

Pyrotechnic Literature Series No. 6

Selected Pyrotechnic Publications of Dr. Takeo Shimizu, Part 3

Studies on Fireworks Colored-Flame Compositions

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Author's Note

These studies were conducted at Hosoya Fireworks Co. in 1958. The papers were originally published by *Journal of the Industrial Explosives Society, Japan* as follows:

Part I in No. 19	pp 308–315	Part V in No. 20	pp 183–190
Part II in No. 19	pp 315–328	Part VI in No. 20	pp 190–191
Part III in No. 20	pp 19–28	Part VII in No. 20	pp 255–264.
Part IV in No. 20	pp 89–102		

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The Journal of Pyrotechnics would wishes to acknowledge the contribution of Dr. Wes Smith for his assistance in copy editing this publication.

For Titles and Abstracts of articles appearing in *Pyrotechnic Publications of Dr. Takeo Shimizu, Part 1* and *Part 2*, see the listing at the end of this volume.

The following photo was taken at the 4th International Symposium on Fireworks in Halifax, Nova Scotia, Canada October 1998. It is of Dr. Takeo Shimizu and Bonnie Kosanke.



A short autobiography of Dr. Takeo Shimizu has been included in this volume. It was compiled by Craig Villeneuve and originally appeared in the *New Hampshire Pyrotechnics Association Newsletter* in March 1991.

Part I. A Theoretical Development of the Line-Reversal Method for Flame Temperature Measurement

ABSTRACT

A fireworks flame generally contains many solid or liquid particles, which cause a continuous spectrum. In order to apply the line-reversal method of temperature measurement to such flames, the author introduced a theoretical equation, which denotes the ratio of the intensity of the resonance lines to that of the neighboring part of the spectrum when a standard light beam is introduced into the spectroscope through the flame.

This equation shows very clearly that as long as the flame does not contain so many particles that it prevents the standard light beam from permeating the flame, the line-reversal method is always effective.

Using this equation, the author proposes a method of measuring flame temperatures that are higher than the maximum brightness temperature of the standard light. The author applied this method to two examples of high-temperature fireworks flames of some magnesium powder compositions and obtained the temperatures of 3,159 and 3,214 K.

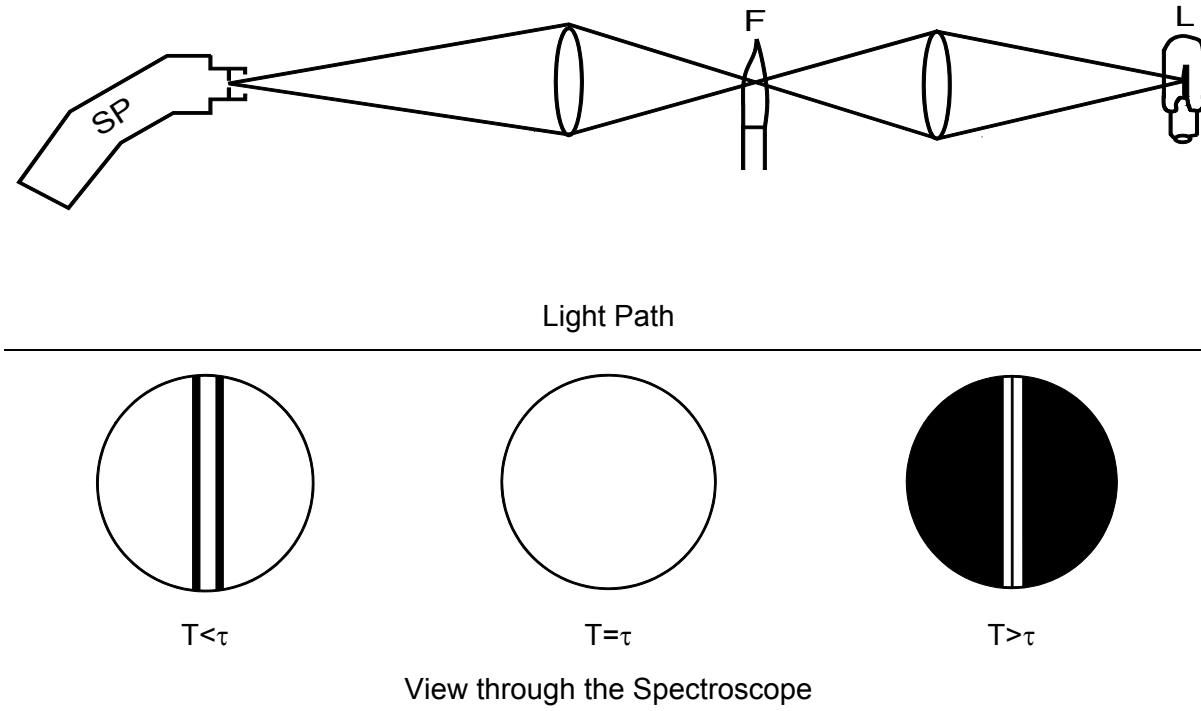
I. Introduction

There are many historical formulations for colored-flame firework compositions. However, they are fragmentary, and the author did not find any literature that described the mechanisms of colored-flame production. The purpose of this paper is to explain experimentally the color-producing mechanism and to have general principles for designing colored-flame compositions for practical uses.

Colored-flame compositions are divided into two types according to their color-producing mechanisms: one uses atomic spectra and molecular spectra from flames and the other uses continuous spectra from solid or liquid materials at high temperature. This paper concerns only the former; the latter may be examined in the future.

Initially it is necessary to measure flame temperatures to explain the color-producing mechanism. There are several flame temperature measuring methods,^[1] however, the author used the line-reversal method, using Na-D lines, which is the most reliable.

When a small quantity of a metal salt of sodium, lithium, thallium, etc., is added to a composition, it produces resonance lines in its flame spectrum. When one observes the spectrum of a standard light, which produces a continuous spectrum, through the sample flame using the device in Figure 1, the resonance lines appear dark when the black body temperature of the standard light (τ) is higher than that of the flame (T). On the other hand, when the black body temperature of the standard light is lower, the lines look bright. Therefore, to read the black body temperature on the scale of the standard light, when the lines disappear while regulating the intensity of the light, this value is equal to the flame temperature, which is defined by the radiation theory.



L	Standard light source
F	Sample flame
τ	Black body temperature of the standard light
T	True temperature of the flame
SP	Spectroscope

Figure 1. The principle of flame temperature measurement using the line-reversal method.

The following two problems need to be addressed before applying the line-reversal method to the measurement of firework flame temperatures.

(1) How does one obtain the theoretical solution when the flame contains solid or liquid particles?

(2) In general, by the ordinary line-reversal method, we cannot measure flame temperatures when they are higher than those of the standard light. How does one obtain flame temperatures that are greater than the maximum black body temperature of the standard light?

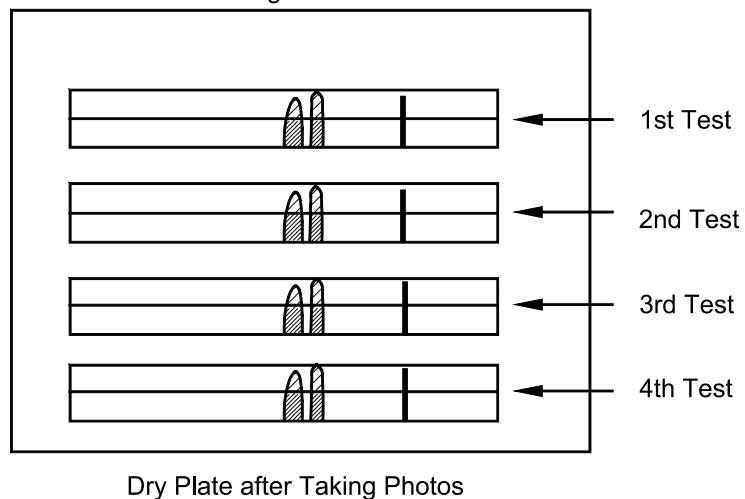
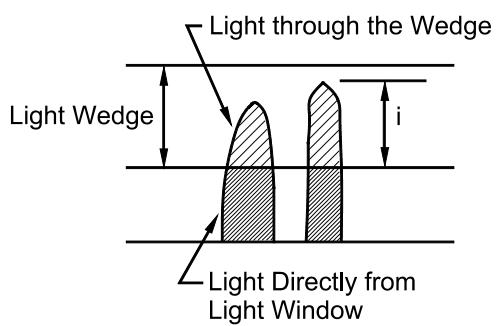
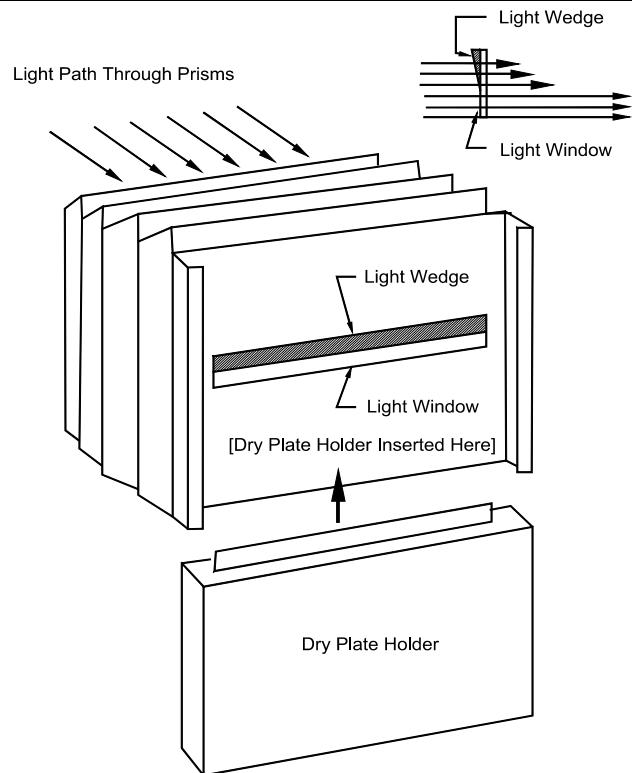


Figure 1a. Diagram of light path and how the plates were made that were used to make the photos.

II. Symbols Used in Equations

T	Temperature of flame in absolute units (K). The flame has a thickness, therefore, it denotes an average value along the path of the beams.
τ	Black body temperature of the standard light (K).
λ	Wavelength of light (cm).
$E(\lambda, T)$	Emissivity of an object at wavelength λ and true temperature T (with no subscript, denotes the black body).
$E(\lambda, \tau)$	Emissivity of an object at wavelength λ and black body temperature τ . It has the same value as the emissivity of black body when $T=\tau$.
$A(\lambda, T)$	Absorption coefficient of a body for light beams of wavelength λ .
$P(\lambda, T)$	Permeability coefficient of a body (equal to zero for an opaque body).
$R(\lambda, T)$	Reflection coefficient for light beams of wavelength λ .
r	Ratio of the light intensity of resonance lines to that of the neighboring background when observed with a spectroscope.
c_1	An emission constant ($11.906 \times 10^6 \text{ erg} \cdot \text{cm}^2 \text{sec}^{-1}$).
c_2	An emission constant (1.4387 cm·deg).
The subscripted symbols are:	
o	Standard light source, it refers to the image of the standard light in the flame.
v	Refers to a flame that is assumed to consist completely of vapor.
s	Refers to a flame that is assumed to consist completely of solid (or liquid) particles.
F	Refers to the sample flame.
n	Refers to the part of the spectrum near the resonance lines.
D	Refers to the resonance lines (e.g., Na-D lines).
F_s	Refers to solid material in the flame.
F_v	Refers to vapor material in the flame.
c	Density of small solid or liquid particles in the flame.

For the symbol c it is assumed that the flame is a thin flat plate that is placed perpendicular to the axis of the beam and that the particles are distributed within the flame, but not outside of the flame.

III. Development of General Theoretical Equations for the Line-Reversal Method

The following conditions are necessary to use the line-reversal method.

- 1) Kirchhoff's law is applicable to the radiation of solid or liquid particles in the flame.
- 2) Kirchhoff's law is also applicable to the radiation of gaseous material in the flame.
- 3) There is no luminescence in the flame.

Condition (1) is empirically always correct. Condition (2) is true only when the radiation of the flame comes from the resonance lines (i.e.,

the absorbed light energy changes to the emission of light with the same wavelength). If there is a luminescence, condition (2) is not applicable.

When light beams of the standard light are introduced into the spectroscope through a sample flame, one observes an overlapping of three light images at the position of the wavelength λ_D of the resonance lines:

- (a) the image that comes from the continuous spectrum of the standard light, whose emissivity is denoted as: $P_F(\lambda_D, T, c) \cdot E(\lambda_D, \tau_o)$.
- (b) the image that comes from the resonance lines, whose emissivity is denoted as: $E_{F_v}(\lambda_D, T, c)$
- (c) the part of the image that is produced by solid or liquid particles and coincides with the wavelength of the resonance lines is denoted as: $E_{F_s}(\lambda_D, T, c)$.

The total sum of the emissivities is denoted as:

$$E_{F_v}(\lambda_D, T, c) + E_{F_s}(\lambda_D, T, c) + P_F(\lambda_D, T, c) \cdot E(\lambda_D, \tau_o) = E(\lambda_D, \tau'_o) \quad (1)$$

Namely, the observed light intensity is proportional to the value $E(\lambda_D, \tau'_o)$ of an imaginary light source.

In the part of the spectrum, outside the resonance lines, (b) is omitted. The sum of the emissivities is:

$$E_{F_s}(\lambda_n, T, c) + P_F(\lambda_n, T, c) \cdot E(\lambda_n, \tau''_o) = E(\lambda_D, \tau''_o) \quad (2)$$

Therefore, the intensity of the observed light is proportional to the value of $E(\lambda_D, \tau''_o)$ of another imaginary light source.

When the flame temporarily consists of only solid or liquid particles, condition (1) becomes as follows, introducing the Kirchhoff's law:

$$E_s(\lambda_D, T) = A_s(\lambda_D, T) \cdot E(\lambda_D, T) \quad (3)$$

$$E_s(\lambda_n, T) = A_s(\lambda_n, T) \cdot E(\lambda_n, T) \quad (4)$$

In the case of the sample flame, the density of the solid or liquid particles in the flame is not

as large as it is with the above formulas. Therefore the sample emission must be realized by multiplying some corrective coefficient to equations 3 and 4. Also the coefficient must be zero when the density of the particles is zero and must be one when the density is highest. Therefore, the coefficient has a relation to the permeability of the flame for light beams of wavelength λ . Temporarily we will use a value $(1 - P_{F_\lambda})$ [any form of the coefficient does not have influence upon the last effect]. See equations 10 and 12. From equations 3 and 4:

$$E_{F_s}(\lambda_D, T, c) = (1 - P_{F_\lambda}) \cdot E_s(\lambda_D, T) = (1 - P_{F_\lambda}) \cdot A_s(\lambda_D, T) \cdot E(\lambda_D, T) \quad (5)$$

$$E_{F_s}(\lambda_n, T, c) = (1 - P_{F_\lambda}) \cdot E_s(\lambda_n, T) = (1 - P_{F_\lambda}) \cdot A_s(\lambda_n, T) \cdot E(\lambda_n, T) \quad (6)$$

Secondly, when the flame consists of only gas (it is a type of transparent gas), it follows, applying equation 2:

$$E_v(\lambda_D, T) = A_v(\lambda_D, T) \cdot E(\lambda_D, T) \quad (7)$$

Normally the flame contains solid or liquid particles, therefore, from the same consideration as above, equation 7 is modified as:

$$E_{F_v}(\lambda_D, T, c) = P_{F_\lambda} \cdot E_v(\lambda_D, T) = P_{F_\lambda} \cdot A_s(\lambda_D, T) \cdot E(\lambda_D, T) \quad (8)$$

When equations 5 and 8 are introduced into equation 1, we have:

$$A_F(\lambda_D, T, c) \cdot E(\lambda_D, T) + P_F(\lambda_D, T, c) \cdot E(\lambda_D, \tau_o) = E(\lambda_D, \tau_o) \quad (9)$$

Here,

$$A_F(\lambda_D, T, c) = (1 - P_{F_\lambda}) \cdot A_s(\lambda_D, T) + P_{F_\lambda} \cdot A_v(\lambda_D, T) \quad (10)$$

denotes the absorption coefficient of the sample flame at the resonance lines. In the same way, when equation 6 is introduced into equation 2, we have:

$$A_F(\lambda_n, T, c) \cdot E(\lambda_n, T) + P_F(\lambda_n, T, c) \cdot E(\lambda_n, \tau_o) = E(\lambda_D, \tau''_o) \quad (11)$$

Here,

$$A_F(\lambda_n, T, c) = (1 - P_{F_k}) \cdot A_s(\lambda_n, T) \quad (12)$$

denotes the absorption coefficient of the sample flame against the light of wavelength λ_n .

The relationship of the absorption coefficient, permeability and reflection coefficient is physically denoted as:

$$A_F + P_F + R_F = 1 \quad (13)$$

This relationship is introduced into equations 9 and 11, and we have:

$$\begin{aligned} & A_F(\lambda_D, T, c) \{E(\lambda_D, T) - E(\lambda_D, \tau_o)\} + \\ & \{1 - R_F(\lambda_D)\} \cdot E(\lambda_D, \tau_o) = E(\lambda_D, \tau'_o) \end{aligned} \quad (14)$$

$$\begin{aligned} & A_F(\lambda_n, T, c) \{E(\lambda_n, T) - E(\lambda_n, \tau_o)\} + \\ & \{1 - R_F(\lambda_n)\} \cdot E(\lambda_n, \tau_o) = E(\lambda_n, \tau''_o) \end{aligned} \quad (15)$$

In these equations it seems that the reflection coefficient R_F is only relative to the solid particles and not to the gaseous materials.^[2] When the wavelengths λ_D and λ_n approach each other, we can have:

$$\left. \begin{aligned} & E(\lambda_D, T) \doteq E(\lambda_n, T) \\ & E(\lambda_D, \tau_o) \doteq E(\lambda_n, \tau_o) \\ & R_F(\lambda_D) \doteq R_F(\lambda_n) \end{aligned} \right\} \quad (16)$$

The operation, using the line-reversal method, compares the brightness of the resonance lines and the near part on the spectrum with each other. Therefore, the equation of comparison obtained by using equation 16 is:

$$\begin{aligned} r & \doteq \frac{E(\lambda_D, \tau'_o)}{E(\lambda_n, \tau''_o)} \\ & = \frac{A_F(\lambda_D, T, c) \left\{ \frac{E(\lambda_D, T)}{E(\lambda_D, \tau_o)} - 1 \right\} + \{1 - R_F(\lambda_D)\}}{A_F(\lambda_n, T, c) \left\{ \frac{E(\lambda_D, T)}{E(\lambda_D, \tau_o)} - 1 \right\} + \{1 - R_F(\lambda_D)\}} \end{aligned} \quad (17)$$

Rearranging the above equation, and introducing a newly defined function $F(r)$, we have:

$$\begin{aligned} \frac{E(\lambda_D, T)}{E(\lambda_D, \tau_o)} & = 1 + \frac{\{1 - R_F(\lambda_D)\}(r - 1)}{A_F(\lambda_D, T, c) - r A_F(\lambda_n, T, c)} \\ & \equiv F(r) \end{aligned} \quad (18)$$

From another source of Wien's radiant equation we have:

$$E(\lambda_D, T) = \frac{c_1}{\lambda^5} e^{-c_2/\lambda_D T} \quad (19)$$

$$E(\lambda_D, \tau_o) = \frac{c_1}{\lambda^5} e^{-c_2/\lambda_D \tau_o} \quad (20)$$

The ratio of the two equations is:

$$F(r) = e^{-\frac{c_2}{\lambda_D} \left(\frac{1}{T} - \frac{1}{\tau_o} \right)} \quad (21)$$

Changing the form, we have:

$$T = \frac{1}{\frac{1}{\tau_o} - 2.303 \frac{\lambda_D}{c_2} \log F(r)} \quad (22)$$

Equation 22 is the common theoretical equation for the measurement of flame temperatures using line-reversal method when the flame contains solid or liquid particles.

IV. Examination of the Common Equation When Flame Temperatures Are Lower Than the Black Body Temperature of the Standard Light (Method 1)

When the flame temperature is lower than the black body temperature of the standard light, it is possible to regulate the temperature of the standard light so that the intensity of the resonance lines becomes the same as that of the near part of the spectrum (brightness regulation). In this case $r = 1$ following equation 17. When this is introduced to equation 18, we have $F(r) = 1$. Since $r = 1$, then

$$E(\lambda_D T) = E(\lambda_D, \tau_o)$$

and from equations 19 and 20 we have:

$$T = \tau_o$$

Therefore, the flame temperature equals the black body temperature of the standard light source.

By the above reason, the line-reversal method is applicable whether or not the flame contains solid or liquid particles.

However, how is it when the particle density is very large? In such a case the value of P_{F_λ} decreases to zero ($P_{F_\lambda} \doteq 0$) and from equations 10 and 12 we have:

$$\begin{aligned} A_F(\lambda_D, T, c) &\doteq A_s(\lambda_D, T) \\ A_F(\lambda_n, T, c) &\doteq A_s(\lambda_n, T) \doteq A_s(\lambda_D, T) \end{aligned}$$

From equation 17 we have $r \doteq 1$. In this situation the errors in the operation of the brightness adjustment increase. Therefore, this method is not good when the particle density is very large.

V. Plan To Measure Flame Temperatures When the Temperature of the Flame Is Higher Than the Black Body Temperature of the Standard Light (Method 2)

For flame temperatures that are higher than the black body temperature of the standard light, it is necessary to develop another method because it is impossible to regulate the temperature of the standard light as high as the temperatures of the flame.

Deforming equation 18 we have:

$$F(r) = 1 + \frac{(r-1)}{\frac{A_F(\lambda_D, T, c)}{1 - R_F(\lambda_D)} - r \frac{A_F(\lambda_n, T, c)}{1 - R_F(\lambda_D)}} \quad (23)$$

Then the following variables are set:

$$x = \frac{A_F(\lambda_D, T, c)}{1 - R_F(\lambda_D)} \quad (24)$$

$$y = \frac{A_F(\lambda_n, T, c)}{1 - R_F(\lambda_D)} \quad (25)$$

where x or y denotes the ratio of the absorbed light energy of the resonance lines or that of the standard light to the light energy that is not reflected. Introducing this equation into equation 23, we have:

$$F(r) = 1 + \frac{(r-1)}{x - ry} \quad (26)$$

This is introduced into equation 21, and we have:

$$e^{-\frac{c_2}{\lambda_D} \left(\frac{1}{T} - \frac{1}{\tau_o} \right)} = 1 + \frac{r-1}{x - ry} \quad (27)$$

In this equation the values of x , y and T do not seem to vary as the black body temperature of the standard light is changed. Therefore, the value of τ_o is changed in three steps, as $\tau_{o_1}, \tau_{o_2}, \tau_{o_3}$, and when the values of r_1, r_2 , and r_3 are measured experimentally, we have three simultaneous equations:

$$e^{-\frac{c_2}{\lambda_D} \left(\frac{1}{T} - \frac{1}{\tau_{o1}} \right)} = 1 + \frac{r_1 - 1}{x - r_1 y} \quad (28)$$

$$e^{-\frac{c_2}{\lambda_D} \left(\frac{1}{T} - \frac{1}{\tau_{o2}} \right)} = 1 + \frac{r_2 - 1}{x - r_2 y} \quad (29)$$

$$e^{-\frac{c_2}{\lambda_D} \left(\frac{1}{T} - \frac{1}{\tau_{o3}} \right)} = 1 + \frac{r_3 - 1}{x - r_3 y} \quad (30)$$

Solving these equations we obtain the values of x , y and T . For simplicity the next symbols are introduced:

$$a = e^{\frac{c_2}{\lambda_D} \left(\frac{1}{\tau_{o1}} - \frac{1}{\tau_{o2}} \right)} \quad (31)$$

$$b = e^{\frac{c_2}{\lambda_D} \left(\frac{1}{\tau_{o1}} - \frac{1}{\tau_{o3}} \right)} \quad (32)$$

$$\frac{x}{y} = z \quad (33)$$

When equation 28 is divided by equation 29 and these symbols are introduced, we obtain:

$$y_1 = \frac{1}{1-a} \left\{ \frac{a(r_2 - 1)}{z - r_2} - \frac{r_1 - 1}{z - r_1} \right\} \quad (34)$$

In the same way from equations 28 and 30 we obtain:

$$y_2 = \frac{1}{1-b} \left\{ \frac{b(r_3 - 1)}{z - r_3} - \frac{r_1 - 1}{z - r_1} \right\} \quad (35)$$

Introducing several values for z and calculating values for y , we have two series of y_1 and y_2 . The subscripts 1 and 2 denote the values of y relating to r_1 , r_2 and r_1 , r_3 . From these relations, two $y-z$ curves are obtained. The values of y and z are obtained at the intersection of the curves. And then, from equation 33 the value of x is obtained. Introducing these values to equation 26, the value of $F(r)$ is obtained. Introducing the value of $F(r)$ and τ_o into equation 22, we obtain the true temperature T of the flame.

At the light intensities of the flame, measured using a spectroscope, the following conditions are necessary.

(1) During the measurement, the values of x and y must not be changed. To meet this requirement during the measurement, the flame must be in a constant state, especially with respect to the density of the atoms of the resonance lines, the density of the solid or liquid particles, and consequently the thickness of the flame.

(2) The width of the slit that regulates the focus does not affect Kirchhoff's law, and it does not affect, in principle, the measurement of the flame temperature. However, the target position of the flame must be unchanged during the measurement.

Also the position of the spectroscope and the light path must be constant.

