation of Shells

The fuses of Shells are cut at the end with a knife so that they are easily ignited. At the same time inspect them to see whether the fuses are fixed firmly to the Shells and repair them if necessary, by winding pasted pieces of hemp around them. Needless to say remind the workers to bring the materials and instrument for such repairs. The Shells are fixed with simple hangers such as those made of papar cord. Sometimes we find a curved fuse, which is shown in Fig.113(F). Be careful to cut it in the proper place, otherwise it causes the Shell to burst low(Tig.146).

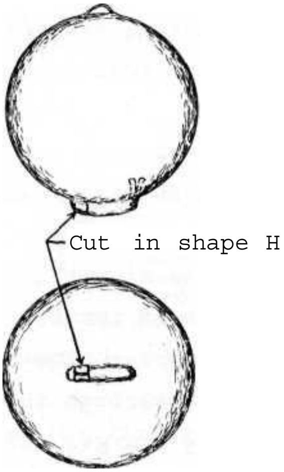


Fig.146. Cutting a curved fuse.

The propellant charge are prepared by packing them one by one in a piece of Japanese paper. The charges must be distinguished for each size of mortar by writing a large number on them(this is not necessary for fast firing which is described later).

26.5. The division of labour

Workers are divided into the following sections: director, firers, carriers, mortar cleaners, shell arrangers and people for firstaid. The scope of the display will determine the number of people in a section. Also in a section for quick shooting an oven keeper is necessary to heat the iron igniters.

26.6. Shooting operations

(1) Ordinary shooting

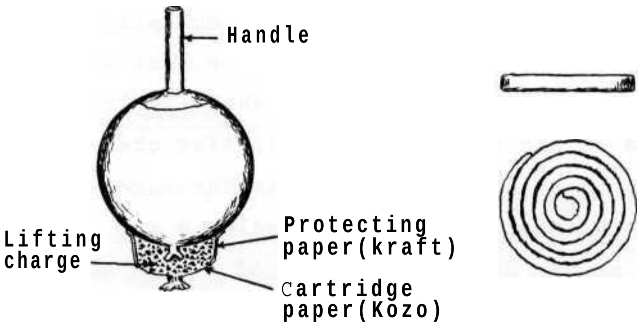
First load the propellant charge into the mortar tearing off the paper packing. The mortar must be inspected before loading to see if any fire remains or not when a shell has already been fired. People have been burnt by an accidental ignition of the propellant charge during such loading. Retaining a small amount of the charge in the hand next load the shell. The shell is fully lowered down to the bottom of the mortar with the help of a piece of cord. Don't drop the shell down to the bottom, otherwise the fuse is very often destroyed and a direct explosion occurs on firing. When the shell has been loaded, the remaining propellant charge in the hand is scattered over the shell to ensure ignition. This is railed "Powder spray".

To ignite the propellant charge, or as some say the "Lifting charge", we use a cut star about 3mm x 3mm x 30mm in size, called "Sindoro"; perhaps the name came from an English word "Cinder". The composition of Sindoro is,e.g., as follows: 62% potassium nitrate, 31% sulphur, 4% realgar, 3% glutinous rice starch. For firing this is ignited with a joss stick or match-cord and thrown into the prepared mortar. The fire propagates first to the powder spray on the shell and then through the gap between the shell and the wall of the mortar to the lifting charge, and the shell is shot.

It is a custom in Japan to arrange people beside the mortar during shooting, but this is not to be recommended. Large shells or shells of high danger such as report shells certainly should be ignited with a fuse or quick match so that the shells are lifted after people have taken shelter. The simplest method is to fix an igniter, Sindoro, to a piece of quick match and hang it on the mouth of the mortar so that the Sindoro is inside and the end of the quick match outside the mortar. The end of the quick match is ignited and the operator quickly runs away from the mortar. After a little while the Sindoro is ignited and falls down to the bottom of the mortar where it ignites the lifting charge. If we are obliged to operate near the mortar, the firer must be protected with a defence plate, e.g. a thick iron plate or a thick mat between the person and the mortar. This is especially necessary for quick shooting described next, because the operator cannot leave his position during the shooting.

(2) Quick shooting

The shells are prepared in the form in Fig.147(A). A quick firing shell is filled with a lifting charge over the fuse and has a handle on the upper part.



(A) Quick firing shell

(B) Ignition metal

Fig.147. Quick firing shell and ignition metal.

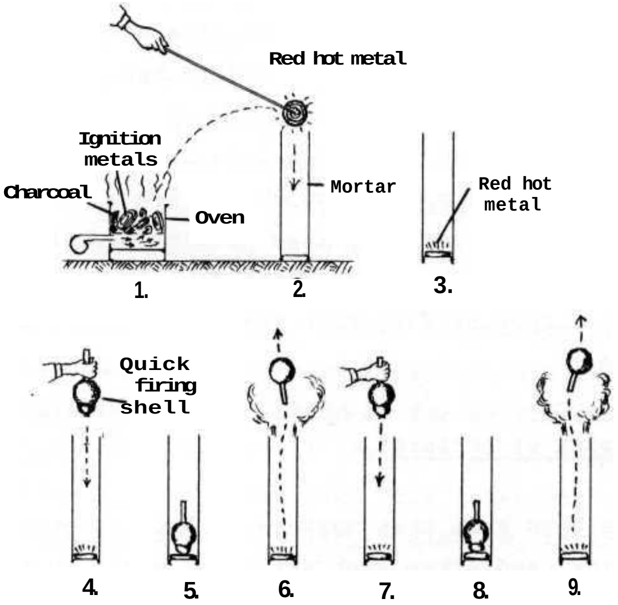


Fig.148. Quick shooting operations.

To fire this shell, first heat "Igniting metals" in a charcoal fire ovenCFig.147(B) and 148,1). The igniting metals are made of iron rod wound in a spiral. Place one of the red hot metals horizontally at the bottom of the mortar(2. and 3.). Then insert the shell so that it falls down to the bottom onto the hot metal(4. and 5.). The shell is lifted by the explosion which occurs at the contact of the lifting charge with the hot metal(6.). The next shell is loaded and shot in the same way(7.,8. and 9.). Thus we can continuously shoot a series of shells, e.g., probably about ten shells per mortar at the most in the case of 6 inch shells. This method is quite popular at present in Japan, because it is possible to shoot a large number of shells with a small number of mortars and it avoids problems like the single shell misfiring and cutting the fuses before the display.

The mortar for quick firing is rather larger than an ordinary mortar in diameter to avoid a shell sticking on the way down the mortar; cinder from the lifting charge is liable to collect on the inside wall. After one series has been fired, the mortar is taken off the support and the mortar is placed upside down and the igniting metal is then taken out. The inside of the mortar is carefully swept for the next firing.

The shells for quick firing are more dangerous than ordinary shells, because the lifting charge is attached to each of the shells and can ignite from even quite a small heat source like a small number of sparks. In addition the firer is compelled to handle the shells amongst the sparks from the lifting charge. Accordingly the firer must keep his place on the windward side of the mortar, using a special container for the shells with a fireproof cover. The shells are placed in the container and protected from fire by covering them with rice chaff. The container should be opened under the fireproof sheet for safety during firing, in order to avert the danger of fire from the mortar. An assistant is required for this operation.

(3) The sweeping of mortars

The point has been made that mortars must be swept after each shot in ordinary shooting, and after each series of shots in quick shooting with a stick attached by a piece of cloth inside the wall. This is to remove the cinder from the lifting charge and to allow the shell to be loaded easily. It is also important to remove the remaining fire which occurs due to the Senko-Hanabi phenomenon in the cinder. After the display is finished wash the mortars with water, especially the inside, and dry them well. When they are completely dry they are oiled. The cinder from black powder dissolves easily in water and has a strong alkaline reaction. When it gets in the eye, it is very painful, but it can be removed by washing the eye in a stream of water.

26.7. Firing precautions

No lift. Sometimes a shell is loaded into the mortar and the ignited Sindoro is thrown into the mortar, but the shell does not come out of the tube. The cause is usually that the fire does not propagate from the Sindoro to the lifting charge because of too narrow gap between the shell and the inside wall of the mortar, or because the lifting charge has not been added and only the shell is loaded due to some error. In the latter the shell is ignited at the fuse without lifting. This is quite dangerous, because the mortar may be broken into pieces by the explosion of the shell in the mortar after a few seconds.

In these circumstances take shelter quickly in a safe place and wait for more than one minute. If no explosion occurs, the cause may be the former. This time throw sufficient powder on the shell in the mortar and throw the ignited Sindoro into the mortar once again. Surely it should work this time. If there is no success even after several attempts, leave it in the mortar untiX the display is finished and remove the shell out of the mortar by turning it upside down.