(3) With the above requirements it is difficult to strictly satisfy that of (1) because the burning state of the colored-flame compositions is not very stable. Therefore, to obtain the value of r with high accuracy, it is recommended to first obtain the values of r for several temperatures of the standard light and create an average line; second, select the values in the line as r_1 , r_2 , and r_3 .

Otherwise some special device is recommended to minimize the time of measurement. One can use a light wedge, setting it directly in front of the slit, although a photograph at the dry plate is useful for the analysis; however, in this case the surface of the light source must be perfectly flat, and the image of the flame must be large and of uniform brightness.

(4) The better the accuracy of the measured data, the better will be the accuracy of the calculated temperatures. Therefore, one must use a photometer as accurately as possible to measure the blackening density of the photographic dry plate when a photographic method is used. In such a case the characteristic curve of the plate must be also considered.

(5) To satisfy the conditions of equation 16, λ_n must be close to λ_D . Therefore, the dispersion of the spectroscope should be as large as possible to make operations of the measurement easy.

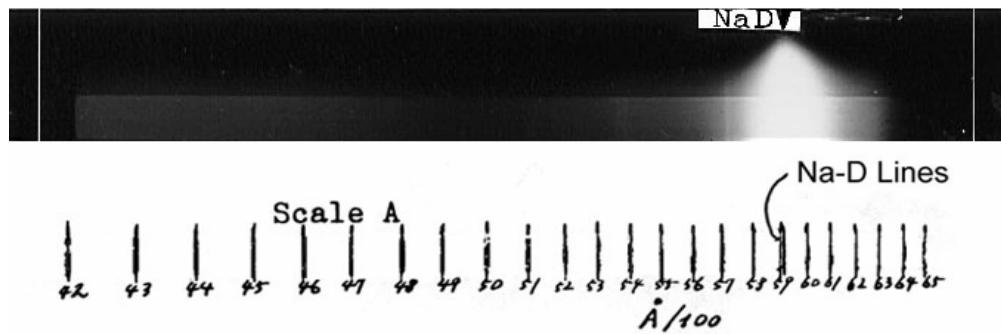


Photo 1. Continuous spectra appeared on both sides of the Na-D lines at lower temperatures.

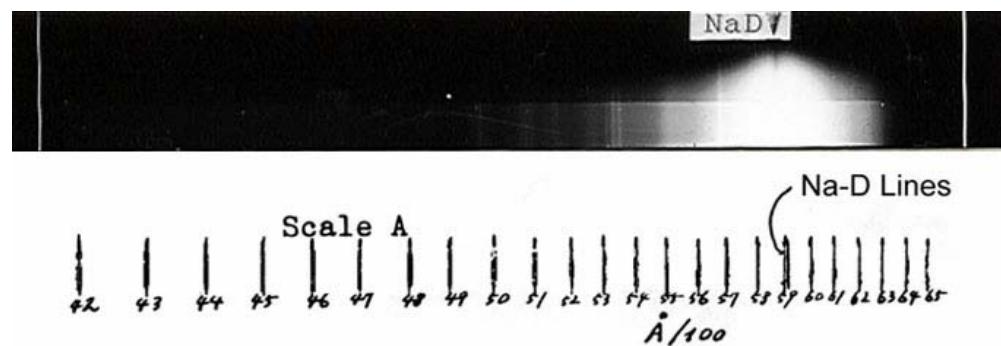


Photo 2. Continuous spectra appeared on both sides of the Na-D lines at higher temperatures.

(6) When the temperatures of the flame are expected to be close to those of the standard light, create a curve of τ_o vs. r and extend it until it intersects the line of $r = 1$. The position of that intersection denotes the rough flame temperature. In this paper a calculated value is given for comparison (denoted with the symbol \odot mark in Figure 2).

(7) There is no need to add a Na source to the sample compositions, especially when flame temperatures exceed about 3000 K. Ordinary ingredients contain Na salts in small quantity as an impurity. Sodium plays a role in the resonance lines. At high temperatures, the Na source must be of very small quantity. If it is large, continuous spectra appear on both sides of the Na-D lines and interfere with measurement operations increasing errors. Photos 1 and 2 show sample results when a fairly large quantity of Na-salt is added.

The compositions used for the photos are:

For Photo 1	
Potassium perchlorate	75%
Colophony	15%
Sodium carbonate (anhydrous)	10%
For Photo 2	
Potassium nitrate	20%
Magnesium	60%
Sodium carbonate (anhydrous)	20%

Example 1. Potassium Perchlorate Composition

Composition:	Potassium perchlorate (for industry use)	45%
	Magnesium (smaller than 149 μ)	45%
	Polyvinyl chloride	10%

Sample cartridge: The composition is loaded into a brown paper tube of 10 mm inside diameter, 96 mm long, having a wall thickness of about 0.5 mm.

Loading density : 1.21 g/cm³

Burning velocity: 3.58 mm/sec

Position of the temperature measurement:

In the middle at a point 10 mm above the flame base.

VI. Measurement and Examples of Calculation Using Method 2

In this paper the author used the photographic method although it is not as accurate. Using a spectroscope of 6.0 Å/mm dispersion at the Na-D lines and changing the temperature of a standard light in four stages, light beams were introduced into the spectroscope after passing through the flame, and the image was photographed. Afterward, a sensitization curve of the dry plate was prepared. On the dry plate the blackening densities of Na-D lines and near the lines were considered as energy values, and the ratio of the two was taken as the value of r . Details of the arrangements of instruments are described in the next part.

Black body temperatures of the standard light were adjusted to a : 2380 K; b : 2490 K, c : 2595 K and d : 2690 K. In each case light beams were introduced into the spectroscope through the flame and photographed on one dry plate as shown in Photo 3.

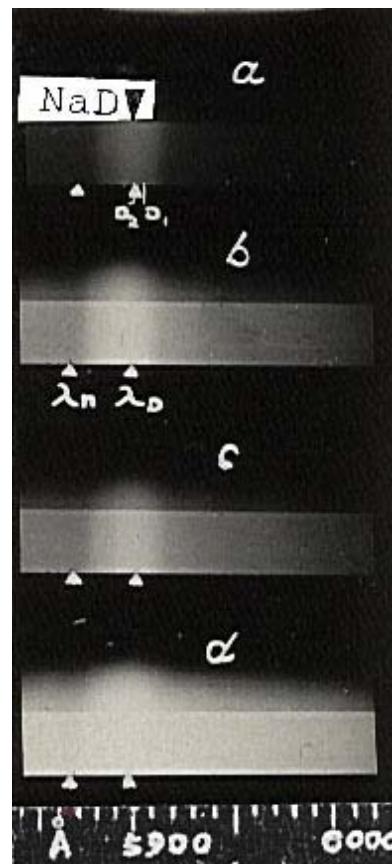


Photo 3. Reflections of the standard light when its temperature was changed in four stages through a sample flame.

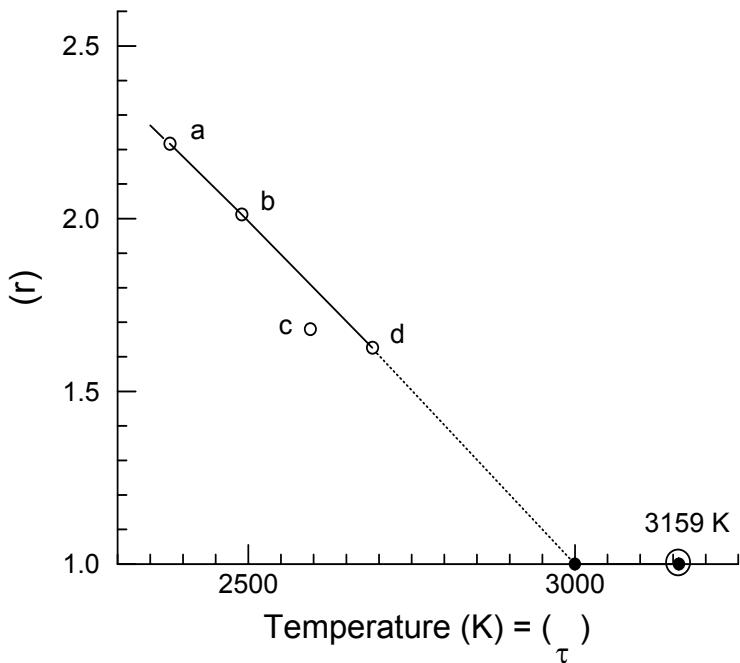


Figure 2. Graphical expression of the data measured.

Measurement:

In the photos, the Na-D₁ and Na-D₂ lines were fairly dispersed. This came from the adjustment of the spectroscope. The \odot symbols denote the measured point of blackening at the wavelength λ_D or λ_n . Attention was paid to the measuring point so that the same points correspond in photos a, b, c, and d. The values thus obtained are shown in Figure 2.

In this case c denotes an irregular value and was omitted for calculation. The values of r which were useable are as follows:

d	$\tau_{o_1} = 2,690 \text{ K}$	$r_1 = 1.626$
b	$\tau_{o_2} = 2,490 \text{ K}$	$r_2 = 2.012$
a	$\tau_{o_3} = 2,380 \text{ K}$	$r_3 = 2.217$

Calculations:

$$1/\tau_{o_1} = 0.0003717$$

$$1/\tau_{o_2} = 0.0004016$$

$$1/\tau_{o_3} = 0.0004202$$

$$\begin{aligned}
 c_2/\lambda_D &= 1.4387/0.590 \times 10^{-4} \\
 &= 2.44 \times 10^4 \\
 a &= e^{\frac{c_2}{\lambda_D} \left(\frac{1}{\tau_{o_1}} - \frac{1}{\tau_{o_2}} \right)} = e^{-0.7296} = 0.4821 \\
 b &= e^{\frac{c_2}{\lambda_D} \left(\frac{1}{\tau_{o_1}} - \frac{1}{\tau_{o_3}} \right)} = e^{-1.1834} = 0.3062 \\
 y_1 &= \frac{1}{1-a} \left\{ \frac{a(r_2-1)}{z-r_2} - \frac{r_1-1}{z-r_1} \right\} \\
 &= 1.931 \left\{ \frac{0.4879}{z-2.012} - \frac{0.626}{z-1.626} \right\} \\
 y_2 &= \frac{1}{1-b} \left\{ \frac{b(r_3-1)}{z-r_3} - \frac{r_1-1}{z-r_1} \right\} \\
 &= 1.441 \left\{ \frac{0.3726}{z-2.217} - \frac{0.626}{z-1.626} \right\}
 \end{aligned}$$

As a test, several values of z are assumed, and when these are introduced to the above equations, we obtain:

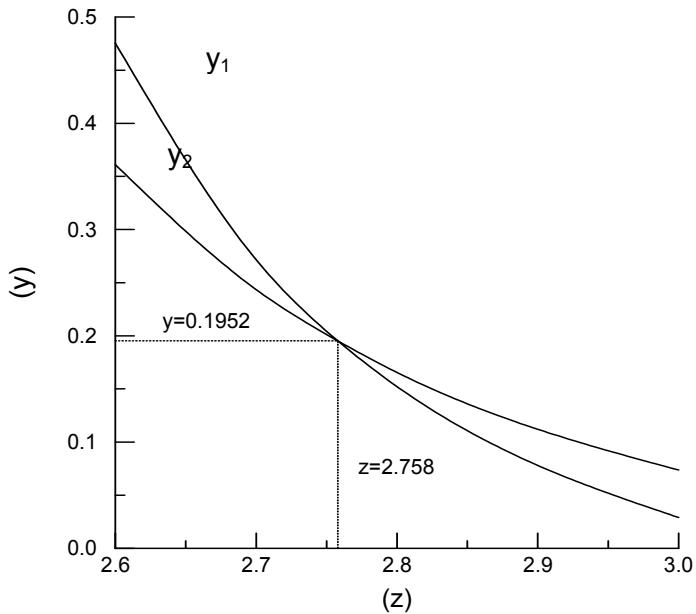


Figure 3. A graphical calculation of the y and z values.

z	y_1	y_2
2.60	0.3611	0.4755
2.70	0.2435	0.2716
2.80	0.1655	0.1522
2.90	0.1120	0.0780
3.00	0.0736	0.0290

From these values of y_1 and y_2 the graph shown in Figure 3 is obtained.

The point of intersection of the curves is at $z = 2.758$, $y = 0.1952$

From these values:

$$x = yz = 0.5384$$

From equation 26:

$$F(r) = 1 + \frac{r-1}{x - ry}$$

Introducing each value, we obtain:

$$F(r_1) = 3.833$$

$$F(r_2) = 7.946$$

$$F(r_3) = 12.503$$

And

$$2.303 \frac{\lambda_D}{c_2} = 2.303 \times \frac{0.590 \times 10^{-4}}{1.4387} \\ = 0.9445 \times 10^{-4}$$

From equation 22:

$$T = \frac{1}{\frac{1}{\tau_o} - 2.303 \frac{\lambda_D}{c_2} \log F(r)}$$

Introducing values for $1/\tau_{o_1}$, $1/\tau_{o_2}$, $1/\tau_{o_3}$ and corresponding values for $F(r_1)$, $F(r_2)$, and $F(r_3)$, we have:

$$\text{from } \tau_{o_1}: T = 3,159 \text{ K}$$

$$\text{from } \tau_{o_2}: T = 3,159 \text{ K}$$

$$\text{from } \tau_{o_3}: T = 3,159 \text{ K}$$

The three data perfectly coincide with each other and show there is no error in the calculations. Namely, the temperature $T = 3,159 \text{ K}$ is the answer.

Example 2. Barium Nitrate Composition

Composition:	Barium nitrate (for industry use)	60%
	Magnesium (smaller than 149μ)	30%
	Shellac	10%

Sample cartridge: The same as in Example 1.

Loading density : 1.42 g/cm³

Burning velocity: 3.25 mm/sec

Position of the temperature measurement:

The same as in Example 1.

Measurement:

The relationship of τ_o to r from photographs is:

$$\tau_{o_1} = 2,690 \text{ K} \cdots r_1 = 1.264$$

$$\tau_{o_2} = 2,595 \text{ K} \cdots r_2 = 1.364$$

$$\tau_{o_3} = 2,380 \text{ K} \cdots r_2 = 1.669$$

Calculation:

$$1/\tau_{o_1} = 0.0003717$$

$$1/\tau_{o_2} = 0.0003854$$

$$1/\tau_{o_3} = 0.0004202$$

$$a = 0.7160, b = 0.3062$$

$$y_1 = 3.521 \left\{ \frac{0.261}{z - 1.364} - \frac{0.264}{z - 1.264} \right\}$$

$$y_2 = 1.441 \left\{ \frac{0.205}{z - 1.669} - \frac{0.264}{z - 1.264} \right\}$$

The relationship of z to y :

z	y_1	y_2
2.1	0.1373	0.2304
2.2	0.1063	0.1499
2.3	0.0842	0.1010
2.4	0.0690	0.0693
2.5	0.0567	0.0476
2.6	0.0472	0.0324

Making a graph of r vs. y , the values of the intersection point are:

$$z = 2.402, y = 0.0687$$

From these:

$$x = yz = 0.1650$$

Introducing the values of x , y and r into the equation for $F(r)$, we have:

$$F(r_1) = 4,376$$

$$F(r_2) = 6,105$$

$$F(r_3) = 14,300$$

Introducing these into the temperature equation, we have:

$$\text{from } \tau_{o_1}: T = 3,214 \text{ K}$$

$$\text{from } \tau_{o_2}: T = 3,213 \text{ K}$$

$$\text{from } \tau_{o_3}: T = 3,214 \text{ K}$$

The three values coincide with each other and show there is no error in the calculation. And $T = 3214 \text{ K}$ is the flame temperature for this example.

VII. Conclusion

The above descriptions are concluded as follows:

- (1) A general theoretical equation was developed that relates the ratios of the spectral light intensities of the resonance lines to that of neighboring positions under the assumption that Kirchhoff's law is applicable even when the flame contains small solid or liquid particles.
- (2) When the density of the solid or liquid particles is too large, the line-reversal method is not useful for measuring flame temperatures. However, in other cases, as long as the brightness of the standard light can be compared to that of the flame, the line-reversal method is useful for measuring flame temperatures. In this case the solid or liquid particles have no influence on the measurement.
- (3) Applying the general theoretical equation, the author planned to measure flame temperatures even when they were higher than those of the standard light.

Acknowledgment

The author would like to acknowledge the help of Dr. Ryohei Ishida at the Institute of Industry, Tokyo, who kindly introduced the author to the line-reversal method.

Literature Cited

- 1) Ryohei Ishida, *Data of Chemical Industries*, Vol. 25 (1957) p 213; Tetsuro Asaba, *Journal of the Explosives Society*, Vol. 18 (1957) p 333.
- 2) Ryohei Ishida, *The Report of the Institute of Industry*, Tokyo, Vol. 51 (1956) p 333; Henning, Tingwaldt. *Z. für Phys.*, Vol. 48 (1928) p 805.
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Part II. Temperature Measurement of Flames by Means of the Line-Reversal Method

ABSTRACT

Using the theory developed in Part I, flame temperatures for various fireworks compositions have been measured by means of line-reversal of the Na-D lines.

(1) For low flame temperature compositions:

Compositions that contain combustible organic materials (i.e., shellac, rosin, pine root pitch, etc.) are commonly used in ordinary fireworks.

The author prepared various combinations of components to see the influence of oxidizers, fuels, color agents, etc. Temperatures are measured by method 1 from Part I. The result shows that the highest temperature appears at the base of the flame. Generally potassium perchlorate gives higher temperatures than ammonium perchlorate. Potassium nitrate always gives lower temperatures than other oxidizers.

The highest temperature is obtained when the ratio of fuel to oxidizer (potassium perchlorate, ammonium perchlorate or potassium nitrate) is about 1:5. For this ratio, the maximum temperatures obtained are as follows:

Oxidizer	Temperature (K)
Ammonium perchlorate	2,480
Potassium perchlorate	2,520
Potassium nitrate	2,000

(2) For high flame temperature compositions:

Compositions that contain magnesium powder can create a very high flame temperature of more than 2,900 K. Temperatures were measured by method 2 from Part I. In this case the photographic method was applied to measure the intensity of spectral lines, and we obtained temperatures of 2,700–3,000 K, but the accuracy of these data are not as good because of the uncertainties of the photographic method due to the instability of the flame.

I. Introduction

In Part I the author tried to develop theoretically the line-reversal method in preparation for the flame temperature measurement. Although the ordinary, colored-fireworks flame contains solid or liquid particles, it was shown that even in such cases the line-reversal method is adaptable.

Moreover, a plan for the measurement of flame temperatures that are higher than the standard light, using the line-reversal method with Na-D lines was described.

In this paper the practical measurements concerning both cases under the theoretical consideration described in the Part I are reported.

II. Selection of the Standard Light and Its Calibration

For the standard light, which is used for temperature measurement, it is desirable to use a bulb that has a ribbon filament with a small flat surface. However, such a bulb was not available. Therefore, the author used a commercially available ‘Spot Light’ based on the recommendation of Dr. Ishida.^[6] The bulb had a power of 100 V, 300 W with a six-coiled filament as shown in Photo 1.

The brightness of the light was the highest at the two center coils, and the lowest at the outside coils. When carefully observing one of the coils, the brightness of the inside surface is higher than that of the outside. Namely, the radiated light beams repeatedly reflected each other inside of the coil as if it were in a tube. Therefore, this phenomenon resembles black body radiation and shows that the bulb can measure higher temperatures than the ordinary flat filament generally used.

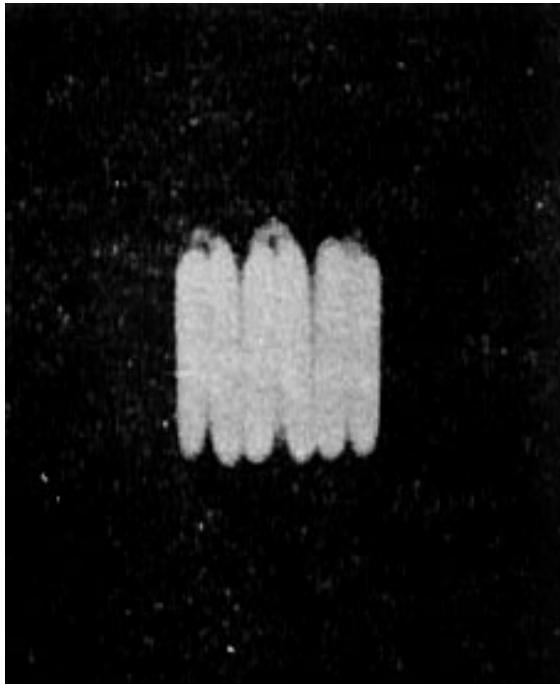


Photo 1. The light from of the standard light.

2.1 The Radiation Pyrometer and Its Calibration

The radiation pyrometer was homemade using an objective lens of 55 mm in diameter with a 110 mm focal length, an ocular lens of 10 mm in diameter with a focal length of 21 mm, and a bulb of 3.5 V. As the filter, a red glass disc wR2 for photographic use was placed in front of the ocular lens assuming that the distance from the object did not affect the data measurements.^[1] The permeability coefficients of the glass disc from the manufacturer's instructions follows:

The Permeability Coefficients $\rho(\lambda)$ of Red Glass wR2.

λ (Å)	$\rho(\lambda)$	λ (Å)	$\rho(\lambda)$
5,800	0.000	6,200	0.835
5,850	0.015	6,250	0.858
5,900	0.050	6,300	0.875
5,950	0.100	6,350	0.888
6,000	0.250	6,400	0.895
6,050	0.500	6,450	0.897
6,150	0.710	6,500	0.900
6,150	0.800	6,550	0.900
		>6,600	0.900

In combination with these and the curve of the international eye sensitivity of the brightness accommodation^[2] and following Wien's equation:

$$E(\lambda, \tau) = c_1 \lambda^{-5} e^{-\frac{c_2}{\lambda \tau}} \quad (1)$$

$$c_1 = 11.906 \times 10^{-6} \text{ erg} \cdot \text{cm}^2 \cdot \text{sec}^{-1}$$

$$c_2 = 1.4387 \text{ cm} \cdot \text{deg}$$

the effective wavelength λ_e for black body temperatures τ were calculated^[3] as follows:

τ (K)	λ_e (Å)
1,273	6,316
2,273	6,259
3,273	6,242
4,273	6,233

For the standard temperature calibration for brightness accommodation, the author used a porcelain electric furnace in place of the black body furnace. The dimensions of the electric furnace were as follows: the internal space was 75 mm in diameter by 115 mm deep (cylindrical in shape); the thickness of the warm wall and bottom was 85 mm. A thermocouple of platinum-rhodium was inserted into the internal space such that it did not touch the inside of the furnace. There was a porcelain lid, which had a 14 mm diameter hole, through which the radiant rays could exit the furnace. While raising the temperature of the furnace, the temperature in the radiant space was not uniform because the bare wire of the electric heater was heated

higher than the wall. Therefore the author raised the temperature to 1200 °C and then switched it off. The calibration of the pyrometer was conducted during the cooling time.

The calibration of the pyrometer was carried out as follows: The small hole was observed through the pyrometer. The brightness of its filament was adjusted so that it coincided with the brightness of the small hole. The electric current of the pyrometer bulb, i mA, and the temperature, denoted by the thermocouple, t °C, was read. These data were recorded and plotted on a graph to obtain an average curve. The largest deviation from the average was 26 °C at 170 mA (Table 1).

Table 1. Calibration Data for Pyrometer.

i mA	160	162	164	166	168	170	172
t °C	712	779	838	892	944	995	1,043

There may be a definite error accompanied with this calibration method. It is thought that the difference between the calibration of this electric furnace and that of the black body furnace is as follows: the radiation loss from the electric furnace is greater than that of black body furnace. However, the thermocouple did not contact the interior surface. If air convection is ignored, the temperatures shown by the thermocouple coincide with that of the temperatures of the black body. To see if the radiation equilibrium is good or not, it was decided to place some small solid material in the electric furnace. When one cannot distinguish this material from the wall of the furnace through the small hole, the radiation is in the black body condition. When calibrating, the brightness of the inner surface and the nichrome wire could not be distinguished.

2.2 Enlargement of the Scale of the Pyrometer

The maximum temperature of the scale obtained from the above calibration was 1,100 °C. For the following use, it must be extended to 1,500 °C. As a base, the values of 170 mA and 995 °C (1,268 K) were used (see Table 1). This is a point near the gold point (1,063 K) and may have the most reliable accuracy for the thermocouple. Therefore, at this point the calibration curve will have high accuracy. The extension method was to use a fan-shaped rotating sector with a direct current bulb and an alternating current bulb.^[4] The results were as follows in Table 2.

Table 2. Extension of the Calibrated Scale.

i mA	170	180	190	200
t °C	1,268	1,470	1,622	1,776

The maximum deviation between the average line and measurement point is 50 °C at 195 mA. There was no difference between the data using direct current and alternating current.

2.3. Calibration of the Standard Light

On the measurement of flame temperatures, the brightness of the image (L_2) at position (F) is the base. The beams come from the standard light (L_1) through the lens (c_1) (see Figure 2 on page 21). Therefore the calibration was carried out by using lens c_1 in the arrangement of measurement taking the distance 1 m from the eye glass of the pyrometer to the position of the image (L_2). With this distance, the deviations, which are caused by the light beam path, are more constant. (The calibration of the pyrometer was carried out in the same way.) To minimize the influence of the spherical aberration of lens c_1 , the distance should be greater. However, the distance should be less when one hopes to regulate the brightness of the standard bulb for the measurement of smaller deviations.

The brightness of the standard light of the pyrometer was not uniform according to the type of the filament because it was a coil type as was that of the standard light used for the line-

reversal measurement process. Therefore, the maximum brightness of the coil was used.