Black shells. These are described in 27.2.

Mid explosion. This is an accident where a shell explodes in the mortar as it ascends due to the action of the lifting charge. This is caused by hot burnt gas from the lifting charge permeating through pinholes into th shell, initiating the explosion of the bursting charge. The pinholes are often found near the fuse and are difficult to see with the naked eye. In ordinary cases, i.e. when the lifting charge is charged normally, the shell explodes as it moves upwards in the mortar, and damage is not so great. The firer must operate in a low position as far as possible when firing.

Bottom explosion. (See "No lift.) This is an accident where a shell explodes in the mortar without ascending. This generally occurs when the lifting charge is missed and the igniter, a Sindoro, is thrown into the mortar. If it is a report shell or chrysanthemum the mortar is broken into pieces, and it is quite dangerous. However if it is a quick firing shell such an accident does not occur.

Early explosion. In this type of accident a shell explodes too early before the shell reaches the expected altitude in the sky. It often occurs, when the composition of the fuse is too soft and causes rapid fire, or when the length of the fuse is too short. When a Poka shell is too weak because of inadequate papering the accident often occurs at the mouth of the mortar. This is caused by shock at the firing.

Unexpected firing. Sometimes this occurs suddenly and unexpectedly in a prepared mortar. This is caused by fire dust particles which fall into the mortar. It is necessary to cover the mouth of the mortar with a lid after it is loaded with the shell.

Shell catch. It can happen that a shell catches the wall of the mortar, when it is loaded. The diameter of the shell may be too large, the sweeping of the mortar may be incomplete, the shell with a handle may be loaded in an inclined position, or the fitting of a Kyokudo to the shell may be incorrect. In ordinary shooting, poke the shell down carefully with a wooden stick. If it does not fall to the bottom, pick out the shell by placing the mortar upside down. If it is a quick firing type, pour a bucket of water into the mortar to cool the hot metal placed in the bottom of the mortar and leave the mortar to stand for a while. After making sure that it is safe, the shell can be taken out of the mortar.

Inspect the diameters of shells by passing them through a gauge. On a display we are often obliged to use mortars from other firework factories which are already set in position, especially in competitions. Before the display it is sensible to make sure that the shell fits the mortar correctly.

The arrangement of the position of riveted or welded parts of a mortar. When a shell accidentally explodes in a mortar, the break occurs at the riveted or welded part normally. In this case the splinters fly in the same direction as the broken side of the mortar and the mortar is blown off in the opposite direction. In view of this the mortar should be set so that the riveted or welded side comes to the left or right of the firer or other people who are nearby. The mortar made of seamless steel tube is the most dangerous, because the splinters fly in all directions on explosion. Mortars made of synthetic resin become brittle as time passes and produce sharp edged splinters, and they are also quite dangerous. Thick paper tube is safer than steel tube for mortars, but tubes are damaged after several firings and weakened by rain.

26.8. The operations for exhibition fireworks

The lance-frames are fixed to a scaffold according to the original picture, and the lance lines of each frame are connected to each other with piped quick match in order to ignite all frames at the same time. When one set of frames is too large to ignite instantaneously or when we are obliged to ignite it from a long distance, it is best to use an electric igniter. When lancework devices are fired at different stages in a display, the ones to be fired first should be placed in a position where sparks cannot be carried by the wind to light the other frames prematurely.

For other kinds of exhibition fireworks almost the same precautions for frame fireworks or shells can be used.

26.9. Control of a great display

In programming a great display it is necessary to give the maximum effect within the limitation of cost. There is also a limit to what the human sight can absorb as time passes with an eventual loss of the ability to recognize the variations of phenomena and colour. Accordingly, for example, at night the elaborate high class shells should be fired at the beginning so that they give people a fresh and deep impression one by one However in the middle part of the display shells of the maximum quantity are used in combination with exhibition fireworks to give a grand sight. At the end thousands of report flashes may be effective to finish the display.

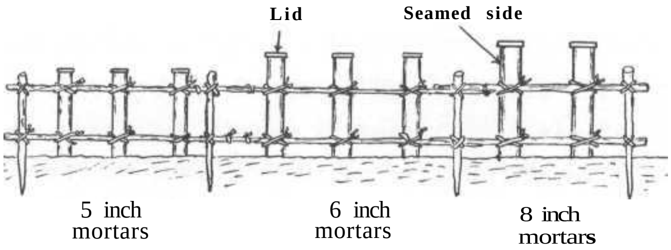
The display site should be a large flat area. There must not be any house, electric wires, electric cars, railways, fuel tanks or other institutions which might cause fire.

The exhibition fireworks produce a large quantity of fire dust sparks as described above and the shells have a large quantity of explosives; these must therefore be separated from each other.

The firing site is in two parts, the store and mortar area. The two positions, properly speaking, must be separated from each other so that the store cannot be attacked directly by a black shell. This requires a distance of not less than 80 metres between the two, but a distance of this length is quite inconvenient to carry the shells. In practice 20 or 30 metres is the most popular just to avoid the fire dust or accidental fall out from the mortar setting station. If possible, use a fireproof store house with a roof of which cannot be damaged by a direct hit from a black shell. Again in practice this is not popular, and we are obliged to only use a tent as a store in most cases. The place must be protected as far as possible and the entrance to the store must be in the opposite direction to the mortars. When we use a tent it must be guarded by a watchman so that he can remove sparks from roof with a long handled broom. The store must be on dry ground and it is sensible to find out in advance if the shells could be damaged by an unexpected water flow from a thunder-storm or unexpected high tide.
The mortar area should be on dry ground of a good size. When we shoot on

board ship, the deck under mortars should be protected by sand bags or thick wooden planks. There was an accident where a ship was cracked by the shock from a mortar causing the ship to take water.

A mortar line for example is arranged at the shooting station as shown in Fig.149. Mortars which have the same diameter should be arranged as one group. When there are more than two calibres of mortar, keep a fairly large distance between the group to distinguish them clearly. There was an accident where a *k* inch shell was loaded into a 5 inch mortar by mistake and the shell exploded on the ground as it only gained a low altitude. For quick firing the mortars should be only fixed to the bar in the upper position, because they need to be detached after each sequence to take out the hot metal. The fixing must be simply released.



An example of a mortar line.

The mortar lines shown in Fig.149 is most popular in Japan due to the economy in labour and materials for a number of mortars. However there is a danger that an accident at one mortar might affect the neighbouring mortars; the independent installation of mortars is much to be recomended whenever circumstances permit(Fig.150).

(A) Middle size mortars

(B) Large size mortars

Fig.150. Independent installation of mortars.

The firing operations at the mortar line are not different from those described in 26.6, but some precautions are necessary. The shell must be fired from the leeward side. It should be forbidden to fire shells simultaneously from more than two mortars in one mortar line. When shooting is in progress, loading must be forbidden except where the quick firing system is used. After all the mortars are loaded, the shooting can begin. After all the mortars have fired, they should be swept out. As soon as all the mortars have been swept, the next loading can then be started. The operations are thus repeated regularly and systematically. Inevitably, in ordinary shooting, a long interval is unavoidable between firings and the spectators are apt to be restless. To minimize the time interval the mortars should be distributed in several mortar stations which are separated from each other and the operators should be allowed to shoot the shells individually, but this requires many men. In recent times in Japan the quick firing system has become popular to avoid the defects of ordinary shooting, but it takes a little time to take or to put in the hot metal, and spare mortars should be provided. Quick firing cuts down the time quite effectively, but requires skillful operators.

26.10. The practical details affecting the firing of shells

The altitude at which the explosion of a firework shell takes place depends on various conditions; i.e. the amount of lifting charge, the weight of the shell, the length and diameter of the mortar, the clearance between the shell and the wall of the mortar, the loaded state of the mortar, the length of the main fuse of the shell etc. These conditions affect each other, and the relations between the conditions are very complicated.

The diameter of a firework flower(chrysanthemum) depends mainly upon the nature of the bursting charge and the paper pasting on the shell, i.e. the strength of the sphere.

Table 27 shows practical data measured by a photographic method. It is clear that there are quite large differences among the values.

We often experience that a shell is lifted to only a low altitude, even when there is no loading error. This may have a wonderful effect, but it is clear that a large part of the lifting charge was blown out of the mortar without burning. Even black powder is rather unignitable under low pressure and therefore mortars which are too short must not be used to avoid this irregularity. Firing in the rain must be avoided to avoid this kind of accident due to moisture in the lifting charge.

Table 27. The practical display data (in Osaka, 1965)

Kind of shell (inch)	Weight of lifting charge (g)	Altitude of explosion (m)	Diameter of chrysanthemum (m)	Weight of shell (g)
5	38-45	95-300	40-180	400-650
6	75-85	110-310	110-240	1150-1500
7	110-130	150-370	100-250	2000-2600
8.5	170-190	160-420	200-360	3200
10	240-280	270-450	160-340	3500-5300
12	450-500	130-440	180-390	8300-9200
24	4125-4875	480-550	490-500	60000-67500

Part 6. Miscellanea

27. The sensitivity of firework compositions

The factors which have a large influence on sensitivity are two; the kind of oxidizers and the fuels(oxidizing agents). The sensitivities may be classified simply as in Table 28 according to the results of many experiments.

Table 28. The classification of the sensitivity of fundamental two component compositions

Fuel / Oxidizer		Red phosphorus	Realgar	Antimony tri-sulphide	Sulphur	Milk sugar	Aluminium	Charcoal
KClO3	S	5	4	3	4	3	1	1
	F	5	4	3	4	1	1	1
NH_4ClO_4	S	4	3	3	3	1	1	1
	F	4	1	1	1	1	1	1
$KClO_4$	S	4	3	2	3	-	2	1
	F	4	1	2	1		1	1
KNO_3	S	3	2	1	3	1	1	1
	F	3	1	1	1	1	1	1

Note: S shows the sensitivity of a composition to shock, F to friction. The figure ,5,4,3,2 or 1, shows the classification of the sensitivity of a composition; 5 is the highest and 1 is the lowest.

Generally speaking, the composition which is sensitive to shock is also sensitive to friction. On the contrary the one which is insensitive to shock is also insensitive to friction, but there are some types which do not follow this rule; a whistle composition consisting of potassium picrate and potassium nitrate is sensitive to shock but insensitive to friction; the thermit compositions, especially red thermit which consists of red lead and ferro-silicon, are quite insensitive to shock but sensitive to friction.

The ratio of the oxidizer to the fuel(by weight) also has an influence upon the sensitivity. Note however that in the case of red phosphorus, realgar, antimony trisulphide or sulphur the influence is quite small, and even when the ratio is 20:80, the sensitivity is almost the same as that of 80:20. Such compositions generally have their maximum sensitivity at 50:50. Other compositions which contain charcoal, aluminium or milk sugar have the maximum at 70:30 and the sensitivity decreases quite rapidly as the ratio decreases(Table 29 and 30).

Firework compositions are so numerous, that the mixing or contact among them causes often higher sensitivity than that of individual compositions. For example, a bursting charge consisting of potassium chlorate and hemp coal is quite insensitive to shock and friction but if it comes in contact with stars which are coated with black powder, by some error at in the loading of Warimono or in a black shell, it would ignite as easily as if a match was rubbed with striker. The author heard that a black shell which contained chlorate bursting charge exploded from shock on the ground, but one with a perchlorate charge did not explode. Clearly, the greatest consideration is necessary in handling chlorate compositions, even when they show quite an insensitive nature.

The readers perhaps notice in Table 28 the fact that, if materials which give a high sensitivity like red phosphorus, realgar, sulphur, antimony trisulphide etc. are rejected from firework compositions, firework manufacture is made much safer. In these circumstances devices are always necessary, the problem being that without these materials ignition can be difficult in fireworks. This is one of the most important themes in fireworks.

Tables 29 and 30 give data of a systematic sensitivity test by the author and confirm the classification in Table 28. So far as other substances are concerned we may be able to judge the sensitivity from the data relating to similar chemical elements. For example, Paris green, which contains arsenic, is rather sensitive in combination with chlorate.

Table 29. Drop hammer test with a 2 kg hammer, non-explosive height in cm for 50 trials

Fuel	Oxidizer	10%	20%	30%	40%	50%	60%	65%	70%	75%	80%	85%	90%	95%	100%
Sulphur	$KClO_3$	23	16	15	15	14	19	25	23	34	15	39	29	39	64
	NH_4ClO_4	38	28	21	23	24	24	25	28	29	34	40	50	49	63
	$KClO_4$	45	39	37	31	30	29	39	34	52	35	75	31	49	138
	KNO_3	60	44	29	30	33	38	35	38	37	43	38	52	67	*
Realgar	$KClO_3$	21	21	23	27	18	36	32	30	28	38	38	31	46	64
	NH_4ClO_4	36	40	40	36	34	41	42	36	43	42	43	43	54	63
	$KClO_4$	85	50	42	25	31	54	38	60	35	69	43	99	55	138
	KNO_3	80	81	50	52	55	67	73	81	82	93	92	120	136	*
Antimony trisulphide	$KClO_3$	41	37	32	35	33	59	43	39	40	36	38	47	58	64
	NH_4ClO_4	55	30	28	29	30	49	60	50	55	48	64	52	85	63
	$KClO_4$	*	63	72	76	75	116	80	*	70	*	68	*	93	138
	KNO_3	71	66	58	63	66	68	67	67	73	74	83	97	98	*
Milk sugar	$KClO_3$	*	*	63	65	50	38	-	43	-	37	-	46	-	64
	NH_4ClO_4	*	*	*	*	75	?	-	43	-	34	-	39	-	63
	$KClO_4$	*	*	*	*	*	*	-	66	-	64	-	76	-	138
	KNO_3	-	-	-	-	-	-	-	-	-	-	-	-	-	*
Aluminium (fine flakes)	$KClO_3$	*	*	98	82	75	79	102	87	92	87	91	83	87	64
	NH_4ClO_4	*	*	138	110	72	63	71	62	67	64	65	61	65	63
	$KClO_4$	*	138	115	93	95	94	*	80	43	70	34	77	48	138
	KNO_3	*	*	110	102	83	78	77	78	75	73	73	75	79	*
Hemp-coal	$KClO_3$	*	*	104	88	81	63	76	65	79	90	108	76	115	64
	NH_4ClO_4	*	138	115	85	90	93	80	91	68	73	63	65	72	63
	$KClO_4$	*	*	*	138	124	120	-	116	58	131	-	124	-	138
	KNO_3	*	*	135	122	112	104	101	95	92	*	-	*	-	*
Picric acid		30													

Note: (1) The first line shows the percentages of an oxidizer, e.g., 30% means that the composition consists of 30% oxidizer and 70% fuel.

(2) The symbol (*) shows that the non-explosive height is higher than 130 cm, but could not be determined.

(3) The temperatures for the tests were 4—28 °C.

(4) A Sakashita-type drop hammer machine at Hosoya Firework Co. was used.

(5) Tests were carried out according to JIS method.

Table 30. Friction test by Yamada's friction, machine, non-explosive weight in kg for 50 trials

Fuel	Oxidizer	5%	10%	15%	20%	25%	30%	35%	40%	45%	50%	55%	60%	65%	70%	75%	80%	85%	90%	95%	100%
Sulphur	$KClO_3$	*	*	*	*	*	*	24.3	22.5	18.7	16.9	13	13	11.2	15	3.7	7.5	5.6	13	13	*
	NH_4ClO_4	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
	$KClO_4$	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
	KNO_3	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Realgar	$KClO_3$	5.58	5.58	2.35	3.72	1.86	1.86	1.20	1.86	<0.93	<0.93	<0.93	<0.93	<0.93	1.86	1.86	3.72	3.72	5.58	18.7	*
	NH_4ClO_4	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
	$KClO_4$	*	*	*	*	*	*	22.5	18.7	13	9.4	13	9.5	15	24.3	28	24.3	*	*	*	*
	KNO_3	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Antimony trisulphide	$KClO_3$	*	22.5	5.6	9.4	7.5	5.6	5.6	5.6	5.6	5.6	4.3	5.6	7.5	13	20.6	*	*	*	*	*
	NH_4ClO_4	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
	$KClO_4$	*	*	*	*	*	*	*	26.1	-	24.3	28	26.1	*	*	*	*	*	*	*	*
	KNO_3	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*

Note: (1) The first line shows the percentage of an oxidizer as in Table 29.

(2) The symbol (*) shows that the non-explosive weight is larger than 70 kg, but could not be determined.

(3) The temperatures for the tests were 15-22 °C.

(4) A Yamada's friction test machine at Hosoya Firework Co. was used.

(5) Aluminium (fine flakes) and Hemp-coal were tested. The non-explosive weights were all larger than 70 kg, but could not be determined.