A fan-shaped rotating sector with two blades (25 rps) was placed directly behind the image position to decrease the light intensity, and the scale of the pyrometer was set to 190 mA (1,622 K) or 200 mA (1,776 K). The openings of the fan angle, φ , were $72^\circ, 44^\circ, 24^\circ, 8^\circ, 5^\circ, 3^\circ$, and 2° . Then the fan was rotated. The brightness of the standard light was adjusted so that it would coincide with that of the filament. At that point, the current and voltage of the standard lamp were read. There was no difference between calibrations in several trials. Therefore, for calibrations, the values of the voltages were used because the voltmeter had a finer scale than the ammeter.

The black body temperatures were calculated using the following formula:^[4]

$$\log \frac{360}{\varphi} = 0.4343 \frac{c_2}{\lambda_e} \left(\frac{1}{\tau_o} - \frac{1}{\tau} \right) \quad (2)$$

where τ_o is the base temperature of the pyrometer, and τ is the black body temperature of the standard light. For the value of λ_e , the author used 6,290 Å, which corresponds to the value of a rough estimate for an anticipated average of the temperatures τ_o and τ . A deviation of about 10 Å does not seriously affect the calculation of the value of τ .

The calibration was carried out three times: before, during and after the measurement. The effect of the first calibration showed the highest temperatures; that of the second, the lowest; and that of the third, the middle at every reading of the current meter. This may be caused by stabilizing the filament of the standard light during use (Figure 1).^[3]

For reference, Dr. Ishida's calibration curve, using a spot light as the standard light, is shown.^[6] The bulb used was different from the author's, and it is difficult to compare the effects with those of this paper; however, the inclination of the curve resembles well the result of this calibration.

2.4. Correction of the Calibration Data Considering Wavelength

Considering the results of calculation from equation 2, a value of wavelength $\lambda_e = 6,290$ Å at 1,500 K for the calibration of the standard light was used. However, for the line-reversal method, the Na-D lines, 5,896 and 5,890 Å were used. The tungsten filament is not a gray body, but the emissivity coefficient depends upon the wavelength of the light used. Therefore, the calibration curve with λ_e must be corrected as it was for the curve with λ_e .

The true temperature of the filament is denoted by T , corresponding to black body temperatures τ_e and τ_D , for wavelengths λ_e and λ_D , and the emissivities by $E(\lambda_e, T)$ and $E(\lambda_D, T)$. Here the answer required is the difference between the values of black body temperatures at λ_e and λ_D at the position of the image of the flame. The glass of the bulb and its reflection has an influence on the value. The relations between these items are shown as follows:

$$E(\lambda_e, \tau_e) = g(\lambda_e) \varepsilon(\lambda_e, T) E(\lambda_e, T) \quad (3)$$

$$E(\lambda_D, \tau_D) = g(\lambda_D) \varepsilon(\lambda_D, T) E(\lambda_D, T) \quad (4)$$

where E denotes the intensity of the sample thermal radiation, g the permeability of the bulb glass multiplied by that of the lens, ε the emissivity coefficient for the black body, E the emission intensity of the black body. When one introduces these relations into Wien's equation 1 we have:

$$\frac{1}{\tau_e} = \frac{1}{T} - 2.303 \frac{\lambda_e}{c_2} \log \varepsilon(\lambda_e, T) g(\lambda_e) \quad (5)$$

$$\frac{1}{\tau_D} = \frac{1}{T} - 2.303 \frac{\lambda_D}{c_2} \log \varepsilon(\lambda_D, T) g(\lambda_D) \quad (6)$$

The reflection coefficient of glass is shown as follows, when the beam lines enter the glass perpendicular to the surface, we have, for one surface:

$$R = \left\{ \frac{n(\lambda) - 1}{n(\lambda) + 1} \right\}^2 \quad (7)$$

where $n(\lambda)$ shows the refractive index of the glass to air as a function of the wavelength λ . In

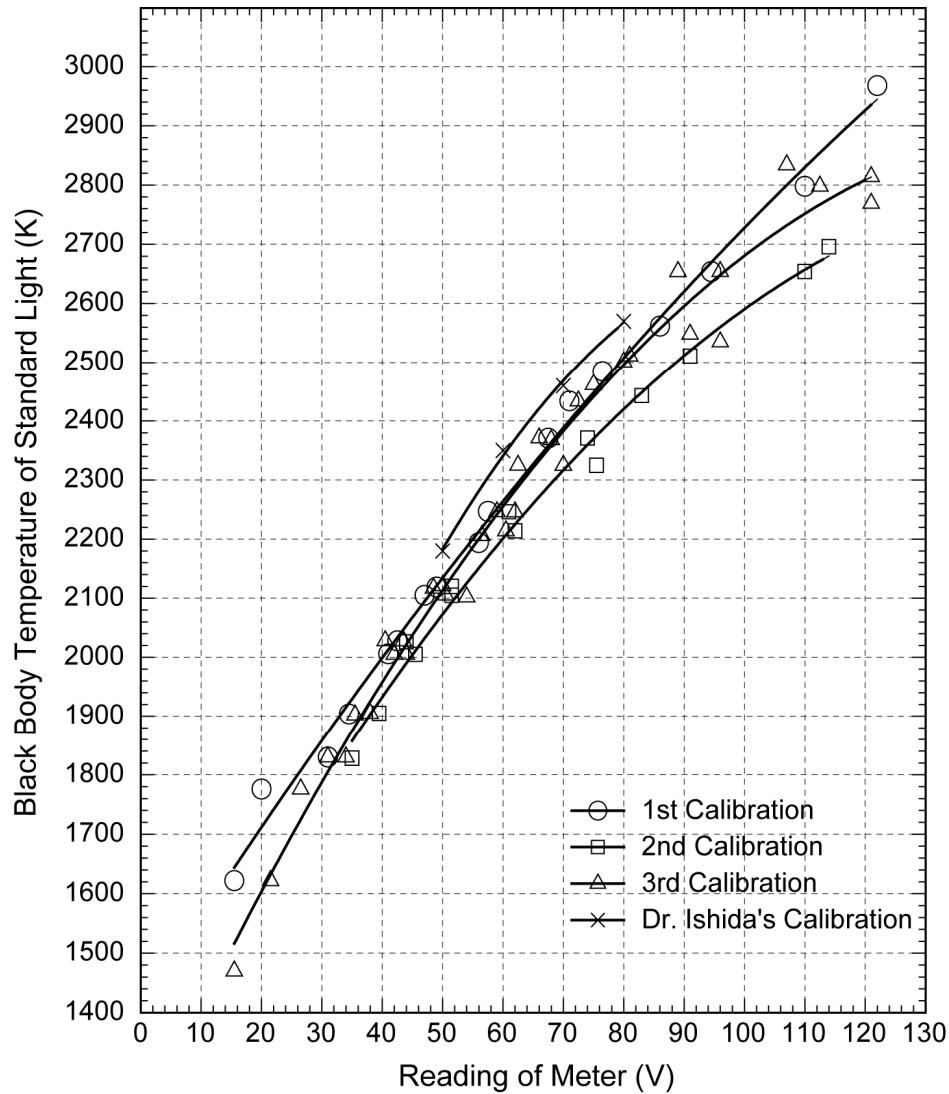


Figure 1. Calibration curves of the standard light.

this case $\lambda_e = 6,290 \text{ \AA}$ and $\lambda_D = 5,890 \text{ \AA}$, and the difference between the two is negligible, so one can use the value $n = 1.52$. Introducing this value to equation 7 we have $R = 0.043$. Therefore, the permeability of one side surface of the glass is calculated as 0.957. There are four surfaces in the beam path, two at L_1 and two at c_1 (i.e., in total 4). Therefore the total permeability is:

$$g(\lambda_e) \doteq g(\lambda_D) \doteq 0.957^4 = 0.839$$

Therefore, we obtain equations 8 and 9 from equations 5 and 6:

$$\frac{1}{\tau_e} = \frac{1}{T} - 0.00009721 \times \log 0.839 \cdot \varepsilon(\lambda_e, T) \quad (8)$$

$$\frac{1}{\tau_D} = \frac{1}{T} - 0.00009433 \times \log 0.839 \cdot \varepsilon(\lambda_D, T) \quad (9)$$

The values of the emissivity coefficient of the ribbon type tungsten filament are shown in Table 3.^[9]

Table 3. The Emissivity Coefficients $\varepsilon(\lambda, T)$ for the True Temperatures T of the Ribbon Type Tungsten Filament.

($\lambda_e = 6,290 \text{ \AA}$, $\lambda_D = 5,890 \text{ \AA}$)

T (K)	$\varepsilon(\lambda_D, T)$	$\varepsilon(\lambda_e, T)$
1,600	0.452	0.457
1,800	0.449	0.453
2,000	0.445	0.450
2,200	0.441	0.446
2,400	0.437	0.443
2,600	0.434	0.439
2,800	0.431	0.436

Introducing these values into equations 8 and 9 we have the values of τ_e , τ_D and the differences $\tau_D - \tau_e$ in Table 4.

Table 4. Black Body Temperatures τ_e, τ_D and $\tau_D - \tau_e$ for the True Temperatures T .^[7]

T (K)	τ_D (K)	τ_e (K)	$\tau_D - \tau_e$
1,600	1,502	1,503	-1
1,800	1,676	1,677	-1
2,000	1,846	1,848	-2
2,200	2,014	2,016	-2
2,400	2,179	2,181	-3
2,600	2,340	2,343	-3
2,800	2,500	2,503	-3

According to Table 4, the calibration curve is usable without correction because the values of $\tau_D - \tau_e$ lie in the range of experimental error. (In this experiment the filament of the standard light was of the coiled type; therefore, the measured temperatures may be nearer the true temperatures and the correction value may be smaller than the values in Table 4.)

III. Spectroscope, Installation of Devices and Measurement Operations

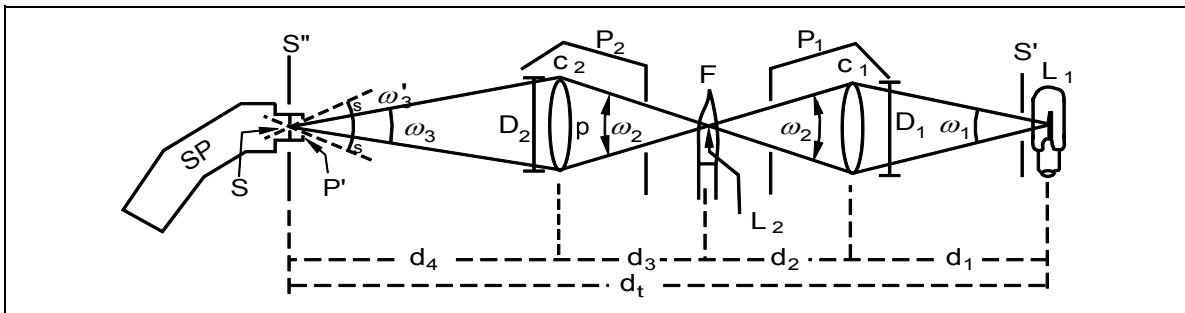
3.1. Dispersion of the Spectroscope

When measuring flame temperatures by means of method 1,^[8] which is based on naked eye observation, the spectroscope should possibly be brighter to minimize the errors, especially if the flame temperatures are low. Therefore, the spectroscope's dispersion (spread of the light beam) should not be very large. When comparing the blackening densities of the dry plate by means of method 2,^[9] a larger dispersion is better for good accuracy, even if the spectroscope is somewhat dark. However, the exposure time should not be very long to avoid a change in state of the flame with time. The dispersions used in the experiment were 60 Å/mm (with three water prisms) for method 1 and 6 Å/mm (with five water prisms) for method 2. The construction of the spectroscope is explained in Part III. (Also see Figure 1a in Part I.)

3.2 Light Path for Measurement

Figure 2 shows the light path for measurement.

The standard light for measurement is not L_1 , but L_2 . Namely, when one sees the light source from p in the direction F and at the solid angle ω_2 , L_2 becomes a light source. Consider when using a light beam of the wavelength λ_i , the energies of the light beams that are emitted from the first light source L_1 in the unit area, in the unit solid angle, and in the unit time is denoted as $E(\lambda_i, \tau_1)$. The total radiation energy per unit time is $E(\lambda_i, \tau_1) \omega_1 s_1$, where s_1 is the total radiation area of the light source L_1 , and the emission surface is a uniform flat surface perpendicular to the axis of the light beam path. The emission surface produces the radiation uniformly (Assumption 1), and the directions of the light beams are uniform in the solid angle ω_1 (Assumption 2). As stated in 2.4, the light beams which pass through the lens c_1 are partially reflected at both sides of the lens. The absorption



L_1	First standard light	p	Center of second collection lens c_2
L_2	Second standard light (the image of L_1)	P'	Protection glass for slit.
F	Flame	P_1, P_2	Lens Protector
c_1	First collection lens	ω	Angles of image
c_2	Second collection lens	s	Light inlet angle
S	Slit	d	Distance between equipment
S'	Shading of random light	D_1, D_2	Diameter of lenses
S''	Screen for making image of the flame	SP	Spectroscope

Figure 2. Installation of the devices for temperature measurement.

of the lens glass is negligible when using visible rays.

When light energy is emitted from the second light source L_2 in the unit solid angle and unit time having a wavelength λ_i , denoted as $E(\lambda_i, \tau_2)$, the total energy is under the same assumption in the unit time is $E(\lambda_i, \tau_2) \omega_2 s_2$, where s_2 is the total radiation area of the light source L_2 . Expressing the reflecting coefficient with $R_{s_1}(\lambda_i)$, the relation of energy is

$$E(\lambda_i, \tau_2) \omega_2 s_2 = \{1 - R_{s_1}(\lambda_i)\} E(\lambda_i, \tau_1) \omega_1 s_1$$

Accordingly, we have:

$$E(\lambda_i, \tau_2) = \frac{\omega_1 s_1}{\omega_2 s_2} \{1 - R_{s_1}(\lambda_i)\} E(\lambda_i, \tau_1) \quad (10)$$

From the relation of optical geometry, we have:

$$\omega_1 s_1 = \omega_2 s_2 \quad (11)$$

Therefore

$$E(\lambda_i, \tau_2) = \{1 - R_{s_1}(\lambda_i)\} E(\lambda_i, \tau_1) \quad (12)$$

Namely, the brilliancy of the light source L_2 is less than that of L_1 based on the quantity of re-

flection by the lens c_1 . The brilliancy of the light source is independent of the size of the lens, and the distance from the standard light L_1 on the image L_2 to the lens. Concerning the lens c_2 the same relation as above is adaptable as:

$$E(\lambda_i, \tau_3) = \{1 - R_{s_2}(\lambda_i)\} E(\lambda_i, \tau_2) \quad (13)$$

Therefore, the brilliancy of the second light source at the slit decreases due to the reflections of the lens c_2 and has no influence on other conditions.

Therefore to decide the dimension of the lenses, their focal lengths, and the distance from the source of the light to the image, the following conditions should be considered.

(1) To meet assumption 1, one should use the middle part of a light source, which has a wider surface.

(2) To meet assumption 2, the diameter of each lens c_1 and c_2 should not be very large for the distance d_1 or d_2 . Therefore the focal length of lens c_1 or c_2 should be larger.

(3) To obtain the highest accuracy, the spectroscope should be very bright. Therefore, the distances d_2 and d_3 , the focal length, and the

diameter of the lenses were determined as follows:

Lens c_1	possibly a large diameter, possibly smaller to enlarge the angle ω_1
Distance d_1	
Lens c_2	the angle ω_3 coincides with the angle of visible range of the spectroscope, and is perfectly covered by the solid angle ω_2 .

(4) The size of the image of light source L_2 on the slit (on the screen S'') should, if possible, be large, and the part of the image of uniform brightness should be aimed at the slit S . In the case of the coiled filament, the most brilliant part should be aimed at the slit.

(5) The chromatic aberration of the lenses does not interfere with the measurement.

(6) Spherical aberration causes a dispersion of the image, decreases its brightness, and the axis of the light path does not coincide with that of the pyrometer. It increases errors during calibration. Therefore, the calibration should be carried out with a pyrometer having a small object lens at a more distant position in the optical axis. However, such a method decreases the accuracy of the calibration.

(7) The flame has a thickness; therefore, the measured area is shown as in Figure 3. The value obtained is an average of that portion within the solid angle ω_2 . Therefore, to obtain accurate values, the solid angle ω_2 should be small.

In the above conditions, some contradict each other; however, they are selected based on the purpose of the experiment, the availability of materials, the location of the experiment, the extent of danger, the protection of devices, etc.

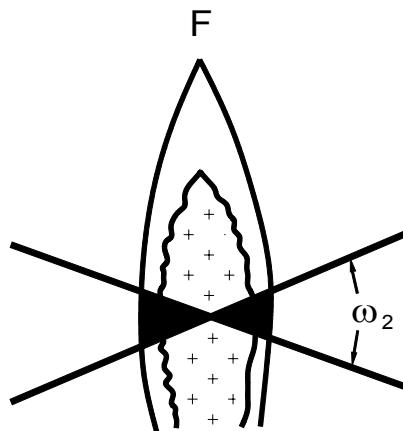


Figure 3. The influences of the thickness of the flame.

3.3 Installation of Devices and Operation

The most important point was how to avoid wind and smoke.

The standard light L_1 , lens c_1 , and lens c_2 were arranged on a long wooden frame. A burning chamber made of tin plates, which protected the flame from wind, was set between c_1 and c_2 . The frame of these instruments was set outdoors so that the wind and smoke did not interfere with the measurement. The light beams from the burning sample and the standard light were fed indoors into the spectroscope through a small window in the measuring room. The sample holder was a tube that was attached to a solid stand, which could be adjusted so that the position of the burning surface of the sample moved up and down during the burning of the sample. A screen was set directly in front of the slit to see the image of the flame and to detect what part of the flame was introduced into the slit. A scale was marked on the screen to see the position of the sample flame. The distances were as follows: $d_1 = 575$ mm, $d_2 = 305$ mm, $d_3 = 310$ mm, $d_4 = 450$ mm. The focal length and the diameter of the lenses were: $f_1 = 195$ mm, $f_2 = 174$ mm, $D_1 = 81$ mm, $D_2 = 74$ mm.

The outdoor operations were as follows: Adjust the sample holder to produce the image of the standard light in the middle of the flame. Adjust the position of the wooden frame so that the maximum intensity of the filament image

from the standard light passed through the slit. During the measurement the position of the image of the filament is somewhat removed and the position is often moved by oscillation. Therefore, the position was checked just before each measurement. The level of the sample was regulated by the handle of the holder so that the temperature of the aimed point of the flame passed through the slit. The length of the tube became shorter and shorter, and attention to this was especially important. On the burning of the samples, protection of the slit and lenses was very important.

IV. Preparation of Samples

4.1 Chemicals

The details are described in Part III; however, the chemicals selected were of as high quality as possible from samples used for spectral analysis.

These were dried at 60–110 °C before mixing. However, a good quality magnesium powder was not available; so a commercial grade was used. It was analyzed as 75.72% Mg, 24.28% Al with no insoluble matter in the HCl solution.

4.2 Sample Compositions and the Specimens

The sample compositions were limited to those that were useful for the spectral analysis of the flames (Tables 6, 9, 10, 11, and 12).

Each mixture was loaded firmly by hand into a double wound brown paper tube.^[10] The dimensions of a completed sample specimen was 10 mm in diameter and 98 mm long. For ignition, a piece of black match was inserted and attached to the top by pasting with thin paper.

V. Temperature Measurement of Low Temperature Flames and Examination of the Results

5.1 The Condition of the Flames, Flame Temperature Data, and Measurement Errors

Examples of low temperature flames are shown in Photo 2. The flames were not as stable as those of a gas burner; however, they were fairly stable. The results are shown in Figures 4–9. The symbols used are:

Δ	loading density, g/cc
v	burn rate, mm/sec
ℓ	length of flame, cm
d	distance from the base to the measuring point of the flame, cm

To determine the temperature, calibration curve 3 was used (Figure 3). The measured data in Figures 4–9 are the average values of four

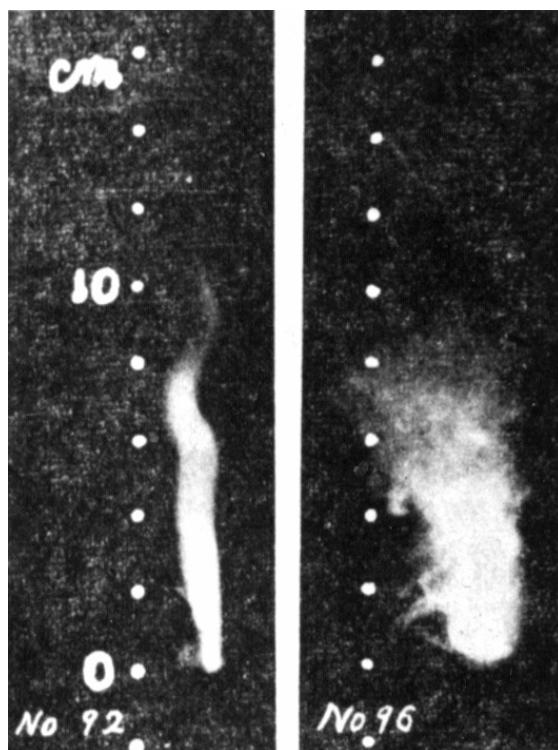


Photo 2. Flames from No. 92, ammonium perchlorate composition and No. 96, potassium perchlorate composition.

time trials at the center of flame.

The probability errors calculated with equation 14 are shown in Table 5.

$$r_T = 0.6745 \sqrt{\frac{\sum e^2}{n-1}} \quad (14)$$

Where r_T is the probability error for the measured values, e is the deviation of each value from the average, and n is the number of the values.

During the measurement, adjusting the brightness of the filament of the standard light was relatively easy. Therefore, errors come mainly from the instability of the flame. Table 5 shows that the position of the most stable points lie 2 cm from the flame base.

Table 5. Probability Errors of Measured Flame Temperature Data r_T (Low Temperature Flames)

τ (K) \ d (cm)	1.0	2.0	3.0	4.0
1,800–2,000	66.7°	28.7°	62.7°	92.9°
2,000–2,200	43.4°	27.1°	33.9°	61.0°
2,200–2,400	44.6°	34.1°	45.1°	36.3°
2,400–2,600	32.3°	25.5°	28.3°	30.9°
2,600–2,800	29.9°	32.5°	—	—

Note: K = Flame temperature in absolute units, Kelvin

d (cm) = distance from the base of the flame along the center line of the flame to the objective point.

5.2 Distribution of Temperatures in a Flame

Figures 4–9 show that temperatures along the center line of the flame were different based on the type of oxidizer, fuel, etc. Generally, temperatures were highest near the base of the flame and decreased along the length of the flame.

5.3 Influence of Oxidizer Type and Mixing Ratios

Flame temperatures were measured with compositions in Table 6. The results are shown in Figures 4 and 5.

Table 6. Sample Mixtures To Study the Effect of Oxidizers, Fuels and Mixing Ratios.

Composition (1)	%
Ammonium perchlorate	x
Shellac	y
Sodium oxalate	10

No.	$x\%$	$y\%$	$\Delta(g/cm^3)$	v (s)	ℓ (cm)
90	65	25	1.15	0.91	12–19
91	70	20	1.15	0.99	<13
92	75	15	1.15	1.07	10–12
93	80	10	1.17	0.93	7–9

Composition (2)	%
Potassium perchlorate	x
Shellac	y
Sodium oxalate	10

No.	$x\%$	$y\%$	$\Delta(g/cm^3)$	v (s)	ℓ (cm)
94	65	25	1.33	1.04	17–19
95	70	20	1.30	1.35	12–13
96	75	15	1.33	1.50	<9
97	80	10	1.30	1.30	6–8

Composition (3)	%
Potassium chlorate	x
Shellac	y
Sodium oxalate	10

No.	$x\%$	$y\%$	$\Delta(g/cm^3)$	v (s)	ℓ (cm)
98	65	25	1.14	2.46	24–26
99	70	20	1.13	2.34	<20
100	75	15	1.11	2.40	<12
101	80	10	1.17	1.86	5–8

Table 6. Sample Mixtures To Study the Effect of Oxidizers, Fuels and Mixing Ratios (Continued).

Composition (4)	%
Potassium nitrate	x
Shellac	y
Sodium oxalate	10

No.	x%	y%	$\Delta(g/cm^3)$	v (s)	$\ell(cm)$
191	65	25	1.29	1.16	—
192	70	20	1.35	1.20	13–14
193	75	15	1.43	2.00	4–8
194	80	10	1.43	—	—

Composition (5)	%
Barium nitrate	x
Shellac	y
Sodium oxalate	10

No.	x%	y%	$\Delta(g/cm^3)$	v (s)	$\ell(cm)$
198	65	25	1.05	1.37	12–13
199	70	20	1.11	1.26	9–12
200	75	15	1.09	1.37	9–10
201	80	10	1.18	1.60	7–9

The loading density was the highest with potassium perchlorate or potassium nitrate, the value was about 1.3 g/cc, and 1.1–1.2 g/cc with ammonium perchlorate and potassium chlorate. The burn rate was greatest for potassium chlorate and decreased in the order of potassium perchlorate, potassium nitrate, and ammonium perchlorate. However, the potassium nitrate composition burned with so much ash (It had to be viewed in a special way). Therefore, it may be difficult to compare with the others.

The maximum flame temperature was 2,518 K with potassium perchlorate and decreased in the order of ammonium perchlorate and potassium chlorate. With potassium nitrate the temperature was lowest, 2,000 K. This might explain the poor ability of color production with potassium nitrate. No relationship was found between flame temperature and oxygen balance.