28. Burning character of some fundamental compositions

The figures on each curve in the following diagrams show the burning durations(Fig.151~156) or the light intensity(Fig.157, 158) at 1 atm. obtained from samples 8.5mm inside diameter and 60mm long in a brown paper tube, in which about 5 grams of composition is charged at a loading density of about 1.5 g/cc.

The system potassium nitrate, carbon powder and sulphur has been used from ancient times. The burning rate and phenomena are rather different according to the kinds of the carbon (Fig. 151~153).

Antimony trisulphide is often used in place of sulphur, because the former causes little degeneration in contact with metal powder or containers(Fig.154).

The system of potassium nitrate, carbon powder and realgar is often used as a dark fuse composition, which produces no visible light or sparks on burning(Fig.156). (S. Lancaster's book on page 248.)

The effect of the barium nitrate in an illuminant composition is clearly shown comparing the light intensity in Fig.158 with those in Fig. 157. The maximum burning rate in Fig. 157 amonunts 4.4 mm/sec and that in Fig.158 6mm/sec.

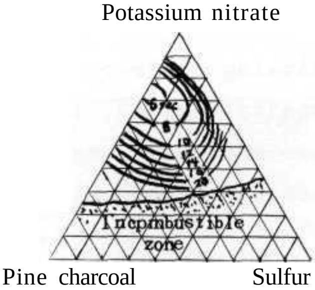


Fig. 151

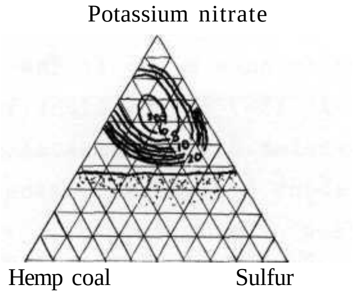


Fig. 152

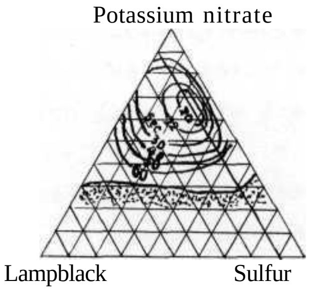


Fig. 153

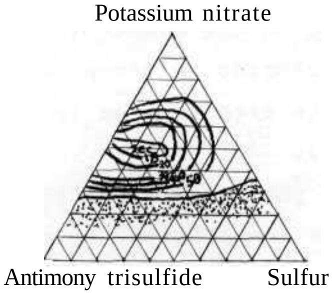


Fig. 154

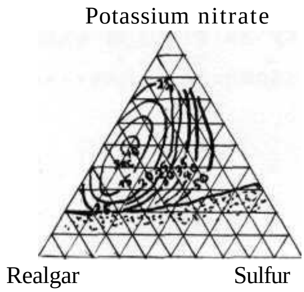


Fig. 155

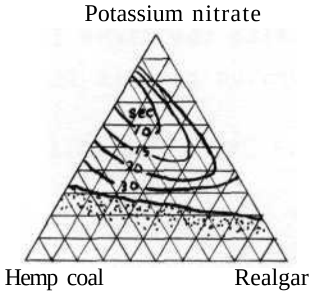


Fig. 156

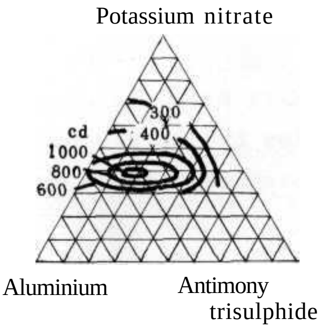


Fig. 157

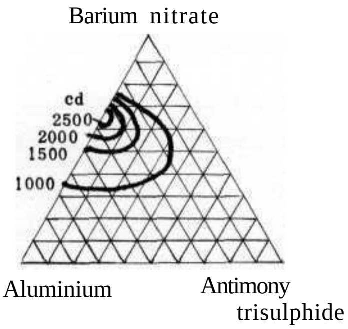


Fig. 158

29. Parachute, flags and balloons

These are paper articles for fireworks. Gampi-paper is the best material, but recently it has been gradually replaced due to the high price by foreign type paper of poorer quality. Sometimes thin cloth is also used for a parachute to hold out against the impact when it opens, but parachutes made of cloth generally fall twice as fast as those made of paper.

Parachute. Cut the paper in the prescribed dimensions and dye it if necessary. If the dimensions are insufficient, paste it with another piece of paper. The paste should be limited to wheat starch, because it allows the pasted part to maintain flexibility. Next sew the edge, especially in the case of a chain with a ring(s.Fig.5), reinforce the edge with string pasting along the paper and folding it back, or paste the string on diagonal lines; in some cases these are all omitted. These constructions are determined by considering the strength of the paper, the dimensions of the parachute, the weight of the hanging articles and the velocity of projection. Generally in the case of a parachute less than 60 cm diameter, the processing can be quite simple. Next crumble the parachute to make it soft; this is quite laborious, but the softer it is, the more it opens without fail. Then fix it with pieces of branch string at the corners as shown in Fig.159. Hemp string is better than cotton string for protection against fire. Sprinkle it with mica or talcum powder to allow it to open well, match the branches of string and fold the parachute as shown in Fig.16o. Bind the matched branches with the main string or wire rope attached to the hanging article. In this case be careful not to miss binding any of the branches. The knot often causes misopening of the parachute due to being caught in the strings. It is best to cover the knot with a piece of paper also winding and pasting it, or some device must be made in folding the parachute.

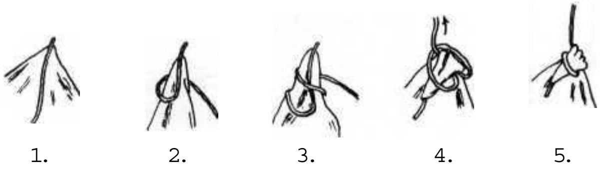


Fig.159. Fixing a branch to a parachute.

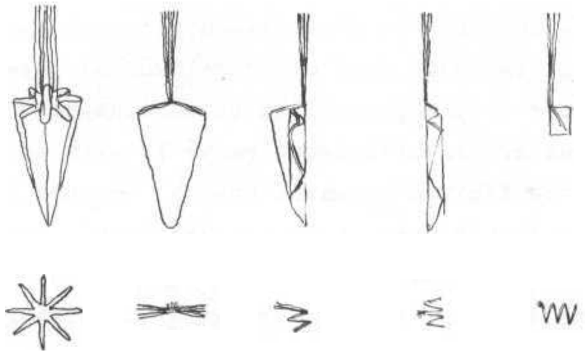


Fig.160. Folding a parachute.

The flag is made as shown in Fig.161,1. The lower edge is reinforced by pasting a piece of string along it and by folding the paper back to avoid tearing the flag when it opens. It is folded firstly along the length (2) and secondly perpendicular to it in a zigzag form (3).

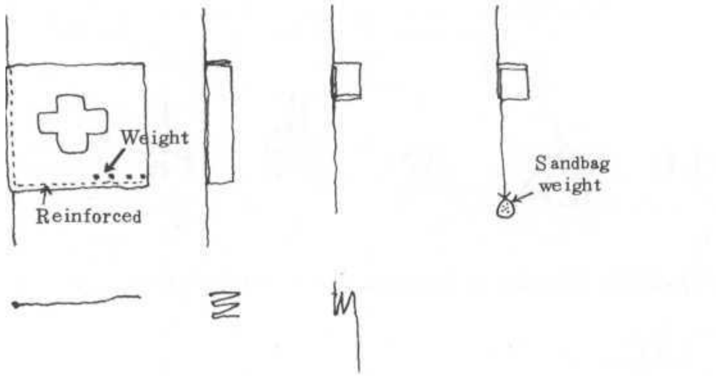


Fig.161. Folding a flag.

The balloon or comic figure is made as follows: Cut the paper in sections by following a pattern. Sew the pieces of the paper together. Crumble it soft and fit it with weight at the edge of the air hole. This is folded like the flag in order to charge it into a shell. Fig.6 shows examples.

Generally articles floating in the air do not fall regularly due to ascending or descending currents. Therefore it is impossible to calculate the falling velocity so that it has any practical value. The following formula is obtained from an experiment in a room using sample parachutes made of Gampi paper less than 1.5m diameter.

$$V = 1.49 \times 10^{-2} - 1.9 \times 10^{-5} p^2 ,$$

where V is the falling velocity of a parachute in m/sec, and

$$p = W/D^2 \ (g/m^2)$$

where W is the total weight(including the hanging article and parachute) in g and D the diameter of the parachute in m.

The space occupied by the folded paper article is calculated by the formula in 17.2.

30. Miscellaneous compositions

(1) Dark fuse

	I	II
Potassium nitrate	36%	56%
Realgar	45	34
Paulownia coal	10	10
Sulphur	9	

Sparks or lights from the fuse are not visible from a long distance.

(2) Thermit

Red iron oxide aluminium composition

Aluminium(fine flake)	45%
Red iron oxide	55

Red thermit

Minium	80%
Ferro-silicon	20

Please note that these compositions, especially the red thermit, are a little sensitive to friction.

(3) Ignition star

Potassium chlorate	70%
Hemp coal	10
Shellac	14
Soluble glutinous rice starch	6
Soluble glutinous rice starch	6

The shaped star is rubbed with a striker, on which the following composition is pasted.

(4) Friction composition

Red phosphorus	63~38%
Antimony trisulphide	13~38
Glass powder	30

10% gum arabic solution in water is added to it to form a slurry and this is pasted on the striker.

(5) Rocket

Potassium nitrate	59~64%
Charcoal	20~31
Sulphur	8~13
Black powder	0~12

(6) Adhesive

Celluloid adhesive

Celluloid or Igner	10~20%
Atnyl acetate or acetone	90~80

Acetone is used for fast drying. This is inflammable even when dried, and is used for binding stars or for making a slurry out of some compositions.

Shellac varnish

Shellac	30%
Ethanol	50

This is widely used to stick pieces of paper, wood etc. Waterproof, but brittle.

Vinyl adhesive

Vinyl acetate	66%
Celluloid	34

It is used by dissolving it in a mixture of ethanol and acetone. It is quite adhesive, but it threads during use and is rather difficult to paste. It is used for waterproof purposes.

Casein adhesive

Casein	77%
Slaked lime(Calcium hydroxide)	16
Sodium carbonate	7

3.8 times its weight of water is added to it when it is used. The adhesive power is quite strong making it suitable for pieces of paper or wood. Once prepared the solution degenerates slowly over two or three days and the adhesive power decreases. It is therefore better to use it as soon as possible.

Sodium silicate solution in water is conveniently used for cardboard cases in spite of the fact that it is not waterproof mainly because it does not get musty.

(7) White smoke

Hexachloroethane	40%
Zinc dust	35
Zinc oxide	25

This must be protected completely from moisture by canning, otherwise it causes a violent reaction generating heat. It is ignited by thermit through a thin brass or plastic plate which is fixed to the tin case in a moistureproof state(s. Lancaster's book on page 239).

(8) White smoke(non-chlor)

Potassium nitrate	48.5%
Sulphur	48.5
Realgar	3.0

This is pressed firmly into a paper tube and the two ends are plugged with gypsum. A small hole is made in it from the outside of the tube and a piece of quick match is inserted into the hole to ignite the composition.

The smoke from (7) or (8) is somewhat poisonous and is forbidden for use in a room or closed chamber where people live, or to protect plants from frost.

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I N D E X

ERRATA AND SUPPLEMENTS

Fireworks, The Art, Science and Technique, 1988, 1996
by Takeo Shimizu

Page IX. Between lines 3 and 4, the following should be inserted:
19: Assembly of Italian type shells. 261

Page 1. Line 1, *Japanese* should read *Japanese.*

Page 86. Line 17 from the bottom, *potassium nitrite* should read *potassium carbonate.*

Page 99. Line 2 and 3, *strontium nitrite*, $Sr(NO_2)_2$ should read *strontium carbonate*, $SrCO_3$.

Page 190. Figure 63. *Contnous* should read *Continuous.*

Page 215. Line 4 from the bottom, *Sodium nitrate* should read *Sodium oxalate.*

Page 225. Line 3 from the bottom, *(cd/cm)* should read (cd/cm^2).

Page 300. Table 26, footnote, the following should be added next to the (2):
(3) The figures show the values which are proportional to electric repulsion angles of tin foil.

APPENDIX

Stabilizing Firework Compositions

1. INTRODUCTION

A firework composition generally consists of several materials, oxidizer, fuel, color producing agent and etc.The state of the mixture is not natural, but artificial. The materials are closely in contact with each other. Therefore, the mixture very often gradually degenerates chemically or sometimes physically to a more stable state. It causes many troubles, moisture absorption, no ignition, low light intensity, spontaneous ignition and etc.

The most important problems at present in the firework field to avoid the degeneration of mixture may be how to select the materials wnich do not react to each other.

For this problem we could have no reliable evidence without experiences in the past. However, with individual experience we cannot foresee the general rule. For example, It is said that "Never mix chlorates with ammonium salts." On the other hand, in the German regulation we find that a mixture of chlorate and ammonium salt is forbidden, however, that of chlorate and ammonium chloride is allowed.2) Another example is that: nitrate with ammonium salt is generally avoided due to producing a hygroscopic substance, but barium nitrate with ammonium perchlorate can be used with no hygroscopic trouble . This articlewill solve such contradictions and give us a general rule on the selection of the materials.

2. THE MINIMUM SOLUBILITY LAW

2.1. General principles and applications

The chemistry originally developed from a dilute solution of some substances in water or from vapor phase. However, our firework mixtures are in solid phase. The degeneration reaction occurs from a solid to solid among the component materials. From our experiences in almost all cases, we know the degeneration of such mixtures occurs from absorption of moisture in the air. Therefore, the state of our mixtures should be thought to be a highly concentrated solution of materials in water, where only the minimum amount of moveable ions of the materials will exist.

A traditional example of producing a precipitate in a dilute solution at 30°C is shown with the reaction of silver nitrate with sodium chloride:

$$\begin{array}{ccccccc} AgNO_3 & + & NaCl & \rightarrow & AgCl\downarrow & + & NaNO_3 \\ 216 & & 36.1 & & 0.00024 & & 96.0 \end{array}$$

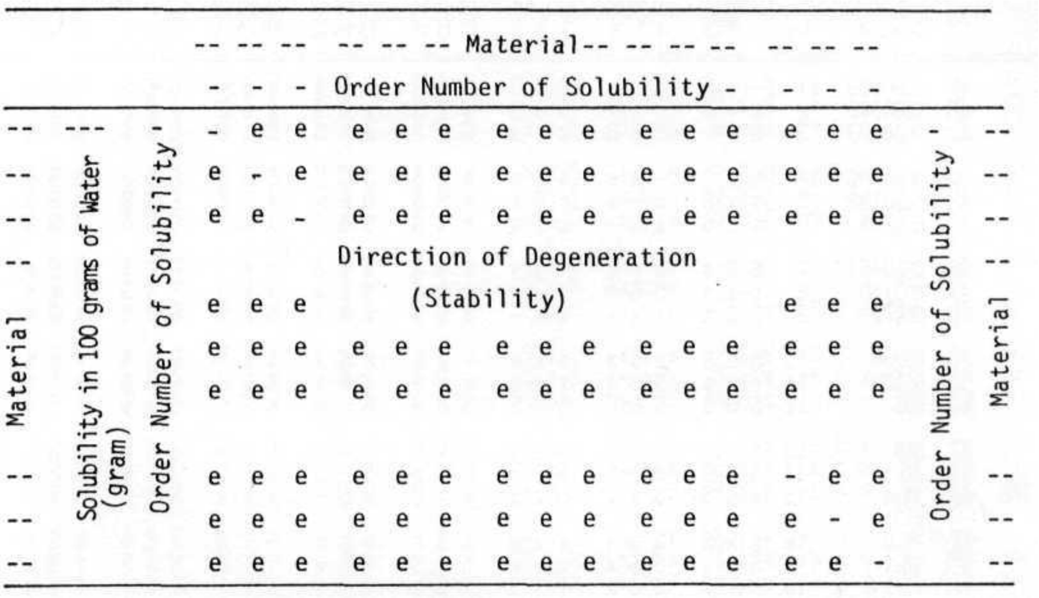
where the figures under symbols show the solubility of each material in 100 grams of water at 30°C, the horizontal arrow the direction of proceeding of the reaction, and the downward arrow the formation of precipitate. These expressions are used hereafter. When the data of solubility of individual substance are not available at 30°C, those of near 30°C are used.

As it is seen in above formula, the reaction proceeds from the left side to the right. In a dilute solution of materials, it is a very common rule of a double decomposition, i.e., the reaction in a dilute solution proceeds to form a substance which has the minimum solubility of all. The firework mixtures, especially when they are consolidated, are not dilute solution, but a solid. However, as described above, they may be thought to be a highly concentrated solution in water because they absorb more or less a very small amount of moisture. Therefore, even in the consolidated state the reaction may proceed to the direction to produce a substance of minimum solubility as it is with the precipitate formation in the dilute solution. However, it takes a long time, several days, months or years because of few active ions. In this article the author calls this reaction rule as the "minimum solubility law."