The temperature gradation from the base of a flame was smallest with the potassium chlorate composition; and potassium nitrate compositions have the same tendency. Other compositions showed steeper gradation and showed a temperature decrease of 50–80 °C per 1 cm of flame length. Barium chlorate compositions showed almost the same characteristics as the potassium chlorate compositions.

The fuel/oxidizer ratio had a great influence on flame temperatures. When the fuel, shellac, was increased, the temperatures of the flame increased to the maximum when the ratio of fuel/oxidizer was 1:5, and the temperatures fell with decreasing ratios.

The relationship of the deficiency of oxygen in the flame and flame temperatures was unknown because the reaction mechanism in the flame was unknown. However, on the assumption of perfect oxidation of the fuels, the quantities of insufficient oxygen are calculated in Tables 7 and 8.

Table 7. Calculated Values of Sufficient or Deficient Oxygen Values for a 100 g Mixture of CO₂ Oxidation.

Composition	%
Oxidizer	x
Shellac	y
Sodium oxalate	10

Oxidizer	Oxidizer (%)			
	65	70	75	80
NH ₄ ClO ₄	-33.6	-20.7	-7.9	+4.9
KClO ₄	-25.6	-12.2	+1.3	+14.7
KClO ₃	-30.2	-17.1	-4.0	+9.1
KNO ₃	-29.9	-16.8	-3.7	+9.4
Ba(ClO ₃) ₂ ·H ₂ O	-36.3	-23.7	-11.0	+1.6

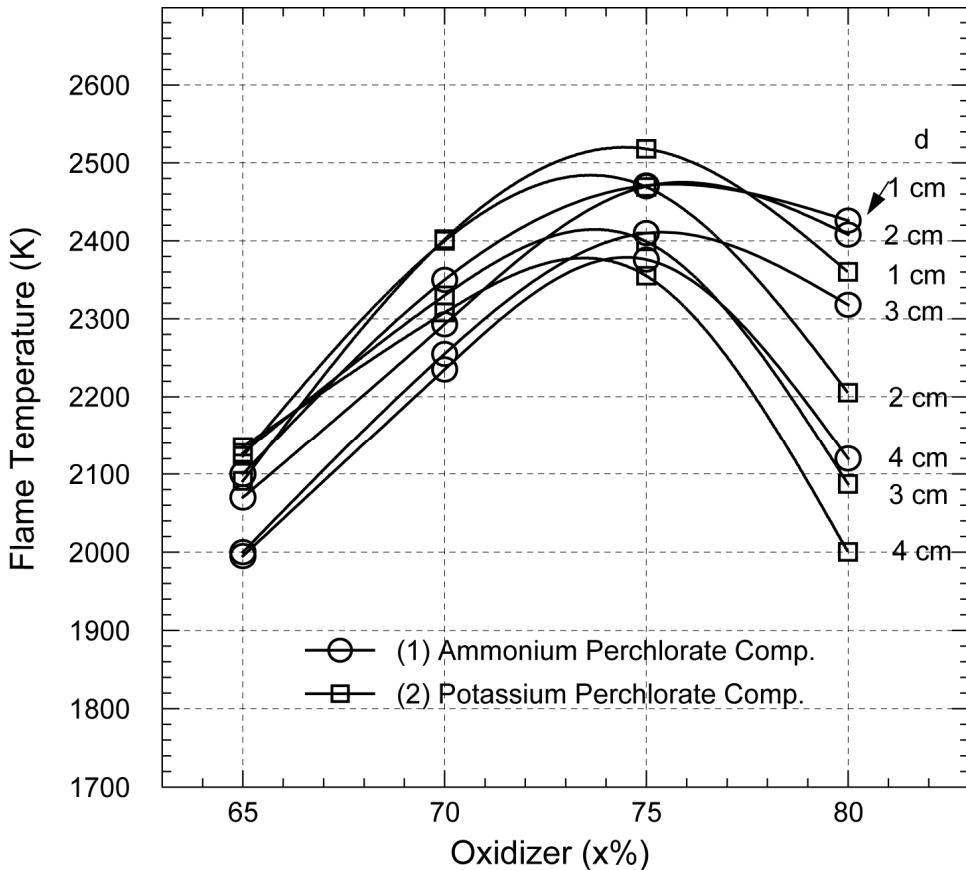


Figure 4. Flame temperatures: the effects of oxidizers, fuels and mixing ratios (I).

Table 8. Calculated Values of Sufficient or Deficient Oxygen Values for a 100 g Mixture of CO Oxidation.

Composition	%
Oxidizer	x
Shellac	y
Sodium oxalate	10

Oxidizer	Oxidizer (%)			
	65	70	75	80
NH_4Cl_4	-11.5	+3.1	+5.4	+13.8
KClO_4	-3.6	+5.5	+14.5	+23.5
KClO_3	-8.1	+0.6	+9.3	+14.9
KNO_3	-7.8	+0.9	+9.6	+18.3
$\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$	-14.2	-6.0	+2.2	+10.4

According to Tables 7 and 8, 75% oxidizer, which gave the highest flame temperature, showed slight oxygen deficiencies except for

potassium perchlorate when CO_2 oxidation took place. However, for CO oxidation, the quantity of oxygen was rich enough to react.

5.4 Influence of the Type of Fuel

Flame temperatures were measured using compositions in Table 9. Together with the results using compositions in Table 6, we see that the flame temperatures were different for the various types of fuel: shellac, colophony, pine root pitch, or wood meal. With ammonium perchlorate pine root pitch gave the highest temperatures, followed by shellac and colophony. However, with potassium perchlorate, pine root pitch gave higher temperatures than shellac. The 1 gram oxygen equivalent value of the fuels are: for colophony, 2.565 grams; for shellac, 2.261 grams; for pine root pitch, 2.376 grams; and for wood meal, 1.370 grams. However, this order does not coincide with the order of temperature values (Figure 6).

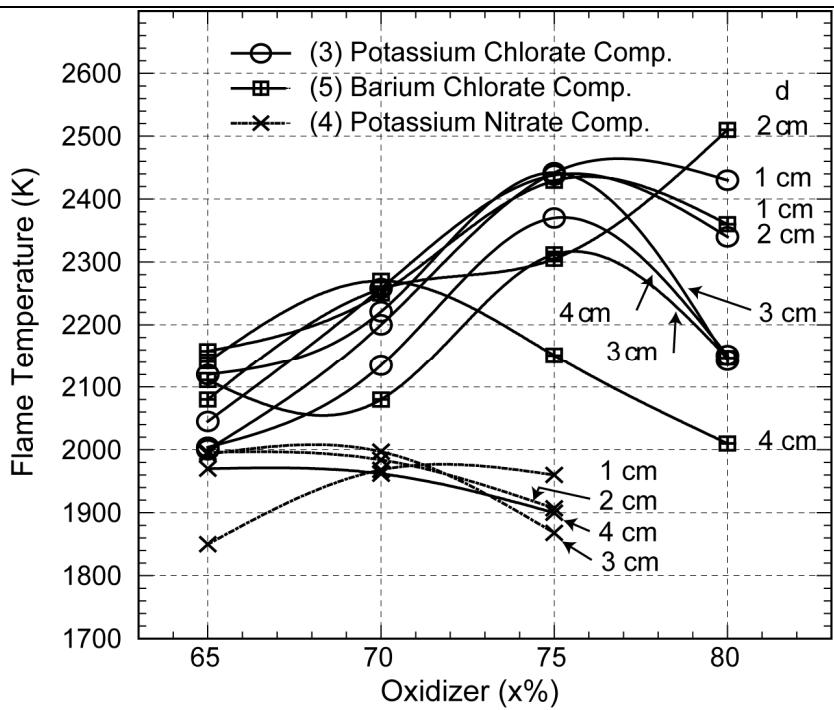


Figure 5. Flame temperatures: the effects of oxidizers, fuels and mixing ratios (2).

Table 9. Effect of Fuel Type.

Composition (6)		%
Ammonium perchlorate		75
Fuel		15
Sodium oxalate		10

No.	Fuel	$\Delta(g/cm^3)$	v (s)	ℓ (cm)
102	Colophony	1.06	0.66	6–9
103	Pine root pitch	1.13	1.98	16–21
104	Wood meal	0.96	0.86	<5

Composition (7)		%
Potassium perchlorate		75
Fuel		15
Sodium oxalate		10

No.	Fuel	$\Delta(g/cm^3)$	v (s)	ℓ (cm)
105	Colophony	—	1.07	10–12
106	Pine root pitch	1.33	3.00	10–12
107	Wood meal	1.26	1.34	3–5

Composition (8)		%
Potassium nitrate		75
Fuel		15
Sodium oxalate		10

No.	Fuel	$\Delta(g/cm^3)$	v (s)	ℓ (cm)
195	Colophony	0.99	—	no flame
196	Pine root pitch	1.13	2.56	—
197	Wood meal	0.95	—	did not burn

Composition (9)		%
Barium chlorate		75
Fuel		15
Sodium oxalate		10

No.	Fuel	$\Delta(g/cm^3)$	v (s)	ℓ (cm)
202	Colophony	1.38	half burnt	—
203	Pine root pitch	1.41	3.24	—
204	Wood meal	1.19	0.66	—

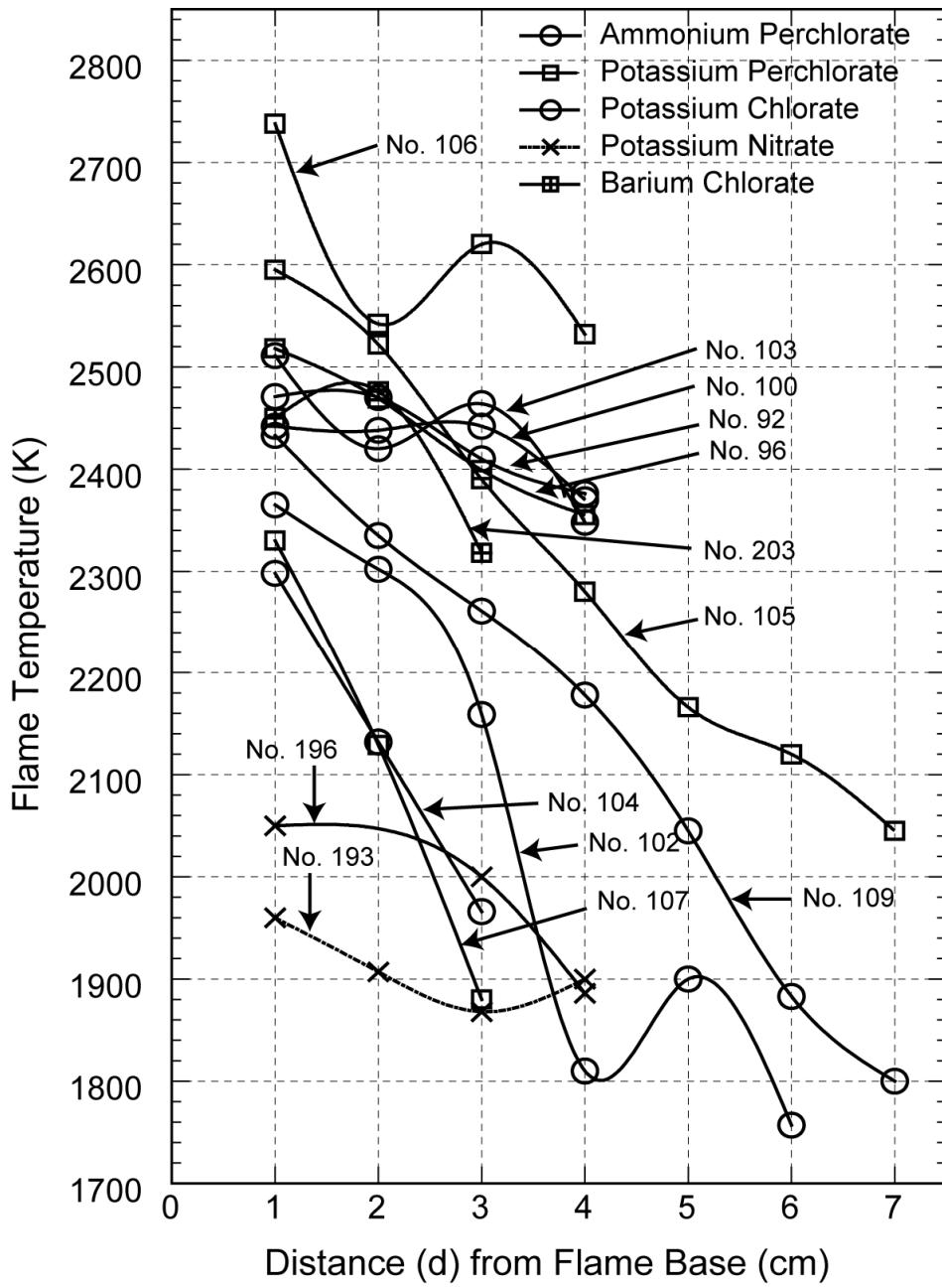


Figure 6. The effect of types of fuel with various oxidizers.

5.5 Effects of Various Color Agents

Flame temperatures were measured with compositions in Table 10 and the results are shown in Figures 7–9.

Table 10. Effects of Color Agents.

Composition (10)	%
Ammonium perchlorate	71
Shellac	14
Color agent	10
Sodium oxalate	5

No.	Color agent	$\Delta(\text{g}/\text{cm}^3)$	$v (\text{s})$	$\ell (\text{cm})$
108	Strontium carbonate	1.16	0.78	6–8
109	Strontium oxalate	1.13	0.79	8–10
110	Strontium chlorate	1.19	0.96	8–10
111	Strontium nitrate	1.19	1.07	9–11
112 ^{*1}	Sodium carbonate	1.13	0.94	5–8
113 ^{*1}	Sodium chloride	1.22	1.08	10–13
114 ^{*1}	Sodium bicarbonate	1.19	0.74	8–10
115	Barium carbonate	1.17	0.80	9–11
116	Barium oxalate	1.13	0.95	10–12
117	Barium chlorate	1.20	0.93	10–12
118	Barium nitrate	1.24	0.98	11–13
119	Basic copper carbonate	1.13	2.28	15–18
120	Copper oxalate	1.12	1.18	18–21
121	Copper sulfate with waters of hydration	1.19	1.00	14–21
122	Paris green	1.13	1.30	17–20
123	Copper arsenite	1.06	1.51	16–22
124	Copper powder 10%	1.19	2.56	17–20
125 ^{*2}	Copper powder 5%	1.21	2.16	16–20

Note *¹: This composition was a mixture of 75% ammonium perchlorate, 15% shellac, and 10% color agent.

*²: 5% copper powder means 95% in total ratios.

Table 10. Effects of Color Agents (Continued).

Composition (11)	%
Potassium perchlorate	71
Shellac	14
Color producing agent	10
Sodium oxalate	5

No.	Color agent	$\Delta(\text{g}/\text{cm}^3)$	$v (\text{s})$	$\ell (\text{cm})$
126	Strontium carbonate	1.28	1.37	9–10
127	Strontium oxalate	1.32	1.07	7–9
128	Strontium nitrate	1.33	1.63	4–6
169 ^{*1}	Sodium carbonate	1.41	1.13	8–10
170 ^{*1}	Sodium chlorate	1.43	1.14	4–6
171 ^{*1}	Sodium bicarbonate	1.41	0.96	9–11
137	Barium carbonate	1.35	1.35	8–10
138	Barium oxalate	1.33	1.32	9–11
139	Barium chloride	1.31	1.26	9–11
140	Barium nitrate	1.31	1.35	9–10
129	Paris green	1.31	1.92	6–9
130	Copper arsenite	1.31	2.00	8–10
131	Copper powder 10 %	1.28	1.76	12–15
132 ^{*2}	Copper powder 5 %	1.23	1.83	9–12
172	Basic copper carbonate	1.33	1.19	10–14
173	Copper oxalate	1.04	1.16	12–14
174	Copper sulfate with waters of hydration	1.31	1.67	3–5

Note : The symbols ^{*1} and ^{*2} are the same as above table.

Composition (12)	%
Ammonium perchlorate	x
Potassium perchlorate	y
Barium nitrate	z
Shellac	15
Sodium oxalate	10

No.	$x\%$	$y\%$	$z\%$	$\Delta(\text{g}/\text{cm}^3)$	$v (\text{s})$	$\ell (\text{cm})$
133	—	60	15	1.31	1.16	9–12
134	—	45	30	1.32	1.02	12
135	60	—	15	1.25	0.57	5–6
136	45	—	30	1.31	0.62	4–5

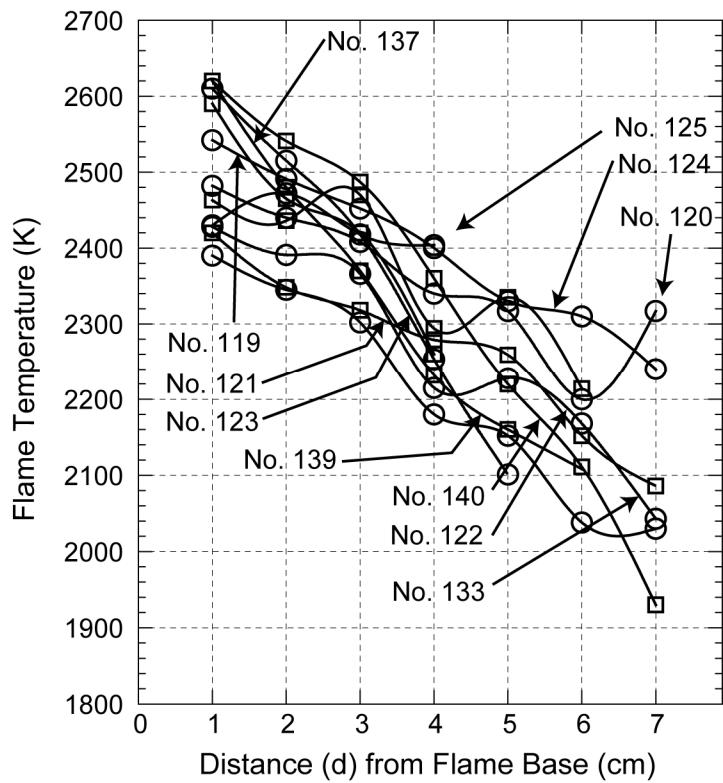
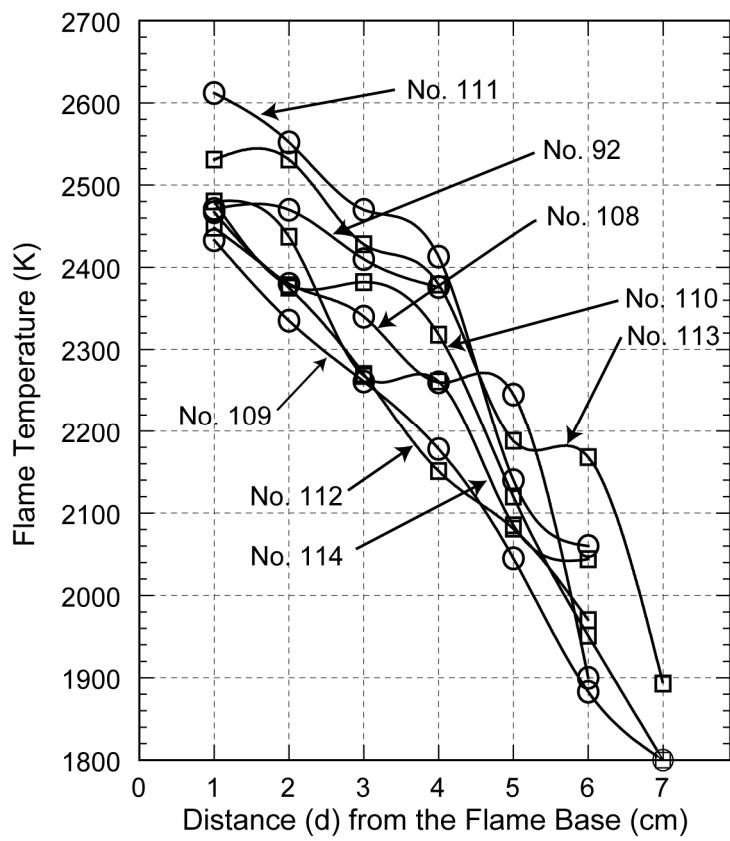


Figure 7. Flame temperatures with compositions of ammonium perchlorate and various fuels.

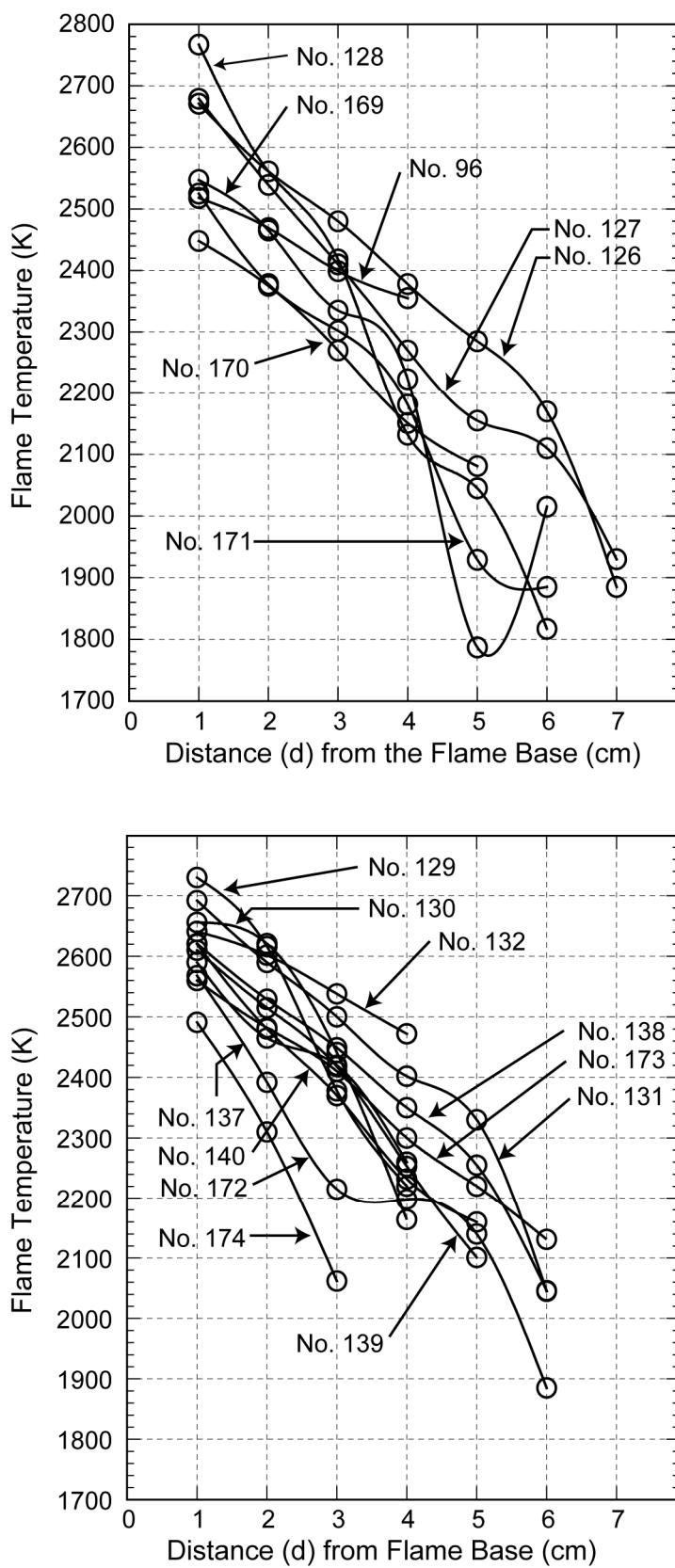


Figure 8. Flame temperatures with potassium perchlorate and various fuels.

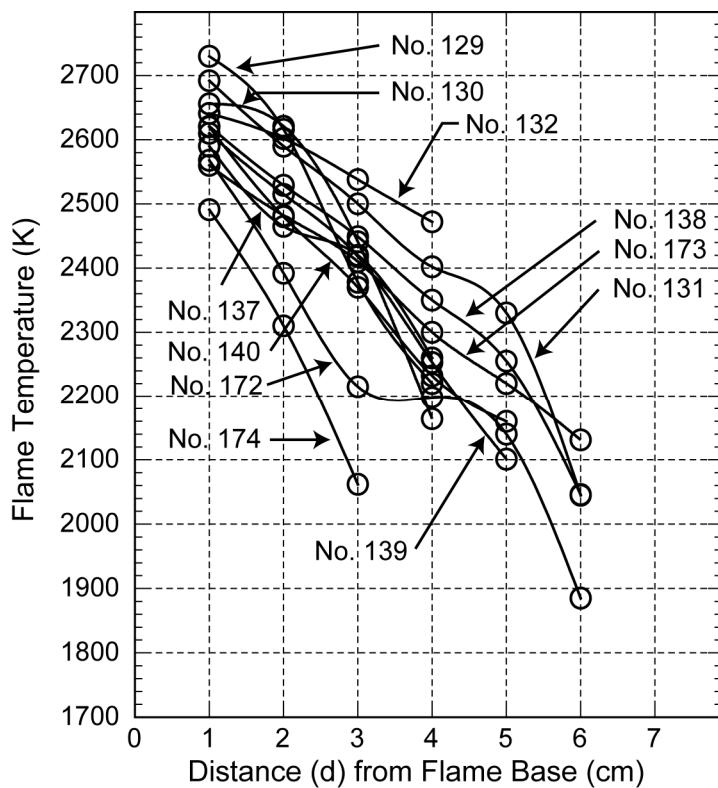


Figure 9. Flame temperatures with mixtures that contain potassium perchlorate, ammonium perchlorate and barium nitrate.