A table was prepared to confirm above theory or to foresee the directions of degeneration reactions (Table 1). In the table, materials are arranged in the order of their solubilities.

Note for Table 1:

a) The arrangement in Table 1 is as follows (e: effect):



Material	Solubility in 100 grams of Water (gram)	Order Number of Solubility	--	--	--	--	--	--	Material	--	--	--	--	--	--	Order Number of Solubility	Material
			-	-	-			Order Number of Solubility						-	-		
--	---	-	-	e	e	e	e	e	e	e	e	e	e	e	e	e	e	-	--
--			e	-	e	e	e	e	e	e	e	e	e	e	e	e	e		--
--			e	e	-	e	e	e	e	e	e	e	e	e	e	e	e		--
--									Direction of Degeneration										--
			e	e	e				(Stability)						e	e	e		
			e	e	e	e	e	e	e	e	e	e	e	e	e	e	e		
			e	e	e	e	e	e	e	e	e	e	e	e	e	e	e		
--			e	e	e	e	e	e	e	e	e	e	e	e	-	e	e		--
--			e	e	e	e	e	e	e	e	e	e	e	e	e	-	e		--
--			e	e	e	e	e	e	e	e	e	e	e	e	e	e	-		--

b) Symbols for materials are denoted in combination of cation with anion:

Cation 1: K^+
2: Na^+
3: Sr^2
4: Ba^{+2}
5: Ca^{+2}
6: NH_4^+

Anion A: NO_3^-
B: $ClO3^-$
C: ClO_4-
D: CO_3^{-2}
F: SO_4^{-2}
G: CrO_4^{-2}

H: $Cr_2O_7^{-2}$
I: Cl^-
J: $C_2O_4^{-2}$

For example, potassium nitrate is denoted by 1A which means KNO_3 or Strontium carbonate by 3D which means $SrCO_3$.

c) General symbols for the effects:

S: no reaction, stable,
s: stable due to common ions between two materials,
x: degenerates, unstable
a: unstable when alkaline,
?: uncertain due to no data of solubility,
*: no data when acid is formed, but certain with experiment,

b) The data of solubility were taken from the references(4).These are the values at or near 30°C.

Table 1. Table for foreseeing degeneration reaction at 30°C with two materials in a solid mixture based on the minimum solubility law.

	Solubility	No.	4F	4G	5J	3D	3F	4D	3J	4J	5D	3G	5F	1C	2J	1B	4A	1F	5G	1H	6C	2I	1I	4I	5G	1J
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
4F	0.00029	1	–	s	S	S	s	s	S	s	S	S	s	S	S	S	s	s	S	S*	S	S	S	s	S	S
4G	0.00046	2	s	–	S	S	x	s	S	s	S	s	x	S	x	S	s	x	s	S*	S	S	S	s	s	S
5J	0.00073	3	S	S	–	S	S	S	s	s	s	S	s	S	s	S	S	S	s	S	S	S	S	S	S	s
3D	0.00090	4	S	S	S	–	s	s	s	S	s	s	S	S	S	S	S	S	S	S	S	S	S	S	S	S
3F	0.00138	5	s	x	S	s	–	x	s	S	x	s	S	S	S	S	x	s	S	S	S	S	S	x	S	S
4D	0.0034	6	s	s	S	s	x	–	x	s	s	x	x	S	S	S	s	x	x	x	S	S	S	s	S	S
3J	0.00461	7	S	S	s	s	s	s	–	s	x	s	x	S	s	S	S	x	x	?	S	S	S	S	S	s
4J	0.0140	8	s	s	s	S	S	s	s	–	x	x	x	S	s	S	s	x	x	?	S	S	S	s	x	s
5D	0.072	9	S	S	s	s	x	s	x	x	–	x	s	S	x	S	x	S	s	S	S	S	S	x	S	x
3G	0.096	10	S	s	S	s	s	x	s	x	x	–	x	S	x	S	x	x	s	?	S	S	S	x	s	x
5F	0.209	11	s	x	s	S	S	x	x	x	s	x	–	S	x	S	x	s	s	S	S	S	S	x	S	x
1C	2.6	12	S	S	S	S	S	S	S	S	S	S	S	–	S	s	S	s	S	s	s	S	s	S	S	s
2J	3.8	13	S	x	s	S	S	S	s	s	x	x	x	S	–	S	x	S	x	S	S	s	S	x	S	s
1B	10.1	14	S	S	S	S	S	S	S	S	S	S	S	s	S	–	S	s	S	s	x	S	s	S	S	s
4A	11.4	15	s	s	S	S	x	s	S	s	x	x	x	S	x	S	–	x	x	x	S	S	S	s	x	x
1F	13.0	16	s	x	S	S	s	x	x	x	S	x	s	s	S	s	x	–	x	s	x	S	s	x	S	s
5G	16.1	17	S	s	s	S	S	x	x	x	s	s	s	S	x	S	x	x	–	S	S	S	S	x	s	x
1H	19.1	18	S*	S*	S	S	S	x	?	?	S	?	S	s	S	s	x	s	S	–	S	S	s	?	S	s
6C	29.9	19	S	S	S	S	S	S	S	S	S	S	S	s	S	x	S	x	S	S	–	S	x	S	s	x
2I	36.1	20	S	S	S	S	S	S	S	S	S	S	S	S	s	S	S	S	S	S	S	–	s	s	S	x
1I	37.1	21	S	S	S	S	S	S	S	S	S	S	S	s	S	s	S	s	S	s	x	s	–	s	S	s
4I	38.3	22	s	s	S	S	x	s	S	s	x	x	x	S	x	S	s	x	x	?	S	s	s	–	x	x
6G	39.9	23	S	s	S	S	S	S	S	x	S	s	S	S	S	S	x	S	s	S	s	S	S	x	–	S
1J	40.1	24	S	S	s	S	S	S	s	s	x	x	x	s	s	s	x	s	x	s	x	x	s	x	S	–
2F	41.2	25	s	x	S	S	s	x	x	x	S	x	s	S	s	S	x	s	x	x	S	s	x	x	S	x
6I	41.4	26	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	s	s	s	s	s	x
4B	41.7	27	s	s	S	S	x	s	S	s	x	x	x	S	x	s	s	x	x	?	S	S	x	s	x	x
2D	45.3	28	S	S	S	s	x	s	x	x	s	x	x	S	x	S	x	S	x	S	S	s	x	x	S	x
1A	45.6	29	S	S	S	S	S	S	S	S	S	S	S	s	S	s	s	s	S	s	x	S	s	x	S	s
6H	46.5	30	?	?	S	?	?	?	?	?	S	?	S	S	S	S	?	S	S	s	s	S	x	?	s	x
6B	53.4	31	S	S	S	S	S	S	S	S	S	S	x	S	S	s	S	x	S	x	s	S	x	x	s	x
6D	55.8	32	S	S	S	s	x	s	x	x	s	x	x	S	x	S	x	S	x	S	s	S	S	x	s	S
3I	58.5	33	S	S	S	s	s	x	s	x	x	s	x	S	x	S	S	x	x	?	S	s	s	s	x	x
6J	59.0	34	S	S	s	S	S	S	s	s	x	x	x	S	s	S	x	S	x	S	s	x	S	x	s	s
1G	66.1	35	S	s	S	S	S	x	S	x	S	s	S	s	S	s	x	s	s	s	S	S	s	x	s	s
6F	77.8	36	s	x	S	S	s	x	x	x	S	x	s	S	S	S	x	s	x	x	s	S	x	x	s	x
5H	83.0	37	?	?	s	?	?	?	?	?	s	?	s	S	x	S	?	x	s	s	S	S	x	?	x	x
2G	88.0	38	S	s	S	S	S	x	S	x	S	s	S	S	s	S	x	S	s	S	S	s	x	x	s	x
3A	88.7	39	S	S	S	s	s	x	s	x	x	s	x	S	x	S	s	x	x	ax	S	S	S	x	x	x
2A	96.0	40	S	S	S	S	S	x	S	S	S	S	S	S	s	S	s	x	S	S	S	s	x	x	S	x
5I	100	41	S	S	s	S	S	S	x	x	s	S	s	S	x	S	S	x	s	S	S	s	s	s	S	x
2B	105	42	S	S	S	S	S	S	S	S	S	S	S	S	s	s	S	x	S	x	S	s	x	x	S	x
1D	114	43	S	S	S	s	x	s	x	x	s	x	x	s	S	s	x	s	x	s	x	S	s	x	S	s
5A	153	44	S	S	s	S	S	S	x	x	s	S	s	S	x	S	s	x	s	S	S	S	S	x	x	x
3B	178	45	S	S	S	s	s	x	s	x	x	s	x	S	x	s	S	x	x	?	S	S	x	S	x	x
2H	192	46	?	?	S	?	?	?	?	?	S	?	S	S	s	S	?	S	S	s	S	s	x	?	S	x
5B	194	47	S	S	s	S	S	S	x	x	s	S	s	S	x	s	S	x	s	x	S	S	x	S	x	x
5C	202	48	S	S	s	S	S	S	x	x	s	S	s	s	x	x	S	x	s	x	s	S	x	S	x	x
2C	219	49	S	S	S	S	S	S	S	S	S	S	S	s	s	x	S	x	S	x	s	s	x	x	x	x
6A	238	50	S	S	S	S	S	S	S	S	S	S	S	S	S	S	s	S	S	S	s	S	S	x	s	S
4C	320	51	s	s	S	S	x	s	S	s	x	x	x	s	x	x	s	x	x	?	s	S	x	s	x	x
3C	327	52	S	S	S	s	s	x	s	S	x	s	x	s	x	x	S	x	x	?	s	S	x	S	x	x