(1) Red color agents (strontium salts)

When using ammonium perchlorate as the oxidizer, strontium nitrate gave temperatures of 100–200 °C higher than other strontium salts. The other strontium salts: chloride, oxalate and carbonate did not show significant differences from each other. When using potassium perchlorate as the oxidizer, strontium nitrate gave higher temperatures than strontium carbonate at the base of each flame. However, in general, one could not find significant differences between the two.

Strontium carbonate produced slightly higher temperatures than strontium oxalate.

(2) Yellow color agents (sodium salts)

When using ammonium perchlorate, sodium chloride gave the highest temperatures of all, with sodium carbonate and sodium bicarbonate about the same. The difference between the chloride and the other sodium salts was about 100 °C.

When using potassium perchlorate as the oxidizer, the gradation of temperatures over the flame length were slightly smaller than with the other oxidizers.

(3) Green color agents (barium salts)

When using ammonium perchlorate, barium nitrate gave higher temperatures than the other oxidizers. The other barium salts, chloride, oxalate, and carbonate had about the same effect. The difference in temperatures between the effect of the nitrate and the others was about 100 °C.

When using potassium perchlorate, the temperature effects were almost the same for each color agent.

(4) Blue color agents (copper salts or copper powder)

Using either ammonium perchlorate or potassium perchlorate the temperature differences were considerable along the flame length among the color agents: 150 °C with ammonium perchlorate and 200 °C with potassium perchlorate. With both oxidizers, copper sulfate with waters of hydration gave the lowest temperatures and copper powder gave the highest. Other blue color agents did not show any special tendency with respect to the type of oxidizer. Paris green and copper arsenite gave lower temperatures with ammonium perchlorate than with potassium perchlorate. The case for basic copper carbonate was the opposite. Copper oxalate always gave higher temperatures.

(5) The effect of mixing ratios of barium nitrate and other oxidizers

This effect will be considered when making green flames (Figure 9). In general potassium perchlorate gave higher temperatures than ammonium perchlorate, and the effects of the mixing ratio of the composition also were larger with potassium perchlorate than with ammonium perchlorate. In both cases the smaller the quantity of barium nitrate, the lower the flame temperature.

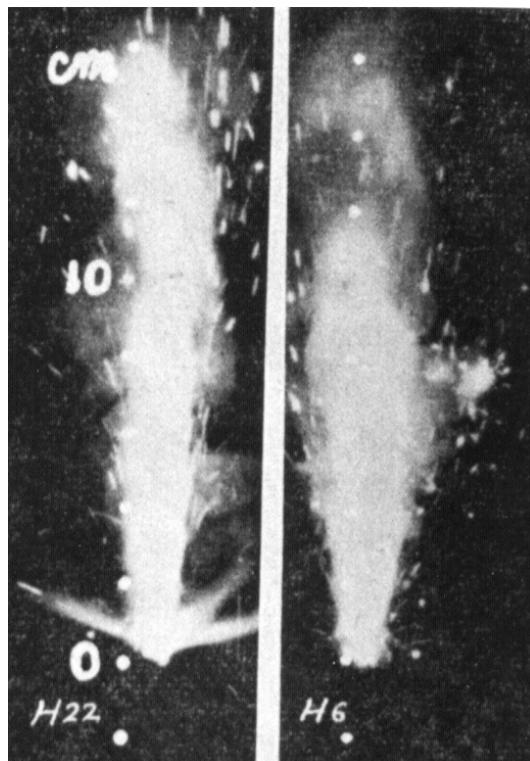


Photo 3. High temperature flames: H22, from an ammonium perchlorate composition and H6, from a potassium perchlorate composition.

VI. Measurements with High Temperature Flames and Discussion of the Results

6.1 Conditions of Flames and Method of Measurement

Examples of high temperature flames are shown in Photo 3. The temperature measuring point was 1 cm from the flame base where it was brightest.

The flame temperatures were measured by method 2 (see Part I). Namely, temperatures of the standard light were changed in four steps and at each step the Na-D lines and neighboring parts of the spectrum were photographed. It was necessary to prepare a characteristic curve of sensitivity of the dry plate that showed the relationship of exposure time and blackening density, from which one could know the relationship of the blackening density to light energy.

(Light energy is proportional to the exposure time on the dry plate.)

The characteristic curve of the dry plate was obtained as follows. Light beams were introduced into the spectroscope with a 0.4 mm wide slit and the dry plate was exposed for $2n$ seconds, where $n = 1, 2, 3, 4 \dots$. Then blackening densities for each image part of the Na-D lines and its neighbors were measured and recorded with the exposure time, and with the resulting curve of n vs. δ , where δ is the blackening density.

The blackening density of the image of the dry plate was obtained as follows. Light beams from the filament of a spot light bulb for photographic use were collected with a 0.4 mm wide slit on an image part of the dry plate, the beams which passed the slit were received by a selenium photometer. The light intensity was measured as the value I . Then a blackening density of no image was measured by the same device as the value I_o . Then the δ value of blackening density δ was obtained as follows:

$$\delta = \log_{10} \frac{I_o}{I} \quad (15)$$

For this method, photographs were used to measure the intensities of the inlet light beams. Small errors might accompany the data at the measurements. However, the errors might be larger than expected, because the stability of high temperature flames was lower than that of low temperature flames.

6.2 Data of the Measurement

The data are shown in Tables 11 and 12. The black body temperatures were changed in four steps: $\tau_1 = 2,380$ K, $\tau_2 = 2,490$ K, $\tau_3 = 2,595$ K, $\tau_4 = 2,690$ K. T is the true temperature of the flame (K).

Table 11. The Effects of the Types of Oxidizer and Mixing Ratios.

Composition (13)		%
Potassium perchlorate	x	
Magnesium	y	
Shellac	10	

No.	x%	y%	$\Delta(g/cm^3)$	v (s)	T (K)
H 5	60	30	1.33	2.42	2,830
H 6	45	45	1.22	3.25	2,830
H 7	30	60	1.14	6.62	2,740
H 8	15	75	0.97	6.96	2,730

Composition (14)		%
Potassium nitrate	x	
Magnesium	y	
Shellac	10	

No.	x%	y%	$\Delta(g/cm^3)$	v (s)	T (K)
H 9	60	30	1.14	1.90	2,775?
H10	45	45	1.01	3.37	2,725?
H11	30	60	1.01	6.62	2,825?
H12	15	75	0.93	did not burn	

Composition (15)		%
Ammonium perchlorate	x	
Magnesium	y	
Shellac	10	

No.	x%	y%	$\Delta(g/cm^3)$	v (s)	T (K)
H21	60	30	1.08	2.41	2,950?
H22	45	45	1.06	4.47	2,875
H23	30	60	1.01	6.23	?
H4	15	75	0.96	9.25	—

Table 11. The Effects of the Types of Oxidizer and Mixing Ratios (Continued).

Composition(16)		%
Barium nitrate		x
Magnesium		y
Shellac		10

No.	x%	y%	$\Delta(g/cm^3)$	v (s)	T (K)
H13	60	30	1.42	3.25	2,975
H14	45	45	1.30	5.25	2,825
H15	30	60	1.13	8.88	?
H16	15	75	1.03	did not burn	

Table 12. The Effects of Compositions Other Than in Table 11.

Composition (17)		%
Potassium perchlorate		x
Magnesium		y
Polyvinyl chloride		z

No.	x%	y%	z%	$\Delta(g/cm^3)$	v (s)	T (K)
H25	45	45	10	1.2	3.58	3,260
H26	50	50	—	1.29	7.62	3,850

Composition (18)		%
Strontium nitrate		x
Magnesium		y
Polyvinyl chloride		z

No.	x%	y%	z%	$\Delta(g/cm^3)$	v (s)	T (K)
H31	45	45	10	0.92	6.49	3,175
H28	50	50	—	1.17	9.30	?

Table 12. The Effects of Compositions Other Than in Table 11 (Continued).

Composition (19)		%
Barium nitrate		x
Magnesium		y
Polyvinyl chloride		z

No.	x%	y%	z%	$\Delta(g/cm^3)$	v (s)	T (K)
H29	45	45	10	1.25	6.81	2,990?
H30	50	50	—	1.41	24.0	3,775

Note: In general, high temperature flame compositions that contained magnesium did not burn smoothly without an organic fuel like shellac. Even when the composition contained 10% shellac, it did not burn smoothly except between 60–30% magnesium, producing many sparks.

Adding a sodium source to the sample compositions was unnecessary, because at high temperatures the Na–D lines always appeared clearly from impurities in the ingredients.

6.3 Examinations of the Results

(1) The effects of oxidizers

Comparing the effect at the same fuel to oxidizer ratio, strontium nitrate gave the highest temperature of all, followed by potassium perchlorate, barium nitrate, ammonium perchlorate, and potassium nitrate.

(2) The effects of the ratio of oxidizer to magnesium

In this experiment, the smaller the ratio of oxidizer to magnesium, the higher the temperature. This is a tendency that comes from the oxygen balance. Namely when the quantity of the magnesium is too large relative to the oxidizer, part of the magnesium is in a vapor state at the flame measuring point.

(3) The effects of fuels other than magnesium

Shellac or polyvinyl chloride were used. Polyvinyl chloride gave higher flame temperatures than shellac.

On the other hand, without any organic fuel, the burn rate of the sample increased to two or three times as large as that with organic fuels, and the temperatures rose to 3700–3800 K. That is, even when a small quantity of organic fuels, other than magnesium, is added to the high temperature composition, the temperatures of the flame decrease remarkably, and the burn rate also decreases.

VII. Conclusion

For low-temperature, colored-flame compositions that contained ordinary organic fuels and for the high temperature compositions that contained magnesium, the flame temperatures were measured by the line-reversal method using the Na-D lines.

The effects of oxidizers, fuels, color agents and the ratios of those components on flame temperatures were examined, and the fundamental data necessary for spectral analysis were obtained.

For high temperature flames, a photographic method was used to obtain the intensities of the spectra. Therefore some errors were unavoidable due to the operation and the instability of the flames. The flames move or oscillate with time; so it will be desirable to use a device to shorten the measurement time in the future.

Acknowledgment

The author thanks Professor Y. Yamamoto, Tokyo University, for his encouragement; Dr. Ryohei Ishida, the Institute of Industry, Tokyo, who kindly taught me about the line-reversal method; and Mr. Mamoru Nonaka, Institute of Electrical Technology, Tokyo, who gave me the data for the emissivity of tungsten.

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“The Curious Artificer” by Craig Villeneuve

CURIOSITY DOESN'T ALWAYS KILL THE CAT

I think that there is one man alive who has brought the art of fireworks a great leap forward in this country and quite likely the whole world. Why is this man a giant in the world of pyrotechny? Mainly because he has chosen to share his vast knowledge and research with the rest of us. Who is this man who shared with us the secrets of the round shell, blue and purple stars without Paris green, the mechanism of strobe phenomena, micro-stars, and dragon eggs? Who is used as a reference in any good book on pyrotechnics published since the seventies? Of course, it's Dr. Takeo Shimizu.

The biographical material that is available on Dr. Shimizu can be found on the dust jacket and preface of his excellent book, *Fireworks: The Art, Science and Technique* printed by Pyrotechnica Publications of Post Falls, TX and in part one of the four part series *Fireworks from a Physical Standpoint* also from Pyrotechnica Publications.

The Library of Congress Cataloging Publication Data states that Dr. Shimizu was born in 1912. From the other sources, 1951 is the year that he became interested in fireworks. About his life before 1951, there is nothing published. That leaves a gap of thirty-nine years, during a period of great turmoil in Japan and the world.

Being a curious sort of person, I wrote to the good Doctor to see if he could provide us with more information about his life and to find out who the people were that influenced him in his life's journey.

What follows is the information he provided. I tried to keep the style and composition as

close to the original as possible, but I did make some changes for the sake of clarity.

AUTOBIOGRAPHY OF A PYROTECHNICIST — DR. TAKEO SHIMIZU

I was born in 1912 in the small village of Takamata in Yamaguchi Prefecture, which is in the middle part of Japan. My father was a farmer. After I finished primary school, I then studied at a middle school in Hagi, a famous town which produced a number of loyalists of the Restoration Period of Meiji, Shoin Yoshida and Shinsaku Takasugi, etc. Hagi faced the Japan Sea and I could hear the sound of the rough sea while I lay in bed at the dormitory of the school on quiet nights.

At school I studied English for the first time. My teacher, T. Ito, had a great respect for English gentlemen. While I was in the fourth year class, an accident happened to me. I was severely scolded by him, and with that I did not do my English homework. I then became slow with the progress of my English. Many of the school boys dreamed of becoming military or naval officers to perform our duty for our country. I passed the famous severe entrance examination of the Military Academy, although I was not so tough but rather delicate.

The Military Academy was divided in two courses. The preparatory course of two years and the regular of one year and ten months. Between the two there was a duty in a regiment for six months. The preparatory course was for liberal arts and the regular was for military affairs. The students were divided into small learning groups of about thirty people.

(Continued on page 56)

Part III. On Backgrounds of Color Flame Spectra

ABSTRACT

Blank runs were made with nominal color-producing compositions to investigate the lines, bands or continuous spectra that appear as background and interfere with the desired spectra of red, yellow, green, etc. These sample compositions consisted of solid materials such as oxidizers (ammonium perchlorate, potassium chlorate, potassium perchlorate, potassium nitrate, etc.), low temperature fuels (shellac, rosin, pine root pitch, etc.), and magnesium powder for the high temperature fuel.

For low flame temperatures sodium D (Na-D) lines (5890 and 5896 Å, caused by impurities contained mainly in the oxidizers), continuous spectra (caused by carbon particles and potassium atoms) and potassium (K) lines (5802, 5783, 5832, 5813; 5340, 5324, 5360, 5343; 5090, 5084, 5113, 5080; 4044, 4048 Å) are observed. For high flame temperatures Na-D lines are also observed, and in addition to the above, MgO bands and continuous spectra (the latter are caused by solid metal oxide particles and K atoms) are found.

The main interfering spectra are the Na-D lines and continuous spectra. Purification of ingredients is very important to remove Na-D lines and to obtain fine colored flames. For high flame temperatures, the addition of chlorine-containing compounds such as polyvinyl chloride, ammonium chloride, etc. to a composition is effective in decreasing the intensity of the continuous spectra, and it is assumed that the metal oxide of the solid phase is converted into the metal chloride of the vapor phase in the presence of chlorine or hydrogen chloride in the flame, but this should be ascertained by further experiments of higher accuracy. The addition of shellac is also effective in weakening the intensity of the continuous spectra and decreasing the black body temperature of the flame.

The permeability coefficients and black body temperature of flames of basic compositions are measured for reference.

I. Introduction

The colored flame compositions used in the manufacture of fireworks are made up chiefly of the usual solid materials such as oxidizing agents, fuels and color agents. In the colored flame, besides the spectrum caused by the color producer, there are also present line spectra, band spectra and continuous spectra arising from products introduced into the flame from the oxidizers and fuels, and also from the various impurities. Together these form a background that interferes with the desired pure color. In order to analyze the colored flame produced from such color compositions, it is necessary, therefore, first of all to carry out tests on blanks made up from all the ingredients, except the color producer. This is the subject of the present report. In this way it can be determined what measures are needed to reduce the strength of this background and to counteract its influence on the desire pure color.

Table 1. Results of Determinations of Elements in the Fuels.

	C (%)	O (%)	H (%)	Ash (%)
Shellac	67.00	23.87	9.00	0.13
Wood rosin	75.77	15.35	8.81	0.07
Pine root pitch	75.12	17.14	6.87	0.87
Coal pitch	91.91	3.25	4.60	0.24

II. Chemicals Used for Production of the Test Samples and Structure of the Charges

1. Oxidizers

Potassium nitrate – commercial reagent grade; potassium chlorate – commercial reagent grade; potassium perchlorate – commercial reagent grade and industrial grade, 5 times recrystallized from distilled water; ammonium perchlorate – industrial grade, 4 times recrystallized from distilled water; barium nitrate – commercial reagent grade; barium chlorate – industrial grade, 3 times recrystallized from distilled water; strontium nitrate – industrial grade, 5 times recrystallized from distilled water, washed with ethyl alcohol, as free as possible of barium chloride.

2. Fuels

Shellac, wood rosin,^[1] pine root pitch, coal pitch – all of commercial grade and of the compositions shown in Table 1.

Magnesium powder A – commercial grade, not showing any high aluminum content when tested, and completely soluble in HCl. Used for determination of penetrating power of flame. Magnesium powder B, compared with A, is of comparatively low purity; Mg 75.73%, Al 24.27%; completely soluble in HCl. Used for general spectral analysis. All passed through a 177 μ sieve.

Aluminum powder – commercial flakes, all passing through a 105 μ sieve. Completely soluble in HCl. No tarry material found.

3. Chlorine Donors

Polyvinyl chloride (CH_2CHCl)_n supplies HCl gas to the flame – commercial grade. The following are the results of analysis: Cl 51.53% (sodium peroxide), ash 0.00% (theoretical chlorine percentage 56.73%).

Benzene hexachloride $\text{C}_6\text{H}_6\text{Cl}_6$ or γ BHC supplies chlorine gas to the flame – commercial grade. The residue after extraction of the γ BHC for insecticides was used. White finely powdered material. Analysis results as follows: Cl 70.90% (sodium method). (Theoretical Cl content 73.14%).

Hexachloroethane C_2Cl_6 supplies chlorine gas to the flame. Commercial product used without further treatment.

Ammonium chloride supplies HCl gas to the flame. Commercial product, recrystallized 3 times from distilled water.

Magnesium chloride is thought to supply chlorine gas or hydrogen chloride gas to the flame^[2] (refer to Section 6.3).

4. Structure of the Sample Charge

This was just as described in Part II. It consisted of a tube made from three layers of brown paper, internal diameter 10 mm and length 97 mm, and ignited at the end. One to three photographs were taken according to the requirements.

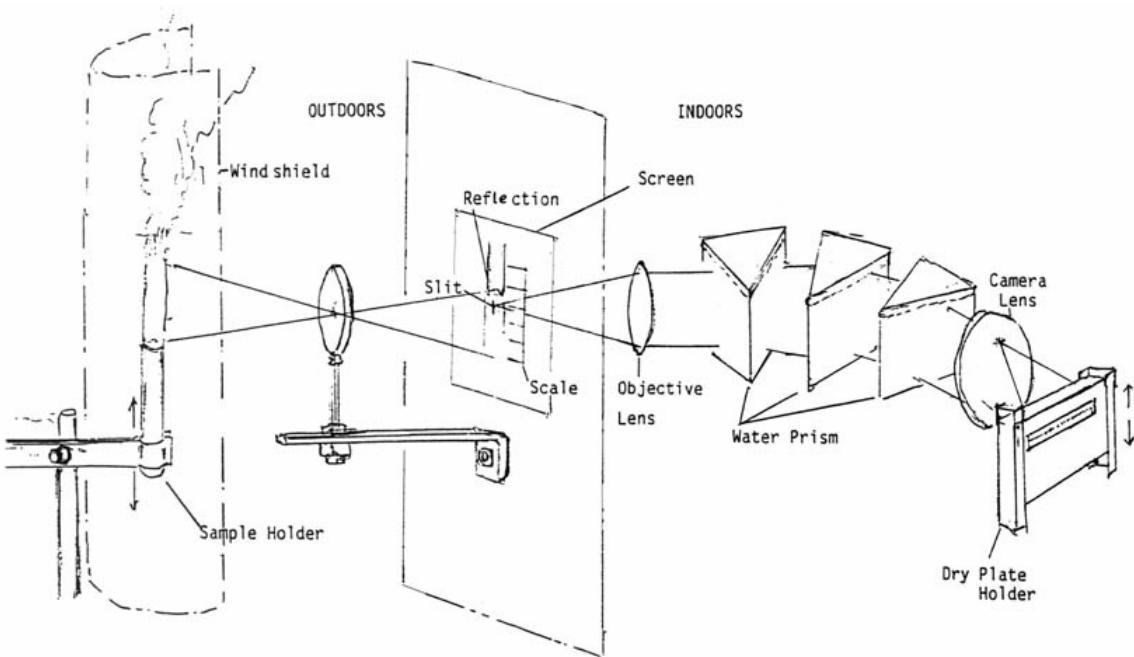


Figure 1. Sketch of the installation of devices for photographing flame spectra. NOTE: There is an error in the illustration. The prisms should be pointing away from not toward the front.

III. Spectrum Apparatus and Auxiliary Equipment

The spectrometer used was a self-setting type with the following characteristics. See sketch in Figure 1.

Prism: This was a water prism consisting of an equilateral triangular vessel made from glass plates and filled with distilled water. Three prisms were used.

Slit: 0.04 mm width, fixed type.

Field of vision: 18° 20'.

Angle of entrant light axis and camera axis: about 50°.

Angle between plane at right angles to the camera light axis and plane of the photographic plate: 16.5°.

Dispersion: initial photographs with 12.5 Å/mm (4000 Å), 20.0 Å/mm (5000 Å), 35.0 Å/mm (6000 Å). Later the more convenient smaller dispersion of 13.0 Å/mm (4000 Å), 30.0 Å/mm (5000 Å), 40.0 Å/mm (6000 Å).

At the focal plane of the camera was a 5.0 mm wide window above which was a 7.0 mm wide light wedge. (Also see Figure 1a in Part I.) The

light passing through both of those could be photographed at the same time and thus enabled comparative judgements to be carried out conveniently.

While photographs were being taken, in order to line up the slit of the spectrometer with the flame, the slit was equipped with a view finder and adjustment was carried out by moving the flame. When high temperatures were used, to include the image in the angle of vision of the spectrometer, a flame length of about 6 cm was used (slit to flame distance 17 cm) while with low temperatures the slit was about 16 cm (slit to flame distance 50 cm). The whole light produced by the flame did not enter the spectrometer. Further, the shape of the flame was rather unstable and so it was impossible to keep a fixed amount of light entering the spectrometer. Hence the photographs taken through the spectrometer are only strictly comparable within each group taken at a given time. However the experimental conditions were kept as constant as possible in order to make the photographs reasonably comparable. Also to assist in the comparison of the individual photographs, calibration was carried out by measuring the light intensity of the flame with a selenium photo-

toelectric cell during the combustion of the sample.

The plates used for taking the photographs were Sakura Pancho-F plates.

Photo 1 shows the sun's spectrum taken with this type of plate and the spectrometer used, and indicates the fundamental spectral and general light sensitivity under the conditions of our experiments.

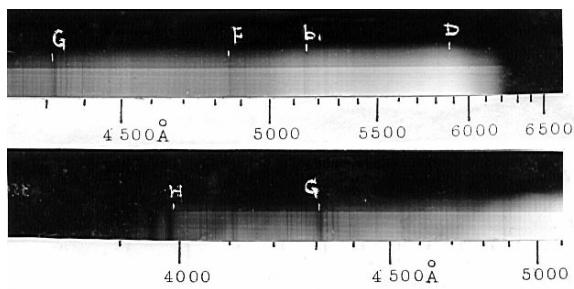


Photo 1. The sun's spectrum in Tokyo, 10 a.m., late in December, 1957.

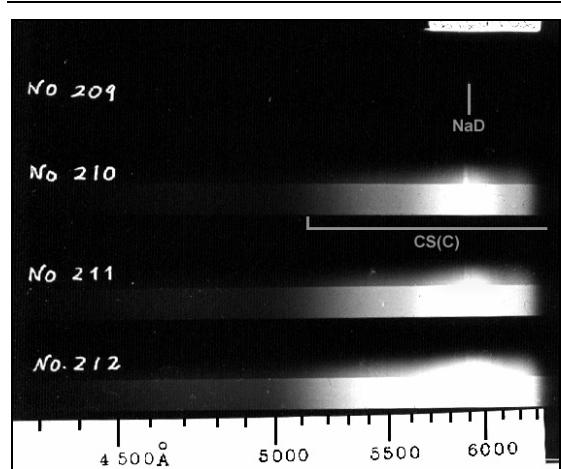


Photo 2. Low flame temperature background using ammonium perchlorate as the oxidizer.

IV. Background with Low Temperature Fuels

For the oxidizers we chose ammonium perchlorate and potassium perchlorate and used shellac, wood rosin, pine root pitch and coal pitch as fuels. These various compositions were burned and measurements carried out on the spectra. The results are shown below and the meaning of the symbols used are as follows:

ω = total weight in grams of material burned for the photograph.

L = the candle-power in candela of the light from the flame, measured with a selenium photo-electric cell.

t = total time in s for combustion.

E = a coefficient related to the light energy emitted by a unit weight of the material in candela·s/g.

$$E = \frac{Lt}{\omega}$$

i = the length of the spectral line on the photograph obtained by passing the light through the light wedge. This gives a coefficient related to the strength of the line at a given wavelength.

d = the density for the plates, with a continuous spectrum, at 5550 Å: the wavelength for maximum sensitivity.

The photographs obtained from these experiments are shown below.

Conclusions

The spectra from the experiment using *ammonium perchlorate* as the oxidizer (Photo 2) gave the following indications.

- It is probable that the sodium D (Na-D) lines, D_1 5890 Å, D_2 5896 Å arise from impurities in the form of Na compounds contained in the oxidizer or the fuel. In the case of shellac the intensity is low, $i = 2.5$, while in the case of the other fuels, it is considerably higher at $i = 4$.
- The continuous spectrum, CS (C) (>5050 Å) is thought to arise from the hot carbon coming from the fuels. This spectrum is almost absent with shellac. With wood rosin and

Table 2. Low Temperature Fuels: Background Characteristics.

Composition (21)		Ammonium perchlorate		80%		
No.	Fuel	ω (g)	L (candela)	t (s)	E (candela·s/g)	d
209	Shellac	263	9	214	7	1.017
210	Wood rosin	268	367	205	281	3.750
211	Pine root pitch	281	767	159	434	4.839
212	Coal pitch	277	1500	115	623	7.500
Composition (22)		Potassium perchlorate		80%		
No.	Fuel	ω (g)	L (candela)	t (s)	E (candela·s/g)	d
213	Shellac	317	45	338	48	1.563
214	Wood rosin	290	500	235	500	3.409
215	Pine root pitch	313	600	140	268	2.586
216	Coal pitch	307	1000	169	550	6.250

pine root pitch it is almost equally in evidence, with $i_{\max} = 3.5$, while with coal pitch it is the highest, giving $i_{\max} = 5.5$.

With potassium perchlorate as the oxidizer (Photo 3) the spectra lead to the following conclusions.

- The Na-D lines at 5896 and 5890 Å are thought to come chiefly from Na impurities in the oxidizer since they are more intense than was the case when using ammonium perchlorate as the oxidizer. Since they are

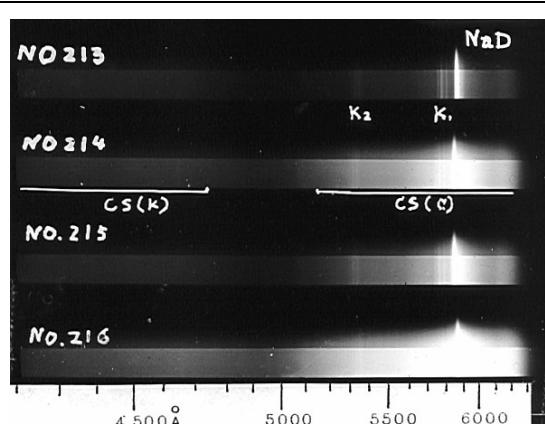


Photo 3. Low flame temperature background using potassium perchlorate as the oxidizer.

present in all cases, they are probably not associated with the fuels. The value of i is approximately 5.9. With such a high value for the intensity, it is probable that the flame temperature in this case is higher than that when using ammonium perchlorate as in Compositions (21) (See Part II).

- The K lines come from the potassium line spectrum, and these are made up of four groups.

K ₁	5802, 5783 Å
	5832, 5813 Å
K ₂	5340, 5324 Å
	5360, 5343 Å
K ₃	5090, 5084 Å
	5113, 5080 Å
K ₄	4044, 4048 Å

Among these K₄ is comparatively strong and the others are quite weak. Since vision sensitivity to K₄ is low, the K lines probably do not constitute an important interfering factor. In these spectra no effect is seen with any of the fuels. (K₄ is not present in Photo 3).

The continuous spectrum, CS (C) (>5030 Å) differs greatly between the various fuels. The value for i_{\max} with shellac is 1, with wood rosin 4,

Table 3. High Temperature Fuel Background Characteristics.

Composition (23)			Ammonium perchlorate			x%		
No.	x%	y%	Fuel	ω (g)	L (candela)	t (s)	E (candela·s/g)	d
121	80	Mg 20	9.4	30	66.0	210	1.06	
122	72	Mg 28	9.6	300	51.5	1,580	2.08	
123	40	Mg 60	8.7	48,000	15.0	82,800	4.35	
124	40	Al 60	9.0	64,000	11.0	78,220	2.94	
<hr/>								
Composition (24)			Potassium perchlorate			x%		
No.	x%	y%	Fuel	ω (g)	L (candela)	t (s)	E (candela·s/g)	d
125	40	Mg 60	8.8	250,000	3.0	85,200	5.88	
126	40	Al 60	9.5	112,000	14.0	165,000	5.45	
<hr/>								
Composition (25)			Potassium nitrate			x%		
No.	x%	y%	Fuel	ω (g)	L (candela)	t (s)	E (candela·s/g)	d
127	40	Mg 60	8.7	160,000	5	91,900	5.17	
128	40	Al 60	9.8	9,600	26	25,500	2.29	

with pine root pitch 3 and with coal pitch 5, and this follows the carbon content of the materials.

- c) The continuous spectrum CS (K) (<4830 Å) is a weak spectrum extending to the ultra-violet and is not influenced by the various fuels. This is thought to be a continuous spectrum arising from the potassium atoms.^[3]

From the above considerations it can be seen that the chief interfering factor is the continuous spectrum CS (C) brought about by the carbon in the fuels. As the carbon content becomes smaller so does this spectral effect.

As far as the oxidizers are concerned there is no direct interference attributable to ammonium perchlorate. With potassium perchlorate the main interfering factor is the continuous spectrum CS (K). [With the naked eye the base of the flame appears to have a white color. This is thought to be due to the CS (K)].

In all the above cases the main interfering factor is that due to the Na-D lines produced by the impurities.

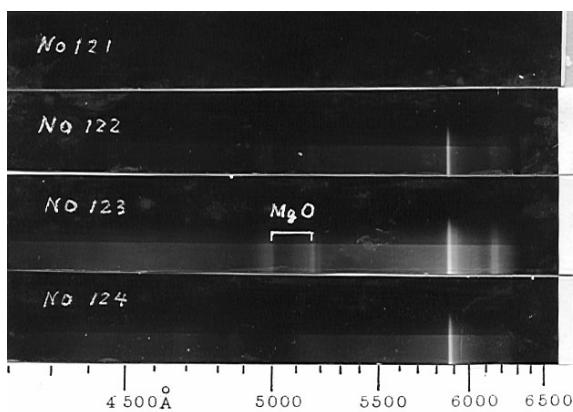


Photo 4. High flame temperature background using ammonium perchlorate as the oxidizer.

V. Background with High Temperature Fuel

For the oxidizers we used ammonium perchlorate, potassium perchlorate and potassium nitrate and for the fuel we used magnesium. Also, for the purpose of comparison, aluminum was used.

The corresponding spectra are shown in Photos 4, 5 and 6.

Conclusions:

Magnesium as the Fuel

The experiments using *ammonium perchlorate* as the oxidizer (Photo 4) gave the following indications.

- The Na-D lines 5896 and 5890 Å are the strongest and are thought to be due to impurities in the oxidizer. Because of the high temperature, the sodium atoms in the flame are excited to a considerable extent and hence, even with a very small quantity of impurity, the intensity of the Na-D lines is increased to produce a very powerful effect. However with No. 121 almost no Na effect is seen; this composition was not difficult to ignite, but burned with an oscillatory flame. The values obtained for i were: No. 122, 5.0; No. 123, 6.0; and No. 124, 5.7; and these intensities are practically proportional to E .

- The MgO band has a peak at the long wave end. In fact there are two peaks, at 5190 Å (0.1) and 5007 Å (0.0). As the magnesium content is increased, the intensity of these lines increases.
- There is a band spectrum observable, which may be from MgCl, at 6165 and 6196 Å. The intensity is proportional to the amount of magnesium contained in the mixture. As will be shown later, this is associated with the presence of chlorine gas in the flame. It can be inferred that this is a MgCl band.
- The magnesium oxide continuous spectrum CS (Mg_xO_y) is observed extending over the visible region. Its intensity is essentially proportional to the magnesium content of the mixture.

Aluminum as the Fuel

- The Na-D lines at 5896 and 5890 Å are due to impurities, and their intensities are fairly high.
- There is an AlO band at 4648 (1.0), 4842 (0.0), 5079 (0.1) Å with a peak towards the short wave end.
- The aluminum oxide continuous spectrum CS (Al_xO_y) can be seen in the visible region.

With *potassium perchlorate* as the oxidizer (Photo 5), apart from the following points, the same type of spectra are observed as with ammonium perchlorate (Photo 4).

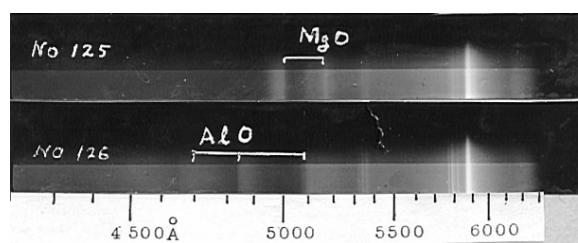


Photo 5. High flame temperature background using potassium perchlorate as the oxidizer.

- There are added K lines and the continuous spectrum CS (K).
- The MgCl? band at 6165 and 6196 Å has disappeared.

Table 4. Background from Compositions Using Chlorine Donors.

Composition (26)		Potassium perchlorate	40%	(additional percent)	
		Magnesium	60%		
		Chlorine donor	15%		
No.	Chlorine donor	ω (g)	L (candela)	t (s)	E (candela·s/g)
349	BHC	9.7	3200	17.0	5,608
350	Hexachloroethane	9.5	8000	13.5	11,388
344	Polyvinyl chloride	8.7	800	16.0	1,471
351	Ammonium chloride	8.7	1600	24.0	4,414
378	Ammonium chloride	7.9	1600	27.0	5,468

- c) In general the intensity of the spectrum is stronger than that obtained when using ammonium perchlorate as the oxidizer.

With potassium nitrate as the oxidizer (Photo 6), the spectrum produced is the same as that for ammonium perchlorate (Photo 4) except for the following differences.

- a) The K lines and the continuous spectrum CS (K) are added.
- b) The MgCl? bands at 6165 and 6196 Å are absent.
- c) When magnesium is used as the fuel, the continuous spectrum is stronger than with ammonium perchlorate as the oxidizer (Photo 4) and is essentially the same as with potassium perchlorate (Photo 5). With aluminum as the fuel, the continuous spectrum is very weak; this is probably because the aluminum melts and the liquid drops are dispersed.
- d) At 5763 Å, on the long wave side, a peak about 60 Å wide can be seen. This is probably brought about by NO_3^- .

As shown above, with these various high temperature fuels, the main interference is caused by the Na-D lines from impurities, as well as from MgO (or AlO) and $\text{MgCl}?$ bands arising from the reactions taking place during combustion. There is also an effect from the Mg_xO_y (or Al_xO_y) and from the potassium continuous spectra. Among these effects the spectra from the magnesium compounds depend on the content of magnesium in the mixture. Of the various oxidizers ammonium perchlorate produces by far the least intense spectra. An influence from HCl in the flame is inferred.

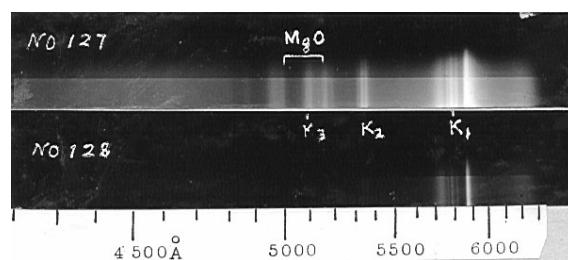


Photo 6. High flame temperature background using potassium nitrate as the oxidizer.

VI. Influence of Chlorine and Hydrogen Chloride Gases on the Background

From the results of numerous experiments on flame spectra it is clear that chlorine and hydrogen chloride gases exert a very important effect in the flame. We now give the results of experiments to study their effect on the background.

The chlorine donors used were as follows:

Chlorine gas producers:

BHC	$C_6H_6Cl_6$	Cl: 73.14%
Hexachloroethane	C_2Cl_6	Cl: 89.85%

Hydrogen chloride gas producers:

Polyvinyl chloride	$(CH_2CHCl)_n$	HCl: 58.34%
Ammonium chloride	NH_4Cl	HCl: 66.89%

The ammonium chloride contains no carbon, and if it is introduced in too large quantities into the mixture, it has the disadvantage of hindering the combustion.

6.1. Low Temperature Flame

In general, with this type of chlorine donor, the results are not very clear. With these various compositions the interfering spectra in the flame come chiefly from carbon, sodium and potassium atoms, and although chlorine gas or hydrogen chloride gas are present, the necessary reactions to produce a reduction in flame color do not occur.

6.2. High Temperature Flame

Experiments were carried out with the above four types of chlorine donors.

In this case the intensity of the continuous spectrum is practically proportional to L , and the smaller the value of L , the lower the intensity of the interfering lines. The effect of polyvinyl chloride is the highest, followed by ammonium chloride, BHC, and hexachloroethane, in that order. That is to say, the effect from hydrogen chloride liberation is more intense than that from the liberation of chlorine gas. To make an accurate assessment of the effectiveness, the value of E must also be considered. On extending t , the time for combustion, L becomes smaller and hence the true effect from HCl or Cl must be to decrease E . Since the order of the chlorine donors as regards the value of E is the same as that for L we may assume that the above assessment is probably correct.

Both oxidizers, ammonium perchlorate and potassium perchlorate, contain chlorine. On combustion of the mixture, the first liberates HCl while the latter liberates neither Cl nor HCl (this is easily confirmed by placing the products of combustion into water and examining the dissolved substances). Hence the activities of these two substances in the flame are different. This is seen with the results from Compositions (23) and (24). If the values of L and E for these two substances, when used in the same compositions, are compared, it can be seen that ammonium perchlorate gives lower values and hence that its activity is higher.

The case of potassium nitrate, which contains no chlorine at all, is interesting. In this case the effect from the addition of chlorine containing compounds is most clear, as shown in Table 5.

From Table 5 it can be seen that the values of L and E for polyvinyl chloride and ammonium chloride are lower than for the others, and the effect of HCl is more conspicuous than that of Cl.

Table 5. Background Using a Non-Chlorine Containing Oxidizer.

Composition (27)		Potassium nitrate	40%	
		Magnesium	60%	
		Chlorine donor		15% (additional percent)
No.	Chlorine donor	ω (g)	L (candela)	t (s)
353	BHC	9.0	2400	19.0
354	Hexachloroethane	8.8	4000	15.0
348	Polyvinyl chloride	8.0	1600	18.5
355	Ammonium chloride	8.5	1600	22
380	Ammonium chloride	7.6	1280	20

Next we compared the results from various compositions containing the substance showing the greatest effect, polyvinyl chloride.

As can be seen from results in Table 6, when the percentage of polyvinyl chloride increases, the values of L and E decrease. Hence the effect of this compound is to reduce the interfering lines. However there is probably some considerable depression of the flame temperature at

the same time, so we must also study this effect on the color developed.

Table 6. Effect from Various Compositions Made up Using Polyvinyl Chloride as the Chlorine Donor.

Composition (28)		Potassium perchlorate	40%	
		Magnesium	60%	
		Polyvinyl chloride		x% (additional percent)
No.	x%	ω (g)	L (candela)	t (s)
341	0	8.5	40,000	8.0
342	5	8.7	32,000	3.5
343	10	8.5	800	13.5
344	15	8.7	800	16.0

Composition (29)		Potassium nitrate	40%	
		Magnesium	60%	
		Polyvinyl chloride		x% (additional percent)
No.	x%	ω (g)	L (candela)	t (s)
345	0	9.0	14,400	5.0
346	5	8.5	4,000	14.5
347	10	8.1	2,400	18.0
348	15	8.0	1,600	18.5

6.3. Chlorine or Hydrogen Chloride Gas: Effect within the Flame

The effect of chlorine or hydrogen chloride gases in decreasing the intensity of the interfering spectra in high temperature flames has been definitely established as discussed above. With compositions containing magnesium the interfering spectra in the flame are from the MgO, MgCl (?) band spectra and the magnesium oxide continuous spectrum. The magnesium oxide continuous spectrum has quite a high intensity in the visible region. Even so, as can be seen from the photographs, the effect of chlorine gas or hydrogen chloride gas in the flame (chlorine gas effect is less) brings about a decrease in the intensity of the magnesium oxide continuous spectrum. For example, using as the chlorine donor polyvinyl chloride, which liberates hydrogen chloride gas, the spectrum obtained is shown in Photo 7 upper (No. 344, potassium perchlorate 40%, magnesium 60%, polyvinyl chloride additional 15%, $\omega = 8.7$, $t = 16.0$). In Photo 7 lower is shown for comparison the spectrum using the same amount of shellac instead of the polyvinyl chloride (No. 377, potassium perchlorate 40%, magnesium 60%, shellac additional 15%; $\omega = 8.0$, $t = 16.0$). It can be seen by comparing these two spectra that when polyvinyl chloride is used, the continuous spectrum is very much less intense.

The lowering of the intensity of the continuous spectrum from magnesium oxide may be due to the following effects.

(1) The chlorine or hydrogen chloride gas reacts in the flame with the solid magnesium oxide MgO to form gaseous MgCl. The result of this is to reduce the concentration of solid particles in the flame.

(2) The chlorine donor causes the temperature of the flame to drop and hence the radiation energy of the solid particles in the flame decreases.

In general, as in Part II, when shellac or other low temperature fuels are added, the flame temperature is markedly reduced, and the intensity of the continuous spectrum is also lowered. (See Part II). From Part II the flame temperature, when using polyvinyl chloride as the chlorine donor is higher than when using shellac. However, the continuous spectrum with polyvi-

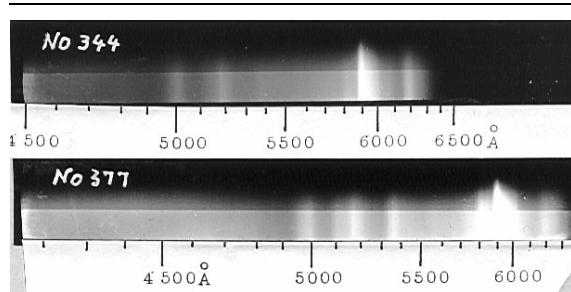


Photo 7. Comparison of effect with polyvinyl chloride and shellac.

nyl chloride is less intense than with shellac. Hence one must assume that effect (2) and effect (1) must be operative at the same time (i.e., reduction of the intensity of the continuous spectrum from the effect of the hydrogen chloride gas).

The following equilibrium reactions have been known for a long time.^[4]



The partial pressures of chlorine and oxygen for various temperatures (°C) are

	50°	250°	550°	750°
Cl ₂	0.3	17.6	79.3	93.3
O ₂	99.7	82.4	20.7	6.7



The partial pressures of hydrogen chloride gas and water vapor at various temperatures (°C) are

	500°	600°	700°
HCl	50.2	75.1	90.2
H ₂ O	49.8	24.9	9.8

These two reactions both have a tendency to proceed from right to left with increasing temperature. This may be in agreement with the idea expressed in effect (1) above. However, the magnesium chloride produced in the flame is probably not in the solid form (MgCl₂) but exists as the vapor of the transient molecule MgCl, and hence whether the above two standard reactions take place in the flame or not is unknown.

The above assessment is not based upon a sufficiently large number of quantitative ex-

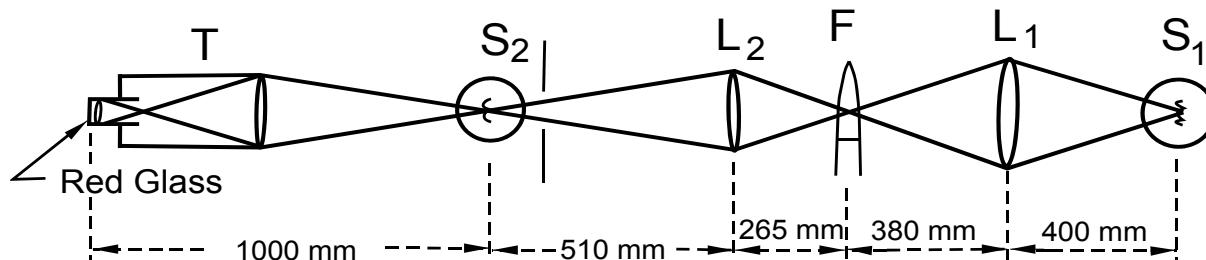


Figure 2. Light path through the measuring apparatus for black body temperatures of flames.

periments, and one can still do little more than conjecture. A further study of this problem with detailed experiments must be made. Some work in this direction is given below.

VII. Measurement of Flame Transmission and Black Body Temperature

The effect of chlorine or hydrogen chloride gases on the flame continuous spectrum has been considered above, and the results suggested that these gases, when present in the flame, reduced the concentration of solid Mg_xO_y particles. Determination of the concentration of these solid particles in the flame or of some quantity related to it would help in clarifying the effect of the chlorine or hydrogen chloride gases. For a measure of the density of the solids in the flame one can use its permeability coefficient and black body temperature. When the density of solids increases, the permeability falls, and, for a given real temperature, the black body temperature rises.

7.1. Method of Measurement

The light path through the measuring apparatus is as shown in Figure 2. However, when only the black body temperature of the standard light S_1 was measured, the lens L_1 was omitted.

The light from the source S_1 passes through the lens L_1 and produces an image within the flame F . The light from the flame F and the image of the source S_1 pass through the lens L_2 to form an image at the position of the filament of a standard lamp S_2 . The image of F and S_1 together with S_2 can be observed through a telescope T . The eye-piece of the telescope is

equipped with red glass as used in a radiation pyrometer. The symbols used later have the following meanings:

p_1 permeability coefficient of lens L_1

p_2 permeability coefficient of lens L_2

p_3 permeability coefficient of the lens of the glass of the standard lamp S_2 on the S_1 side.

P_F permeability coefficient of the flame

λ_e effective wavelength of the red glass

$E(\lambda_e, \tau_{S_1})$ radiation emissivity with light source S_1 of wavelength λ_e and black body temperature τ_{S_1}

$E(\lambda_e, \tau_F)$ radiation emissivity with flame wavelength λ_e and black body temperature τ_F .

The brightness of the image of S_1 , which has passed through the flame, at the position of the filament of S_2 is added to the brightness of S_2 . The relationship between this quantity and the reading of the black body temperature at S_2 denoted by $\tau'_{F_{S_1}}$, in terms of emissivity, is shown by the following expression:

$$E(\lambda_e, \tau_{S_1}) \cdot P_F \cdot p_1 \cdot p_2 \cdot p_3 + E(\lambda_e, \tau_F) \cdot p_2 \cdot p_3 = E(\lambda_e, \tau'_{F_{S_1}}) \quad (1)$$

If the light source S_1 is now extinguished, leaving only the flame brightness added to S_2 , and denoting the black body temperature of S_2 by τ'_F the relationship between the emissivities becomes

$$E(\lambda_e, \tau_F) \cdot p_2 \cdot p_3 = E(\lambda_e, \tau'_F) \quad (2)$$

If the flame is now extinguished, with only the brightness from the point light source from

S_1 added, and if the black body temperature of S_2 is denoted by τ'_{S_1} we have, in the same way:

$$E(\lambda_e, \tau'_{S_1}) \cdot p_1 \cdot p_2 \cdot p_3 = E(\lambda_e, \tau'_{S_1}) \quad (3)$$

If equations 2 and 3 are now substituted into equation 1 and the whole rearranged, we obtain the flame permeability coefficient as in the following equation:

$$P_F = \frac{E(\lambda_e, \tau'_{F_{S_1}}) - E(\lambda_e, \tau'_F)}{E(\lambda_e, \tau'_{S_1})}$$

If the Wien equation (Part II) is now introduced we get

$$P_F = e^{-\frac{c_2}{\lambda_e} \left(\frac{1}{\tau'_{F_{S_1}}} - \frac{1}{\tau'_{S_1}} \right)} - e^{-\frac{c_2}{\lambda_e} \left(\frac{1}{\tau'_F} - \frac{1}{\tau'_{S_1}} \right)} \quad (4)$$

The measuring apparatus formerly used for line-reversal method (Part II) was possibly used. However, as mentioned above, when measuring black body temperatures of the standard light, the lens L_1 was omitted and the light S_1 was directly observed. In this case, the calibration curve used in Part II was also used without alteration. That is permissible for the following reason.

The relationship between the reading τ' from the calibration curve and the black body temperature of the standard light source τ'' is given by the following equation:

$$E(\lambda_e, \tau'') \cdot p_1 = E(\lambda_e, \tau') \quad (5)$$

Introducing the Wien equation and rearranging, this becomes

$$\frac{1}{\tau''} = \frac{1}{\tau'} + 2.303 \frac{\lambda_e}{c_2} \log p_1 \quad (6)$$

Hence when calculating P_F from equation 4, one must substitute $1/\tau''$, instead of $1/\tau'$. If this is done, the correction value disappears and has no influence on the P_F calculation.

Next, to get the black body temperature of the flame, the Wien equation is substituted into equation 2. We then get the following expression, as with equation 6.

$$\frac{1}{\tau_F} = \frac{1}{\tau'_F} + 2.303 \frac{\lambda_e}{c_2} \log p_2 \cdot p_3$$

In order to make a correction for the reading of the calibration curve, the value $1/\tau'_F$ must be modified by $1/\tau''_F$ from equation 6 and if this is done, we get

$$\frac{1}{\tau_F} = \frac{1}{\tau'_F} + 2.303 \frac{\lambda_e}{c_2} \log p_1 \cdot p_2 \cdot p_3 \quad (7)$$

Now if we put $p_1 = p_2 = p_3 = 0.916$ (the permeability coefficient of one glass surface was taken to be 0.957), and if these values are substituted in the above equation, then

$$\begin{aligned} \frac{1}{\tau_F} &= \frac{1}{\tau'_F} + 2.303 \frac{0.0000626}{1.438} \log 0.916^3 \\ &= \frac{1}{\tau'_F} - 0.0000115 \end{aligned} \quad (8)$$

The density of the photograph can be used as the magnitude defining the density of the solids in the flame using the following equation:

$$c = \frac{k}{w} \log \frac{1}{P_F} \quad (9)$$

Here c is a value proportional to the density of solid particles in the flame, k is a constant, and w the width (in cm) of the flame in the transmitted light path.

7.2 Results of Measurements and Discussions

The results of measurements carried out in the manner described are given below. The structure of the samples was the same as that described in Section V. The value v shows the rate of combustion.