1:K^+, 2:Na^+, 3:Sr^{+2}, 4:Ba^{+2}, 5:Ca^{+2}, 6:NH_4^+

A:NO_3^-, B:ClO_3^-, C:ClO_4^-, D:CO_3^{-2}, F:SO_4^{-2}, G:CrO_4^{-2}, H:$Cr_2O_7^{-2}$, I:Cl^-, J:$C_2O_4^{-2}$

Symbols

S:stable; sxommon ions, stable; x:unstable; a:unstable when alkaline; ?:uncertain; *:certain

2F 25	6I 26	4B 27	2D 28	1A 29	6H 30	6B 31	6D 32	3I 33	6J 34	1G 35	6F 36	5H 37	2G 38	3A 39	2A 40	5I 41	2B 42	1D 43	5A 44	3B 45	2H 46	5B 47	5C 48	2C 49	6A 50	4C 51	3C 52	No.	
s	S	s	S	S	?	S	S	S	S	S	s	?	S	S	S	S	S	S	S	S	?	S	S	S	S	s	S	1	4F
x	S	s	S	S	?	S	S	S	S	s	x	?	s	S	S	S	S	S	S	S	?	S	S	S	S	s	S	2	4G
S	S	S	S	S	S	S	S	S	s	S	S	s	S	S	S	s	S	S	s	S	S	s	s	S	S	S	S	3	5J
S	S	S	s	S	?	S	s	s	S	S	S	?	S	s	S	S	S	s	S	s	?	S	S	S	S	S	s	4	3D
s	S	x	x	S	?	S	x	s	S	S	s	?	S	s	S	S	S	x	S	s	?	S	S	S	S	x	s	5	3F
x	S	s	s	S	?	S	s	x	S	x	x	?	x	x	x	S	S	s	S	x	?	S	S	S	S	s	x	6	4D
x	S	S	x	S	?	S	x	S	s	S	x	?	S	s	S	x	S	x	x	S	?	x	x	S	S	S	x	7	3J
x	S	s	x	S	?	S	x	x	s	x	x	?	x	x	S	x	S	x	x	x	?	x	x	S	S	s	S	8	4J
S	S	x	s	S	S	S	s	x	x	S	S	s	S	x	S	s	S	s	s	x	S	s	s	S	S	x	x	9	5D
x	S	x	x	S	?	S	x	s	x	s	x	?	s	s	S	S	S	x	S	s	?	S	S	S	S	x	s	10	3G
s	S	x	x	S	S	x	x	x	x	S	s	s	S	x	S	s	S	x	s	x	S	s	s	S	S	x	x	11	5F
S	S	S	S	s	S	S	S	S	S	s	S	S	S	S	S	S	S	s	S	S	S	S	s	s	S	s	s	12	1C
S	S	x	s	S	S	S	x	x	s	S	S	x	s	x	s	x	s	S	x	x	s	x	x	s	S	x	x	13	2J
S	S	s	S	s	S	s	S	S	S	s	S	S	S	S	S	S	s	s	S	s	S	s	x	x	S	x	x	14	1B
x	S	s	x	s	?	S	x	S	x	x	x	?	x	s	s	S	S	x	s	S	?	S	S	S	s	s	S	15	4A
s	S	x	S	s	S	x	S	x	S	s	s	x	S	x	x	x	x	s	x	x	S	x	x	x	S	x	x	16	1F
x	S	x	x	S	S	S	x	x	x	s	x	s	s	x	S	s	S	x	s	x	S	s	s	S	S	x	x	17	5G
x	S	?	S	s	s	x	S	?	S	s	x	s	S	ax	S	S	x	s	S	?	s	x	x	x	S	?	?	18	1H
S	s	S	S	x	s	s	s	S	s	S	s	S	S	S	S	S	S	x	S	S	S	S	s	s	s	s	s	19	6C
s	s	S	s	S	S	S	S	s	x	S	S	S	s	S	s	s	s	S	S	S	s	S	S	s	S	S	S	20	2I
x	s	x	x	s	x	x	S	s	S	s	x	x	x	S	x	s	x	s	S	x	x	x	x	x	S	x	x	21	1I
x	s	s	x	x	?	x	x	s	x	x	x	?	x	x	x	s	x	x	x	S	?	S	S	x	x	s	S	22	4I
S	s	x	S	S	s	s	s	x	s	s	s	x	s	x	S	S	S	S	x	x	S	x	x	x	s	x	x	23	6G
x	x	x	x	s	x	x	S	x	s	s	x	x	x	x	x	x	x	s	x	x	x	x	x	x	S	x	x	24	1J
–	x	x	s	x	S	S	S	x	x	x	x	x	s	x	s	x	s	x	x	x	s	x	x	s	S	x	x	25	2F
x	–	x	x	x	s	s	s	s	s	x	s	S	x	S	x	s	x	x	S	S	x	S	x	x	s	x	x	26	6I
x	x	–	x	x	?	s	s	x	x	x	x	?	x	x	x	x	s	x	x	s	?	s	S	S	x	s	S	27	4B
s	x	x	–	S	S	S	s	x	x	S	x	x	s	x	s	x	s	s	x	x	s	x	x	s	S	x	x	28	2D
x	x	x	S	–	x	x	S	x	x	s	x	x	S	s	s	S	S	s	s	x	x	x	x	x	s	x	x	29	1A
S	s	?	S	x	–	s	s	?	s	x	s	s	x	?	S	x	S	S	S	?	s	S	x	x	s	?	?	30	6H
S	s	s	S	x	s	–	s	x	s	x	s	x	x	S	S	x	s	x	S	s	x	s	x	x	s	x	x	31	6B
S	s	s	s	S	s	s	–	x	s	x	s	x	x	x	x	x	x	s	x	x	x	x	x	x	s	x	x	32	6D
x	s	x	x	x	?	x	x	–	x	x	x	?	x	s	x	s	x	x	S	s	?	S	S	x	x	x	s	33	3I
x	s	x	x	x	S	s	s	x	–	x	s	x	x	x	x	x	x	x	x	x	x	x	x	x	s	x	x	34	6J
x	x	x	S	s	x	x	x	x	x	–	x	x	s	x	x	x	x	s	x	x	x	x	x	x	x	x	x	35	1G
x	s	x	x	x	s	s	s	x	s	x	–	x	x	x	x	x	x	x	x	x	x	x	x	x	s	x	x	36	6F
x	S	?	x	x	s	x	x	?	x	x	x	–	x	?	S	s	S	x	s	?	s	s	s	S	x	?	?	37	5H
s	x	x	s	S	x	x	x	x	x	s	x	x	–	x	s	x	s	x	S	x	s	x	x	s	x	x	x	38	2G
x	S	x	x	s	?	S	x	s	x	x	x	?	x	–	s	x	S	x	s	s	?	S	S	S	s	x	s	39	3A
s	x	x	s	s	S	S	x	x	x	x	x	S	s	s	–	x	s	x	s	x	s	S	S	s	s	x	x	40	2A
x	s	x	x	S	x	x	x	s	x	x	x	s	x	x	x	–	x	x	s	x	x	s	s	x	x	x	x	41	5I
s	x	s	s	S	S	s	x	x	x	x	x	S	s	S	s	x	–	x	x	s	s	s	S	s	x	x	S	42	2B
x	x	x	s	s	S	x	s	x	x	s	x	x	x	x	x	x	x	–	x	x	x	x	x	x	x	x	x	43	1D
x	S	x	x	s	S	S	x	S	x	x	x	s	S	s	s	s	x	x	–	x	x	s	s	x	s	x	x	44	5A
x	S	s	x	x	?	s	x	s	x	x	x	?	x	s	x	x	s	x	x	–	?	s	S	x	x	x	s	45	3B
s	x	?	s	x	s	x	x	?	x	x	x	s	s	?	s	x	s	x	x	?	–	x	x	s	x	?	?	46	2H
x	S	s	x	x	S	s	x	S	x	x	x	s	x	S	S	s	s	x	s	s	x	–	s	x	x	x	x	47	5B
x	x	S	x	x	x	x	x	S	x	x	x	s	x	S	S	s	S	x	s	S	x	s	–	s	x	s	s	48	5C
s	x	S	s	x	x	x	x	x	x	x	x	S	s	S	s	x	s	x	x	x	s	x	s	–	x	s	s	49	2C
S	s	x	S	s	s	s	s	x	s	x	s	x	x	s	s	x	x	x	s	x	x	x	x	x	–	x	x	50	6A
x	x	s	x	x	?	x	x	x	x	x	x	?	x	x	x	x	x	x	x	x	?	x	s	s	x	–	s	51	4C
x	x	S	x	x	?	x	x	s	x	x	x	?	x	s	x	x	S	x	x	s	?	x	s	s	x	s	–	52	3C