Table 7. Black Body Temperature of the Flame $\tau_F(\lambda_e = 6260 \text{ \AA})$; Permeability Coefficient P_F ; and $c = 100/w \times \log(1/P_F)$.

Composition (29); low temp.; ammonium perchlorate 75% + fuel 15%.

No.	Fuel	τ_F (K)	P_F	w (cm)	c	v (mm/s)
141	Shellac	1526	1.00	1.27	0	1.43
142	Wood rosin	1711	0.87	1.20	5	1.65
143	Pine root pitch	1790	0.60	1.64	14	1.82
144	Wood flour	1474	0.96	1.04	2	1.40

Composition (30); low temp.; potassium perchlorate 75% + fuel 15%

No.	Fuel	τ_F (K)	P_F	w (cm)	c	v (mm/s)
145	Shellac	1677	0.84	1.04	8	1.35
146	Wood rosin	1776	0.70	1.19	13	1.88
147	Pine root pitch	1671	1.00	1.90	0	1.94
148	Wood flour	1542	0.78	1.77	6	1.65

Composition (31); low temp.; potassium chlorate 75% + fuel 15%.

No.	Fuel	τ_F (K)	P_F	w (cm)	c	v (mm/s)
149	Shellac	1630	0.97	1.54	1	1.55
150	Wood rosin	1620	0.66	1.40	13	1.43
151	Pine root pitch	1682	0.96	1.92	1	3.20
152	Wood flour	1506	0.99	1.09	0	2.87

Composition (32); high temp.; ammonium perchlorate 45% + magnesium 45% + added material 10%

No.	Added Material	τ_F (K)	P_F	w (cm)	c	v (mm/s)
153	None	1980	0.66	1.90	10	4.80
154	Polyvinyl chloride	1973	0.73	2.29	6	4.80
155	Ammonium chloride	1873	0.43	1.45	25	3.78
156	Shellac	1766	0.73	1.14	12	4.92

Table 7. Black Body Temperature of the Flame $\tau_F(\lambda_e = 6260 \text{ \AA})$; Permeability Coefficient P_F ; and $c = 100/w \times \log(1/P_F)$ (Continued).

Composition (33); high temp.; potassium perchlorate 45% + magnesium 45% + added material 10%

No.	Added Material	τ_F (K)	P_F	w (cm)	c	v (mm/s)
157	None	2565	0.72	?	?	2.80
158	Polyvinyl chloride	2141	0.32	1.56	32	6.03
159	Ammonium chloride	2113	0.29	1.61	33	5.07
160	Shellac	2055	0.76	2.08	6	5.49

Composition (34); high temp.; potassium nitrate 45% + magnesium 45% + added material 10%

No.	Added material	τ_F (K)	P_F	w (cm)	c	v (mm/s)
161	None	2379	?	?	?	22.7
162	Polyvinyl chloride	1982	0.73	2.41	6	5.05
163	Ammonium chloride	2063	0.57	2.50	10	5.33
164	Shellac	1891	0.57	2.08	12	5.35

Composition (35); high temp.; barium nitrate 45% + magnesium 45% + added material 10%

No.	Added material	τ_F (K)	P_F	w (cm)	c	v (mm/s)
165	None	2565	?	?	?	28.0
166	Polyvinyl chloride	2037	0.48	1.82	18	7.12
167	Ammonium chloride	1996	0.50	1.61	19	6.23
168	Shellac	2037	0.52	?	?	6.43

Composition (36); high temp.; ammonium perchlorate 40% + magnesium 40% + added material 20%

No.	Added material	τ_F (K)	P_F	w (cm)	c	v (mm/s)
175	Polyvinyl chloride	1901	?	2.34	?	3.56
176	Ammonium chloride	no burning	—	—	—	—
177	Shellac	1711	0.69	1.14	14	2.78
178	BHC	1871	0.56	1.04	24	3.20

Composition (37); high temp.; potassium perchlorate 40% + magnesium 40% + added material 20%

No.	Added material	τ_F (K)	P_F	w (cm)	c	v (mm/s)
179	Polyvinyl chloride	1979	0.61	2.08	10	2.11
180	Ammonium chloride	no burning	—	—	—	—
181	Shellac	1713	0.52	1.43	19	2.44
182	BHC	2028	0.69	1.66	10	?

Table 7. Black Body Temperature of the Flame τ_F ($\lambda_e = 6260 \text{ \AA}$); Permeability Coefficient P_F ; and $c = 100/w \times \log(1/P_F)$ (Continued).

Composition (38); high temp.; potassium nitrate 40% + magnesium 40% + added material 20%

No.	Added material	τ_F (K)	P_F	w (cm)	c	v (mm/s)
183	Polyvinyl chloride	1906	0.61	1.94	11	2.92
184	Ammonium chloride	1856	0.74	2.75	5	2.59
185	Shellac	1753	0.70	3.69	4	2.41
186	BHC	2081	0.57	2.16	11	2.60

Composition (39); high temp.; barium nitrate 40% + magnesium 40% + added material 20%

No.	Added material	τ_F (K)	P_F	w (cm)	c	v (mm/s)
187	Polyvinyl chloride	1890	0.68	2.55	7	5.19
188	Ammonium chloride	1910	0.61	2.13	10	2.91
189	Shellac	1789	0.45	2.60	13	3.70
190	BHC	2033	0.33	1.92	25	4.00

The measured part of the flame was 1 cm from the base, in the middle.

Discussion

- (1) The value of c , indicating the density of solids in the flame, is subject to a large experimental error (obtained from three determinations), and hence it is difficult to deduce any definite rules from the results shown. Hence to study the effect of chlorine or hydrogen chloride gases on the background it is necessary for more accurate determinations to be made on the permeability coefficient.
- (2) For determination of the density of the solids in the flame it is better to use the black body temperature τ_F which gives an approximate assessment. This is because τ_F can be obtained from a single measurement. However, where the true temperature of the flame is not known, one can only get a rough idea of the value.
- (3) Comparing high temperature and low temperature flames, in general, the permeability coefficient of the flame with the low temperature is greater. Consequently the solids density is lower. This is the result expected with no metallic compounds in the flame.

The black body temperature is higher with high temperature.

- (4) Of the materials added to the high temperature mixtures, shellac and polyvinyl chloride produce a much lower flame brightness than the others. Consequently, the black body temperature is also lower. That is to say, with these substances, it is possible to reduce the continuous spectrum intensity in the background to some extent. Judging only from these results, irrespective of the oxidizer used, the effect of shellac is in general the higher. Using chlorine or hydrogen chloride gas liberators, such as polyvinyl chloride, ammonium chloride and BHC, one gets a black body temperature 100–200 °C higher than when using shellac (with 20% composition). The flame permeability coefficient varies with the various compositions.

VIII. Conclusions

The line, band and continuous spectra entering the structure of the background spectrum of the light from the combustion of various basic compositions were studied, together with their causes. Among these, the main interfering factors in the colored light spectrum arose from the Na-D lines, from impurities in the materials used to make up the mixtures, and the continuous spectra arising from heated solid particles in the flame. Their intensity was especially high with the high temperature fuel.

To get a pure colored light it is necessary to counteract or reduce these effects. To get rid of the Na-D lines, the only method available is to make sure that the components are thoroughly purified. To get rid of the continuous spectra from solid particles in the flame, the addition of materials that liberate chlorine or hydrogen chloride gases are of practical use when dealing with high temperature flames. Also the addition of shellac and other organic materials is effective in reducing the temperature of the high temperature flames. (See author's note.)

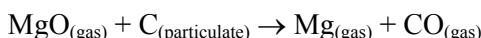
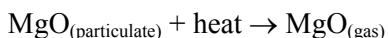
In concluding this report I would like to thank Mr. Yamamoto of Tokyo University, Technology Department for general guidance, and Mr. Makishima for great help in analysis of the spectra. Also for analysis of the raw materials I thank Mr. Takada and Mr. Hosotani.

Literature

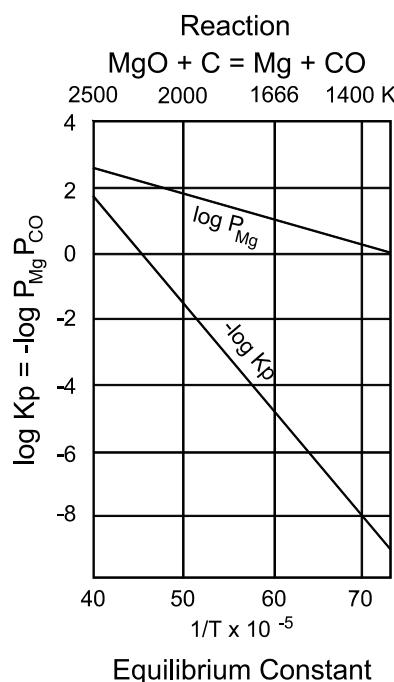
- 1) T. Shimizu, *Hanabi* (1957) p 57.
- 2) J.W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, IV (1923) p 300.
- 3) J.W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, II (1923) p 463.
- 4) Ibid. (2).

Author's Note

With later investigations it was confirmed that the continuous spectrum of MgO is eliminated by using an organic material (e.g., shellac, wood rosin, etc.) even when the material does not contain chlorine. This effect is not caused by decreasing the true (real) flame temperatures by the addition of the material. The reaction should be:



at high temperatures.



Reference

T. Shimizu, *Fireworks from a Physical Standpoint*, Part II, Pyrotechnica Publications (1983) p 88 and Photographs 129, 131, and 132 on p 78.
Handbook of Inorganic Chemistry (in Japanese), Gihodo Shuppan Co. (1990) p 1215.

Autobiography of a Pyrotechnist — Dr. Takeo Shimizu

(Continued from page 38)

Soon after I entered the preparatory course, the teacher read my paper as a superior style in a lesson of composition. I was very much delighted; however, such a case never came again in all my life at the Academy. I only once won at Judo with my friend, Mr. Kondo, who looked much tougher than me; however, I never won in competitions or games in all other cases. Therefore, even at present I have no passion for games of chance. After the preparatory course, I arrived at the Saseho Heavy Artillery Regiment in Nagasaki-ken. There I met Lieutenant K. Eguchi and other young officers. They were men of great diligence and would read books of tactics even on their horses. They did not like to spend time on worthless matters. After the duty of hard training, I was certainly changed into a more diligent young man when I returned to the Academy to study further in the regular course.

All of the students, called cadets, wore a uniform with shoulder-straps of sergeant and the gorget patches with the numbers of the regiment. They also seemed changed from the idle students in the preparatory course. I liked the regular course because I was not bothered by mathematics, physics, etc. I was good in the lessons of tactics, weapons, and surveying. In July 1933 I came down from the Academy at Ichigaya Hill with a diploma. I started again for my post with the Saseho Heavy Artillery Regiment and in November I was commissioned a sub-lieutenant. Young officers in the regiment were trained with cannon firing. When the black smoke from a shell was found before the target, we had to increase the range of the next shell so that it would fall behind the target. It might seem easy, but for me it was very difficult because I would



Takeo Shimizu, lieutenant at Saseho Heavy Artillery Regiment (1933).

suddenly forget the position of the black smoke. I was very disappointed and thought I might not be suitable as a company commander on a battlefield. I decided to change the direction of my future life and began the hard study of mathematics, physics, and chemistry in spare moments from my duty.

(Continued on page 102)

Part IV. Flame Spectra of Red, Yellow and Green Color Compositions

ABSTRACT

Flame spectra of red, yellow and green color compositions are examined under various conditions.

a. Red Flame

A red flame is produced by bands from strontium (Sr) salts. These bands consist of five main bands [i.e., α (6013), β (6203), γ (6300), δ (6428) and ε (6558)], where each number represents the wavelength of the maximum intensity in Angstroms (\AA). The influence of chlorine on the α band is quite different from the others, namely the α band is weakened by chlorine, whereas chlorine intensified the others, and this effect is greater with hydrogen chloride gas than with chlorine gas. This is very clearly observed especially in low temperature flames. The influence of strontium salts is very small. The effect of oxidizers that produce either chlorine or hydrogen chloride gas is quite remarkable. If we add ingredients that have chlorine, they can intensify each band only in high temperature flames. The effects of calcium (Ca) salts were also examined.

b. Yellow Flame

A yellow flame is produced by sodium (Na) salts. The spectrum consists of mainly Na-D lines, but in addition, a continuous spectrum from Na atoms appears between 5,800 and 6,100 \AA and makes the flame color rather white, especially at high flame temperatures.

c. Green Flame

Only BaCl bands can produce green flames when barium (Ba) salts are used as the color agents. Compositions without chlorine cannot produce green color because only BaO bands appear, giving white color to the flames. In the presence of chlorine both BaCl and BaO bands appear. The effect of chlorine or hydrogen chloride gas in a flame seem to weaken the BaO bands and to intensify the BaCl bands. The ef-

fect of chlorine gas is less than that of hydrogen chloride gas. And so, ammonium perchlorate produces a better green color than potassium perchlorate. Adding some kind of chlorine compound (chlorine donor) is also effective to intensify the green color.

1. Introduction

The author examined the spectra that should appear as the background of the colored flame spectra when the compositions contained no color agent in Part III of this study. In this section spectra were examined with the fundamental compositions of colored flames when they contained the color agents. The effects of chemicals used and the mixing ratios were confirmed, and methods of modifying the compositions were considered.

In this paper the author used symbols α , β , ... for the names of spectral bands. They did not come from spectroscopy, but they were used only for convenience sake.

2. Preparation of Chemicals for Samples and Instruments

The color agents used were as follows. The other chemicals were as described in Part III.

a) Red

Strontium carbonate: A water solution of purified strontium nitrate was added to ammonium carbonate, and the precipitate was washed with distilled water until the Nessler reagent reaction was invisible.

Strontium oxalate: A water solution of purified strontium nitrate was added to ammonium oxalate, and the precipitate was washed with distilled water until the Nessler reagent reaction was invisible.

Strontium chloride: A 12 N hydrochloric acid solution for chemical use was added to a quantity of slightly excess strontium carbonate, which was prepared by the above method; then the residual strontium carbonate was filtered out. The solution was vaporized and crystals of strontium chloride were obtained.

Strontium nitrate: A commercial item was purified by recrystallizing three times.

Calcium carbonate: Commercial item of precipitate.

b) Yellow

Sodium carbonate: Anhydrous commercial reagent.

Sodium oxalate: Commercial reagent of special class (>99.5% purity).

Sodium bicarbonate: Commercial reagent.

Sodium chloride: Commercial reagent of special class (>99.5% purity).

c) Green

Barium carbonate: A water solution of barium nitrate of commercial reagent of special class (>99.0% purity) was added to ammonium carbonate. The precipitate was filtered from the solution and washed with distilled water until the Nessler reagent reaction was invisible.

Barium oxalate: A water solution of barium nitrate of commercial reagent of special class (>99.5% purity) was added to ammonium oxalate. The precipitate was filtered from the solution and washed with distilled water until the Nessler reagent reaction was invisible.

Barium chloride: Commercial reagent of the first class (>95.0% purity).

Barium nitrate: Commercial reagent of special class (>99.0% purity).

Barium chlorate: Commercial item which was purified three times with distilled water.

The construction of the sample specimens, the instruments for the experiment, and the method of experiment were the same as those in Part III.

3.0 Flame Spectra for Red Flame Compositions

As the color agent, strontium salts or occasionally calcium salts have been used. In this paper mainly strontium salts were studied with only a cursory look at calcium salts.

3.1 Flame Spectra of Strontium Salts

The flame spectra obtained from several representative compositions are shown in Photo 1.

- | | |
|----------|--|
| No. 249: | Low flame temperature
75% ammonium perchlorate
15% shellac
10% strontium carbonate |
| No. 269: | Low flame temperature
75% potassium perchlorate
15% colophony
10% strontium carbonate |
| No. 130: | High flame temperature
33.3% strontium nitrate
66.7% magnesium |
| No. 131: | High flame temperature
30% strontium nitrate
60% magnesium
10% shellac |
| No. 132: | High flame temperature
30% strontium nitrate
60% magnesium
10% polyvinyl chloride |

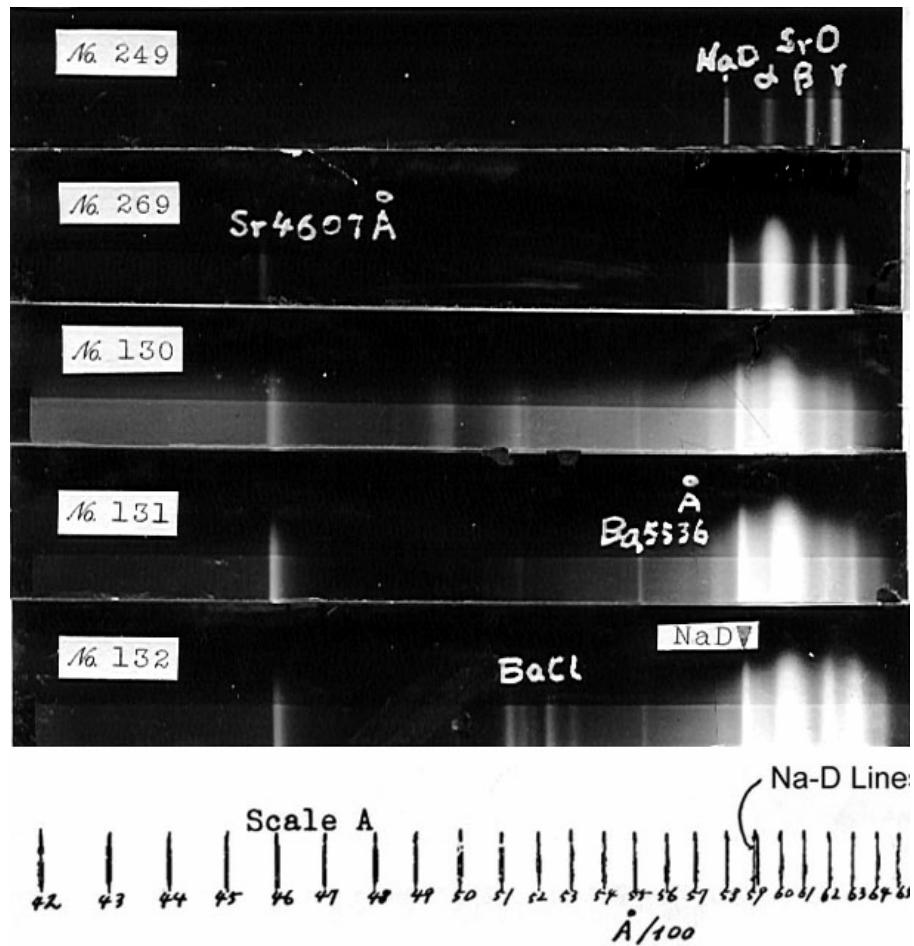


Photo 1. Flame spectra of strontium salts.

The main spectra observable in the five photographs are as follows:

1. *Sr 4607 Å (atomic spectrum)*: This line interferes with red. It is weak at low flame temperatures, but fairly strong at high flame temperatures. It is weaker than the SrO band and can be ignored.
2. *Na-D 5896 and 5890 Å (atomic spectra)*: These lines interfere with red. They come from impurities in the chemicals. These lines are present even when using oxidizers that have been purified. In general these lines appear stronger than the Sr 4607 Å.
3. *SrO band (molecular spectra)*: This band is very strong and the main source of red light. Five line groups were observed with almost the same wave intervals. The dry plate method was not sensitive enough for wavelengths greater than 6400 Å; it could not de-

tect two of them. The groups are shown with their shortest wavelength as follows:

SrO band	Å
α	6013
β	6203
γ	6300
δ	6428*
ε	6558*

* out of sensitivity range of the dry plate

The bands can be assumed to come from the SrO molecule because they were visible when the sample composition did not contain chlorine (Photo 1: Nos. 130 and 131).

4. *Ba lines or bands*: These come from a very small quantity of barium compound in the chemicals of the composition. These interfere with red.

Authors Note: After these experiments were completed in 1958, the author obtained A. G. Gaydon's paper (Monique Charton and A. G. Gaydon, "Band spectra emitted by strontium and barium in arcs and flames", *Proc. Phys. Soc.* 7-A (1956) p 520). They attributed the α band to SrOH and the β , γ , δ , and ε bands to SrCl. In the latter case, the BaCl molecule came not only from ammonium perchlorate, but also from potassium perchlorate, although in the latter case Cl or HCl could not be found in the flame. However, the author has adopted the physicist's judgment since that time, because he perceived that it was difficult to determine the structure of emitters with only a chemical experiment like in this paper. From this standpoint, the observed effects in this paper are confirmed as follows:

The α band comes from SrOH and is interfered with by Cl or HCl that is produced by NH_4ClO_4 and even by KClO_4 , especially at lower flame temperatures; however, at higher flame temperatures, the interference decreases.

The β , γ , δ , and ε bands come from SrCl. When no Cl or HCl is present in the flame, they do not appear (see Photo 2: No. 153).

At present, 1998, a question still remains in the author's mind as to why the spectra β or γ appeared in the non-chlorine flame like it is in the flame of non chloride compositions (see Photo 1: Nos. 130 and 131).

3.2 The Effects of Chlorine or Hydrogen Chloride on the SrO Bands

It could be thought that when Cl or HCl is present in the flame, the intensity of SrO bands would decrease. But it is not true. The influences of Cl or HCl are quite different for the α band than for the others: β , γ , δ , and ε . In Photo 1—No. 249 of the low flame temperature—was supplied with HCl gas from ammonium perchlorate in its flame. In this case the α band was very weak. On the contrary, in No. 269 the α band was very intense. The HCl or Cl gas in the flame was very weak because potassium perchlorate was the oxidizer. The flame of a potassium perchlorate composition does not produce HCl or Cl gas. This was experimentally confirmed

by blowing the flame onto the surface of water. Analysis of the water showed that it did not contain HCl or Cl.

If such a phenomenon with the α band occurred as a result of the effect of temperatures, the flame color would change from the flame base to the tip, however, such an effect was not observed.

On the contrary, at high flame temperatures, the intensity of the α band did not change as much with compositions. However, the intensity of the other bands was very weak when the flame contained no Cl or HCl gas, and very intense in the opposite case.

The δ and ε bands were not clearly photographed; however, they would have the same characteristics as β and γ by naked eye observation.

From the above observations it was thought that Cl and HCl are involved with the excitation of the SrO molecule. As a result, the α band was limited and the β , γ , δ , and ε bands were intensified. Comparison of the effects of Cl and HCl will be described later.

The limiting effect of the α band appeared more at low flame temperatures than at high flame temperatures.

Table 1. Influence of Oxidizer and Fuel Mixing Ratios.

Composition (40)	%
Ammonium perchlorate	x
Shellac	y
Strontium carbonate	10

No.	x%	y%	Oxygen balance	ω	Δ	v	L	E	CS	SrO band
217	50	40	-0.674	23.5	1.05	0.63	10	193	weak	slight
218	60	30	-0.402	25.7	1.16	0.83	20	264	strong	invisible
219	70	20	-0.130	26.7	1.20	0.99	10	107	strong	invisible
220	80	10	+0.142	27.7	1.26	2.46	1	4.1	weak	strong

Note: Oxygen balance is the excess or deficiency of oxygen in grams per 1 gram of oxidizer.

Symbol	Description (units)
ω	weight of sample composition (g)
Δ	loading density (g/cm ³)
v	burn rate (mm/sec)
L	flame length (cm)
E	light energy [candle power (Cd) × burn time (sec) ÷ ω]
CS	continuous spectrum

3.3 Low Temperature Red Flames

(1) The Effect of Oxidizer and Fuel Mixing Ratios

In Table 1 the oxygen balance is shown as the excess or lack of oxygen in grams for CO₂ oxidation of a 1 gram sample. CS is a continuous spectrum. The symbols are common in the following tables.

With the results from Part II plus Table 1, the continuous spectrum CS disappears at high flame temperatures with excess oxygen, and the SrO bands appear.

Table 2. Effects of Color Agents with Shellac as the Fuel.

Composition (41)	%
Ammonium perchlorate	75
Shellac	15
Color agent	10

No.	Color agent	Sr%	ω	Δ	v	L	E	α	β	$\alpha-\beta$	CS
249	Strontium carbonate	5.94	27.3	1.23	1.10	13	122	4.4	5.0	-0.6	0
250	Strontium oxalate	4.98	28.1	1.29	0.94	6	63	4.0	4.8	-0.8	0
251	Strontium chloride	3.29	28.3	1.27	1.02	8	79	3.0	4.3	-1.3	0
252	Strontium nitrate	4.14	27.2	1.22	1.32	13	103	4.4	5.3	-0.9	0

(2) The Effects of Various Color Agents

In Table 2 Sr% means the content of strontium in the mixture denoted by weight percentage. α , β and CS are the maximum blackening length i by light beams through the light wedge on the photograph in mm (with CS being the longest). The other symbols and definitions are the same as in Part II or III.

All color agents have about the same effect. Only the presence of HCl gas makes the α band weak. With the naked eye these looked somewhat white. This comes from the strong Na-D lines from impurities and the low density of Sr ions.

The width of the α band, $\Delta\lambda$, was about 70 Å in every experiment.

Comparing Table 3a with Table 2, we see that the α band intensities in Table 3a are higher than those in Table 2 and the widths of the α bands in Table 3a are larger than those in Table 2 ($\Delta\lambda$ = about 130 Å). In Table 3a the spectral bands are covered by the continuous spectrum CS(C) or CS(K). The flames of Composition (42) looked more pink than those of Composition (41). Light intensities of the flames of Composition (42) were stronger than those of Composition (41).