A few examples of foreseeing the degeneration reactions are presented from Table 1.

The reaction of potassium chlorate(1B) and ammonium perchlorate (6C) is found at the crossing point of the horizontal line of 1B with the vertical line of 6C as a symbol x which denotes unstable. This reaction is expressed as:

$$\begin{array}{lcccccccr} \text{Reaction:} & KClO_3 & + & NH_4ClO_4 & \rightarrow & KClO_4\downarrow & + & NH_4ClO_3 & (1) \\ \text{Solubility(g):} & 10.1 & & 29.9 & & 2.6 & & 53.4 & \end{array}$$

In the same way with potassium chlorate(1B) and ammonium chloride(5I) the crossing point denotes stable with a symbol S:

$$\begin{array}{cccccccr} KClO_3\downarrow & + & NH_4Cl & \leftarrow & KCl & + & NH_4ClO_3 & (2) \\ 10.1 & & 41.4 & & 37.2 & & 53.4 & \end{array}$$

The reaction (1) proceeds toward the right side because the $KClO_4$ has the minimum solubility of all. This reaction creates very dangerous ammonium chlorate which easily causes a spontaneous decomposition. On the other hand, the reaction (2) causes no reaction because $KClO_3$ at the left side has the minimum solubility of all. These are to explain the German regulation forbids the mixture of potassium chlorate and ammonium salts, but allows that of potassium chlorate and ammonium chloride.[3)][2)]

With the reactions of ammonium perchlorate and nitrates in the same way:we find:

$$\begin{array}{cccccccr} NH_4ClO_4(6C) & + & KNO_3(1A) & \rightarrow & NH_4NO_3(6A) & + & KClO_4(1C)\downarrow & (3) \\ 29.9 & & 45.6 & & 238 & & 2.6 & \end{array}$$

$$\begin{array}{cccccccr} 2NH_4ClO_4(6C) & + & Ba(NO_3)_2(4A) & \leftarrow & 2NH_4NO_3(6A) & + & \overset{(4C)}{Ba(ClO_4)_2} & (4) \\ 29.9 & & 11.4\ \downarrow & & 238 & & 320 & \end{array}$$

(3) and (4) explain our experiences: when ammonium perchlorate is mixed with potassium nitrate, the mixture gradually absorbs moisture in the air to become muddy due to the high hygroscopic nature of the ammonium nitrate. On the other hand, when ammonium perchlorate is mixed with barium nitrate, no reaction occurs. The reason is .that the reaction (3) proceeds to the right due to the formation of $KClO_4$, which has the minimum solubility, while the latter (4) stops in the left due to the minimum

solubility of $Ba(NO_3)_2$.

2.2. Dichromate reactions

A special attention should be paid with reactions of dichromate to apply the minimum solubility law. Dichromate salts are important to protect metals, especially magnesium, from corrosion. With ammonium perchlorate the reaction proceeds as follows:

$$\begin{array}{ccccccc} \mathrm{K_2Cr_2O_7} & + & \mathrm{2NH_4ClO_4} & \rightarrow & \mathrm{2KClO_4}\downarrow & + & \mathrm{(NH_4)_2Cr_2O_4} \\ 19.1 & & 29.9 & & 2.6 & & 46.5 \end{array} \tag{5}$$

In this case the reaction proceeds in the same way as the reaction (1) This is an ordinary reaction which follows the minimum solubility law. (In this reaction the volume of the right side mixture increases five percent from the left. Therefore, it is better to use the ammonium dichromate in place of the potassium dichromate to avoid cracking of stars during the store.) However, when using dichromates, they often create acid. The values of solubility of materials in acid are not always clear. In such cases, the direction of degeneration reaction must be experimentally confirmed. Examples are shown as follows (the solubilities noted are the values in water):

$$\begin{array}{ccccccccccc} \mathrm{K_2Cr_2O_7} & + & \mathrm{Sr(NO_3)_2} & + & \mathrm{H_2O} & \rightarrow & \mathrm{K_2CrO_4} & + & \mathrm{SrCrO_4}\downarrow & + & \mathrm{2HNO_3} \\ 18.1 & & 88.7 & & & & 66.1 & & 0.096 & & \end{array} \tag{6}$$

$$\begin{array}{ccccccccccc} \mathrm{K_2Cr_2O_7} & + & \mathrm{SrSO_4}\downarrow & + & \mathrm{H_2O} & \leftarrow & \mathrm{K_2CrO_4} & + & \mathrm{SrCrO_4} & + & \mathrm{H_2SO_4} \\ 18.1 & & 0.00138 & & & & 66.1 & & 0.096 & & \end{array} \tag{7}$$

$$\begin{array}{ccccccccccc} \mathrm{K_2Cr_2O_7} & + & \mathrm{SrCO_3}\downarrow & + & \mathrm{H_2O} & \leftarrow & \mathrm{K_2CrO_4} & + & \mathrm{SrCrO_4} & + & \mathrm{H_2CO_3} \\ 18.1 & & 0.00090 & & & & 66.1 & & 0.096 & & \end{array} \tag{8}$$

$$\begin{array}{ccccccccccc} \mathrm{K_2Cr_2O_7} & + & \mathrm{Ba(NO_3)_2} & + & \mathrm{H_2O} & \rightarrow & \mathrm{K_2CrO_4} & + & \mathrm{BaCrO_4}\downarrow & + & \mathrm{2HNO_3} \\ 18.1 & & 11.5 & & & & 66.1 & & 0.00046 & & \end{array} \tag{9}$$

$$\begin{array}{ccccccccccc} \mathrm{K_2Cr_2O_7} & + & \mathrm{BaSO_4}\downarrow & + & \mathrm{H_2O} & \leftarrow & \mathrm{K_2CrO_4} & + & \mathrm{BaCrO_4} & + & \mathrm{H_2SO_4} \\ 18.1 & & 0.0029 & & & & 66.1 & & 0.00046 & & \end{array} \tag{10}$$

$$\begin{array}{ccccccccccc} \mathrm{K_2Cr_2O_7} & + & \mathrm{BaCO_3} & + & \mathrm{H_2O} & \rightarrow & \mathrm{K_2CrO_4} & + & \mathrm{BaCrO_4}\downarrow & + & \mathrm{H_2CO_3} \\ 18.1 & & +.0022 & & & & 66.1 & & 0.00046 & & \end{array} \tag{11}$$

Of these reactions, (7), (8), (9) and (11) follows the minimum solubility law in water, (6) follows the law when the mixture is alkaline, and (10) does not follow experimentally.

This article is concluded as follows:

(1) The author presented the "minimum solubility law", having an idea that the chemical reactions or degenerations inside of a consolidated firework mixture may be thought as it is those among substances of a highly concentrated solution in water.

(2) The number of ions which can move in a consolidated mixture will be so small that the reactions proceed very slowly. Therefore, it has been very difficult to foresee the direction of reaction without experiences. However, with the help of this law we could overcome the difficulty.

(3) However, this method may not be applied to substances which do not dissolve into ions, metals or to acid or alkali forming substances, the solubilities of which in the acid or alkali are unknown.

(4) All the materials arranged in Table 1 are thought to have some relation in the firework field. The reactions with symbols are not all experimentally confirmed, but a few.

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