In the above experiment no other special spectrum other than those of Sr molecules in Photo 1 was found. Namely, strontium salts do not give different spectra caused by negative ions of carbonate, oxalate, chloride or nitrate.

Table 3a. Effect of Color Agents with Colophony as the Fuel.

Composition (42)	%
Potassium perchlorate	75
Colophony	15
Color agent	10

No.	Color agent	Sr%	ω	Δ	v	L	E	α	β	$\alpha-\beta$	CS
269	Strontium carbonate	5.94	31.6	1.50	1.46	118	687	7.9	6.8	1.1	3.6
270	Strontium oxalate	4.98	32.2	1.54	1.33	67	426	7.5	6.5	1.0	3.0
271	Strontium chloride	3.12	31.7	1.47	0.88	32	815	7.6	6.7	0.9	2.2
272	Strontium nitrate	4.14	31.6	1.47	1.77	960	2680	9.5	7.8	1.7	5.0

Table 3b. Effect of the Addition of HCl or Cl Producing Substance to the Composition.

Composition (43)	%
Potassium perchlorate	70
Colophony	10
Strontium carbonate	15
Fuel addition	5

No.	Fuel additive	Cl %	HCl %	ω	Δ	ν	L	E	α	$\Delta\lambda_\alpha$	β	$\Delta\lambda_\beta$
233	—	—	—	30.0	1.41	1.95	128	593	5.7	4.0	3.1	1.0
234	Polyvinyl chloride	—	2.92	31.7	1.50	1.81	160	752	5.4	3.9	3.6	1.5
235	BHC	3.66	—	31.2	1.52	1.41	58	342	3.7	2.9	2.2	1.0
236	Ammonium chloride	—	3.34	31.9	1.54	1.35	58	355	4.4	3.2	2.6	0.8

Therefore, selection of the color agent from the various salts may vary depending on the purpose; however, it should be noted that the value of E is the largest with strontium nitrate. However, from the standpoint of moisture resistance, strontium carbonate is the best. The relationship between the Sr density and E was not found.

(3) The Effect of the Addition of HCl or Cl Producing Substance to the Composition

The flame spectra was photographed after adding HCl or Cl producing substances to the composition, and the effects were examined.

$\Delta\lambda_\alpha$ is the width of the α band, and $\Delta\lambda_\beta$ is the width of the β band on the dry plate in mm.

In Table 3b, compared with Composition (41) in Table 2, the effect of HCl or Cl was not very strong; it may be because their density in the flame is less than when using ammonium perchlorate.

Table 4. Effect of Additives at High Flame Temperatures.

Composition (44)	%
Strontium nitrate	30
Magnesium	60
Additive	10

No.	Additive	Sr%	Cl%	HCl%	ω	Δ	v	L	E	α	β	γ	CS	α -CS
130	—	13.8	—	—	8.8	1.16	24.2	48000	21800	7.7	6.4	5.8	6.3	1.4
131	Shellac	12.4	—	—	8.3	1.09	3.59	4800	15600	8.0	6.9	5.8	4.2	3.8
132	Polyvinyl chloride	12.4	—	5.83	8.2	1.08	8.43	9600	13500	7.7	7.9	7.0	5.0	2.7
137	BHC	12.4	7.31	—	8.3	1.11	11.9	28800	27800	7.4	7.6	7.5	5.3	2.2
138	Hexachloroethane	12.4	8.99	—	8.3	1.10	24.0	32000	15400	7.1	6.7	7.8	4.5	2.6
139	Ammonium chloride	12.4	—	6.69	8.7	1.14	6.93	12800	20600	8.5	7.9	7.4	5.0	2.9
140	Magnesium chloride	12.4	3.49	—	8.2	1.09	8.00	12800	18700	7.9	7.4	7.8	5.5	2.4
147	Ammonium sulfate	12.4	—	—	8.4	1.10	28.3	32000	12300	8.0	7.0	6.1	6.1	0.9
148	Camphor	12.4	—	—	8.6	1.11	21.3	32000	14400	7.6	7.0	6.1	6.0	1.0

3.4 High Temperature Red Flames

The intensities of the SrO band spectra of high temperature flames are generally much higher than those of low temperature flames. Of the spectra, the α band is the strongest ($\Delta\lambda$ = about 130 Å). Therefore, it has the most powerful influence upon the red color.

(1) The Effects of Fuels

Table 4 shows the results of experiments for high flame temperature compositions.

α band: The strength of the α band was always high with almost no difference whether or not the compositions contained Cl or HCl compounds. Of these additives, however, ammonium chloride gave the strongest value.

β and γ bands: The effects were different for the compositions that contained Cl or HCl compound and those that did not. In the former case, the β band was almost as strong as the α band. (Compare Nos. 131 and 132 in Photo 1.)

Continuous spectrum CS: This comes from solid particles of MgO and interferes with the color of the flame. Shellac was the most effective in removing this spectrum, and then the chlorine compounds in the order of ammonium chloride, polyvinyl chloride, hexachloroethane,

magnesium chloride, and BHC. Therefore, reducing the effect of the continuous spectra was more effective when using HCl compounds than Cl compounds.

Other interfering spectra: Most of the interfering lines came from impurities contained in the materials of the composition. The following were the most intense: Na-D 5896, 5890, Sr 4607, and Ba 5535.5 Å. These lines always appeared regardless of type of fuel or additive. The Na-D lines were always intense. The BaCl band appeared clearly even when the additives were chlorine compounds (Photo 1: No. 132). These effects were especially intense with polyvinyl chloride and ammonium chloride. This came from the barium impurity in strontium nitrate.

Table 5. Effect of Oxidizer and Additives.

Composition (45)	%
Oxidizer	20
Magnesium	60
Strontium carbonate	10
Additives	10

No.	Oxidizer	Additive	Sr%	Cl%	HCl%	ω	Δ	v	L	E	α	β	γ	CS
149	NH_4ClO_4	—	6.60	0.00	6.69	8.7	1.14	8.81	24000	264000	8.3	7.9	7.7	6.8
150	NH_4ClO_4	Polyvinyl chloride	5.94	0.00	12.15	8.4	1.10	8.08	4800	100800	6.7	7.1	6.6	4.5
151	KClO_4	—	6.60	0.00	0.00	9.0	1.19	16.0	40000	240000	8.4	8.0	7.4	5.7
152	KClO_4	Polyvinyl chloride	5.94	0.00	5.83	9.0	1.18	5.11	4800	91200	6.9	7.2	7.0	4.7
153	KNO_3	—	6.60	0.00	0.00	9.7	1.26	7.54	8000	104000	7.7	0.0	0.0	5.2
154	KNO_3	Polyvinyl chloride	5.94	0.00	5.83	7.0	1.03	4.90	4800	96000	6.8	6.1	5.0	3.5
155	KNO_3	Ammonium chloride	5.94	0.00	6.69	8.6	1.10	5.00	4800	96000	7.4	7.3	6.3	4.4
156	KNO_3	Shellac	5.94	0.00	0.00	8.1	1.05	3.38	800	23200	6.6	0.0	0.0	3.9

Photo 2 corresponds to Table 5.

The effects of Composition (45) in Table 5 show the same tendencies as those of Composition (44) in Table 4. In particular, it must be noted that the β and γ bands did not appear; only the α band appeared, when there was no Cl or HCl as in the case of KNO_3 in Composition Nos. 153 and 156. At high flame temperatures, the effects of Cl are not distinguishable.

(2) The Effects of Various Oxidizers

From Tables 4 and 5 we know that the addition of Cl- or HCl-producing material like polyvinyl chloride or ammonium perchlorate or potassium perchlorate do not intensify the α , β , and γ bands, but rather it makes the bands weak. However, it is effective in diminishing the continuous spectra which interferes with the flame color (Photo 2). Therefore, from a practical standpoint, the addition of such a material may always be useful.

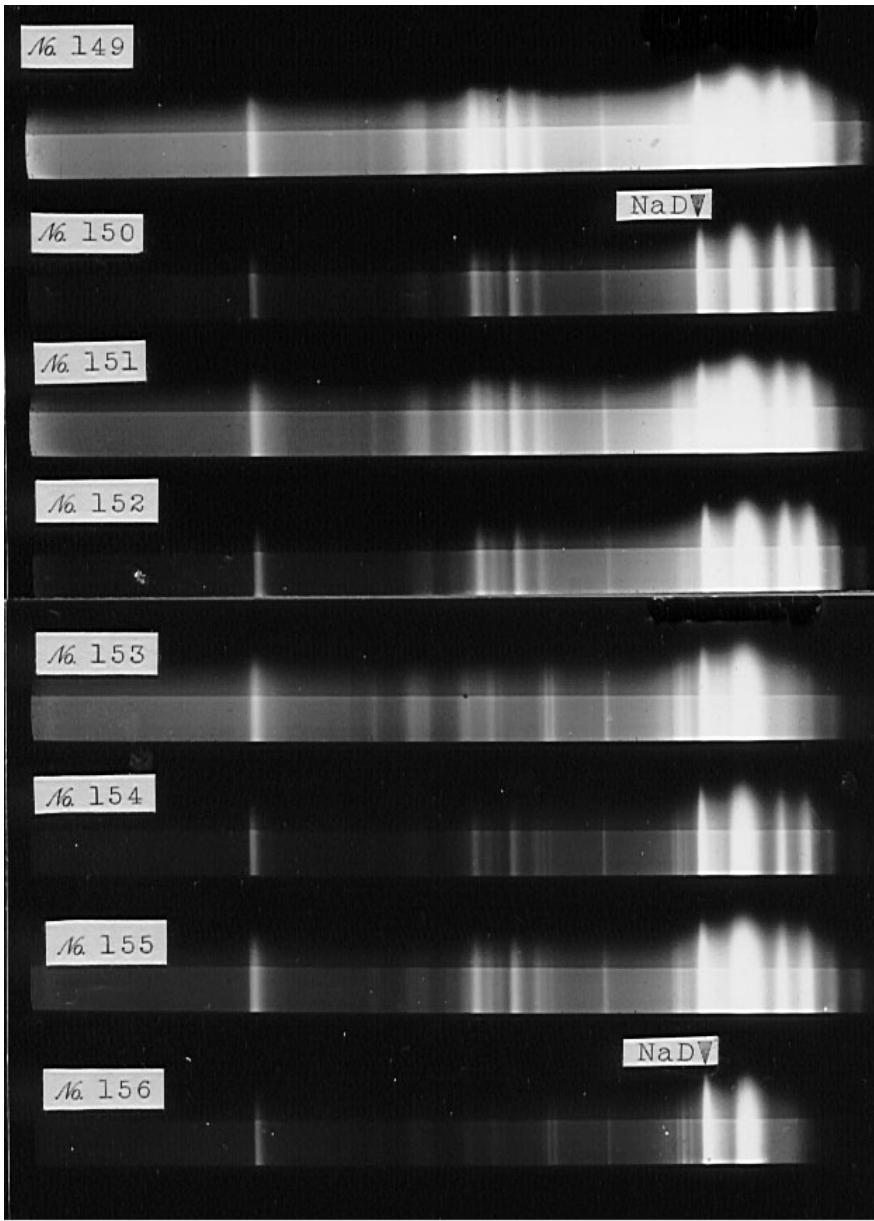


Photo 2. The effect of various oxidizers and additives on red flame spectra at high temperatures.

Table 6. Effect of Changing Magnesium and Oxidizer Mixing Ratios.

Composition (46)		%
Strontium nitrate		x
Magnesium		y

No.	x%	y%	ω	Δ	v	L	E	α	β	γ	CS
129	50	40	9.6	1.25	19.6	32000	167000	7.6	6.7	5.0	7.0
130	30	60	8.8	1.16	24.2	48000	318000	7.7	6.5	5.4	5.0

Composition (47)		%
Ammonium perchlorate		x
Magnesium		y
Shellac		10
Strontium nitrate		10

No.	x%	y%	ω	Δ	v	L	E	α	β	γ	CS
165	60	20	9.0	1.17	2.65	320	2050	5.5	6.4	5.7	0.0
166	30	50	8.2	1.07	6.53	3200	12130	8.1	8.4	8.2	4.4

(3) *The Effects of the Mixing Ratio of Magnesium to Oxidizers*

Flame temperatures are affected by the mixing ratio of magnesium to oxidizers (see Part II). Accordingly, the spectra may be also fairly affected by the ratio.

For the non-chloride Composition (46) there was no notable difference between the intensities of α , β and γ bands. The higher strontium nitrate content produced a more intense continuous spectra. It may be thought that the higher strontium nitrate content may give higher flame temperatures (see Part II). With the naked eye, the flame of No. 130 was redder than that of No. 129.

Of the Compositions (47) that contained ammonium perchlorate, No. 165 did not produce continuous spectra, and the red was weak like that of low temperature flames. No. 166 produced an intense red; however, the intensity of the continuous spectra was also high.

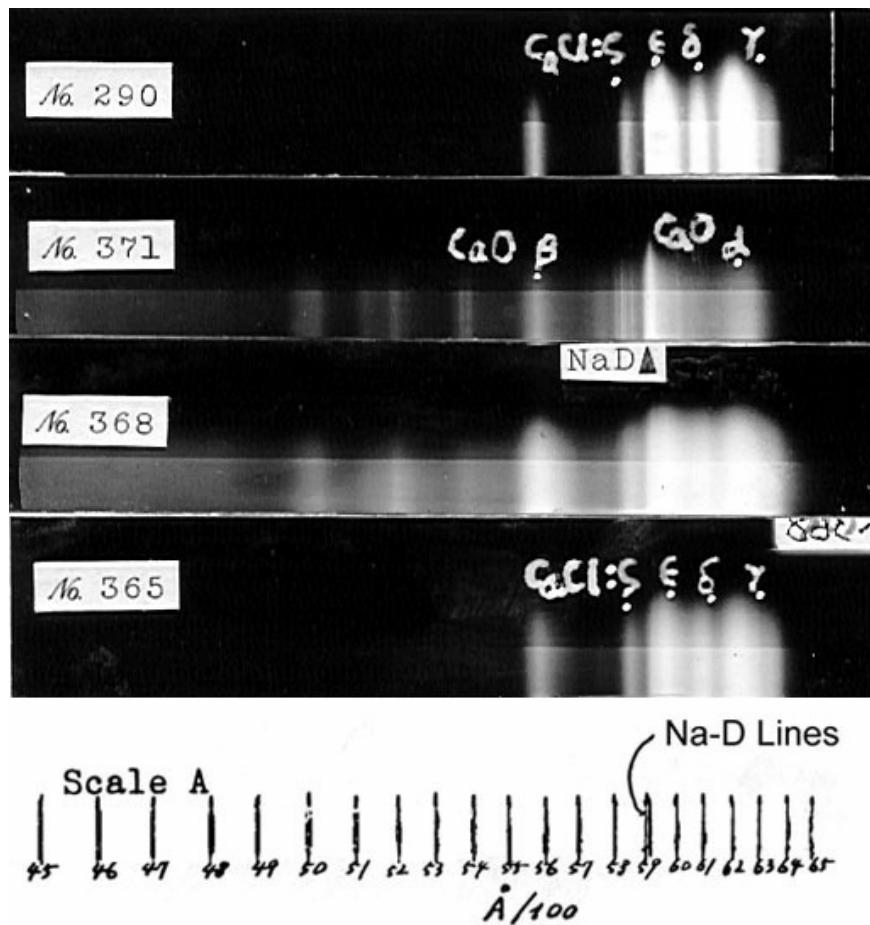


Photo 3. Flame spectra produced by calcium salts.

3.5 The Flame Spectra from Calcium Salts

The calcium flame spectra produced by representative compositions are shown in Photo 3.

Compositions:

No. 290: Low flame temperature
75% ammonium perchlorate
15% shellac
10% calcium carbonate

No. 371: High flame temperature
20% potassium nitrate
70% magnesium
10% calcium carbonate

No. 368: High flame temperature
22.2% potassium perchlorate
66.6% magnesium
11.2% calcium carbonate

No. 365: High flame temperature
20% ammonium perchlorate
60% magnesium
10% polyvinyl chloride
10% calcium carbonate

The calcium flame spectra in Photo 3 are as follows:

(1) *CaO band*: This was clearly observed when using the non-chlorine Composition No. 371. It consists of two bands: α (6150–6270 Å, $\Delta\lambda = 120$ Å) and β (5500–5580 Å, $\Delta\lambda = 80$ Å). When we wish to obtain red flame, the β band interferes with red. These bands always appear in compositions with or without chlorine and are the main calcium spectra.

(2) *CaCl band*: This appeared only with compositions that contained chlorine.

Table 7. Effect of Oxidizers on Calcium Spectra.

Composition (48)		%	Composition (49)		%
Ammonium perchlorate		22	Potassium chlorate		75
Magnesium		66	Shellac		15
Calcium carbonate		12	Calcium carbonate		10

Composition	No.	ω	Δ	L	v	E	α	β	γ	δ	ϵ	ζ
(48)	371	9.0	1.18	3200	5.71	54400	4.7	4.3	—	—	—	—
(49)	290	26.6	1.16	11.0	1.08	112	7.3	4.2	4.6	5.5	6.8	4.5

γ	6294–6360 Å	$\Delta\lambda = 66 \text{ Å}$
δ	6030–6078 Å (two)	$\Delta\lambda = 48 \text{ Å}$
ϵ	5915–5986 Å	$\Delta\lambda = 71 \text{ Å}$
ζ	5803–5838 Å	$\Delta\lambda = 35 \text{ Å}$

The ϵ and ζ bands interfere with red. The intensity of ϵ band is large.

When using calcium salts as red color agents, the results can be nearly red flames or yellowish flames depending on the intensity and width of the bands. Therefore, one should select the composition according to the purpose to obtain a good effect. Regardless, the intensity of the β band is the problem.

3.6 The Effects of Various Compositions on Calcium Spectra

(1) The Effects of Various Oxidizers

Examination of Table 7 and comparing with Photo 3, Composition (48) is a high temperature flame and a non-chlorine mixture. The flame

appears yellow. This is caused by the high intensity of the both α and β bands. Composition (49) produces a slightly red flame. This composition also contained chlorine; however, the β band was smaller than the α band, and it produced γ , δ , ϵ , and ζ bands. (It is impossible to compare the data of Compositions (48) and (49) because the distance between the flame and the spectroscope were different. Also the quantities of the sample were different.)

In examining Table 8, the bands of CaO (α and β) both appeared. Of the CaCl bands, only ϵ and ζ bands appeared clearly in No. 376 at low flame temperature. γ , δ , and ϵ bands all appeared in No. 368 at high flame temperature. These phenomena make the flame reddish colored at low temperatures and yellowish at high temperatures. These phenomena are mainly concerned with the ϵ and ζ bands. Therefore, the effect of potassium perchlorate may be between ammonium perchlorate and potassium nitrate.

Table 8. Effect of Varying Fuel and Oxidizer on Calcium Spectra.

Composition (50)		%
Potassium perchlorate		x
Fuel		y
Calcium carbonate		10

No.	$x\%$	Fuel	$y\%$	ω	Δ	v	L	E	α	β	γ	δ	ϵ	ζ	CS
376	75	Shellac	15	32.4	1.44	3.60	—	—	7.2	5.8	0	0	6.4	3.6	0
368	20	Magnesium	60	9.5	1.24	9.80	24000	25270	7.8	5.0	5.3	6.7	7.2	6.1	4.5

Table 9. Experiments Using Polyvinyl Chloride as the Additive.

Composition (51)	%
Oxidizer	20
Magnesium	60
Polyvinyl chloride	10
Calcium carbonate	10

No.	Oxidizer	ω	Δ	v	L	E	α	β	γ	δ	ε	ζ	CS
365	NH_4ClO_4	8.5	1.13	4.80	11200	224000	7.0	5.8	4.8	6.0	7.0	5.5	4.0
366	KClO_4	9.0	1.24	5.76	8000	136000	6.4	5.9	4.7	6.4	6.5	6.3	4.4
367	KNO_3	8.5	1.11	4.26	2400	55200	6.2	5.6	3.0	6.1	5.7	6.3	4.0

(2) The Effect of Fuels

The three compositions, which had different oxidizers, each perfectly produced the CaO (α and β) and CaCl (γ , δ , ε , and ζ) bands. Therefore, in this case, the addition of the Cl compound increases the interference and makes the flame yellowish.

4.0 Flame Spectra with Yellow Flame Compositions

To obtain yellow flames, sodium salts were used as the additives.

4.1 Flame Spectra Produced by Sodium Salts

Observable lines were Na-D lines and Na 5688 Å. The latter was very weak when compared to the former. The main yellow light came from the Na-D lines.

Na-D lines: Always very strong and easily reversible. They absorb light of the same wavelength from continuous spectra. They emit the same light with no change in the wavelength and with an intensity that depends on the flame temperature. However, when using sodium compounds as an additive, a continuous spectrum appears on both sides of the Na-D lines and the Na-D lines appear dark as they are absorbing

lines. The higher the flame temperature, the wider the wave range and the stronger the intensity. Therefore, the color of the flame looks yellow at low temperatures, and somewhat red or white at high temperatures. Photo 4 shows the yellow flame spectra.

No. 224: Low flame temperature:
80% ammonium perchlorate
10% shellac
10% sodium carbonate

No. 274: Low flame temperature:
75% potassium perchlorate
15% colophony
10% sodium oxalate

No. 178: High flame temperature:
47.1% potassium perchlorate
35.3% magnesium
11.8% polyvinyl chloride
5.8% sodium oxalate

No. 203: High flame temperature:
20% potassium nitrate
60% magnesium
20% sodium carbonate

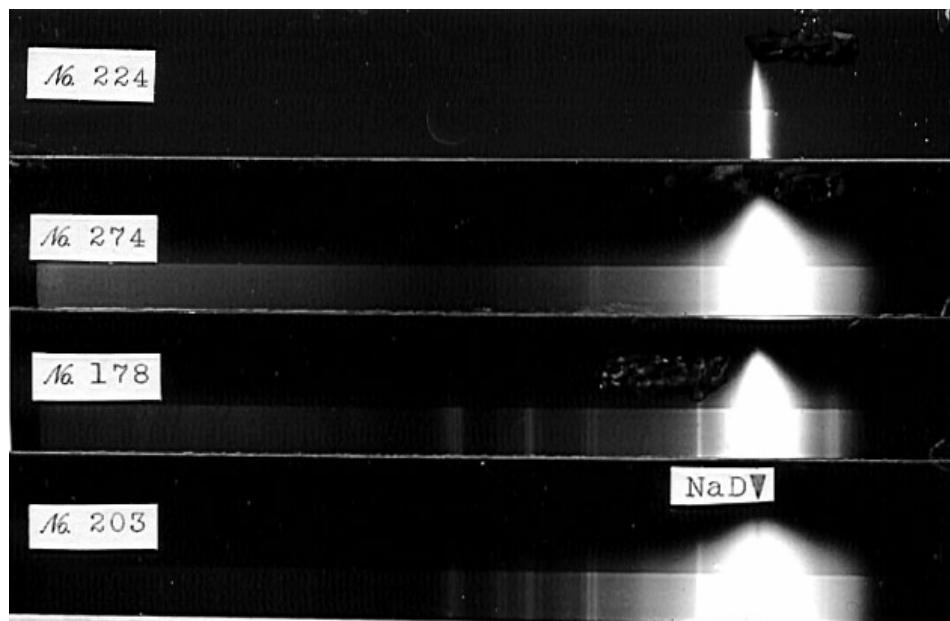


Photo 4. Flame spectra with sodium salts.

4.2 Low Temperature Yellow Flames

(1) The Effect of Mixing Ratios of Oxidizers and Fuels

In Table 10 the definition of the oxygen balance is the same as in Table 1. CS(D) denotes the maximum height of the Na continuous spectrum that was photographed through the prism.

The intensity of Na-D lines is highest with

Nos. 223 and 224, and in other cases decreased with decreasing quantities of x . This may be caused by flame temperature decreasing. In these compositions the CS(D) did not appear, which may also be caused by the low flame temperatures.

Table 10. Influence of Mixing Ratios of Oxidizers and Fuels.

Composition (52)	%
Ammonium perchlorate	x
Shellac	y
Sodium nitrate	10

No.	$x\%$	$y\%$	Oxygen balance	ω	Δ	v	L	E	D	CS(D)
221	50	40	-0.674	28.7	1.33	1.8	10	53.0	5.5	0
222	60	30	-0.402	24.2	1.09	2.5	10	47.5	5.5	0
223	70	20	-0.130	25.7	1.16	2.3	10	47.1	6.1	0
224	80	10	+0.142	25.8	1.15	2.5	2	9.3	6.0	0

Table 11. Effects of Color Agents and Oxidizers.

Composition (53)	%
Potassium perchlorate	75
Shellac	15
Color agent	10

No.	Color agent	Na %	ω	Δ	v	L	E	D	$\Delta\lambda_1$	$\Delta\lambda_2$
273	Sodium carbonate	4.34	32.5	1.45	?	82	—	7.00	143	227
274	Sodium oxalate	3.43	31.0	1.40	1.00	80	730	7.40	160	202
275	Sodium chloride	3.93	32.2	1.48	0.60	61	881	7.00	108	167
276	Sodium bicarbonate	2.74	32.0	1.46	0.80	64	720	6.60	35	187

(2) *The Effects of Various Color Agents and Oxidizers*

In Table 11, $\Delta\lambda_1$ and $\Delta\lambda_2$ are the widths of the continuous spectrum in Å.

$\Delta\lambda_1$ is from Na-D to shorter wavelengths, and $\Delta\lambda_2$ is from Na-D to longer wavelengths. In Table 11 the intensities of the Na-D lines were similar to each other in the case of such small densities.

The continuous spectrum CS(D) always extended towards longer wavelengths rather than shorter. Therefore, when using potassium perchlorate, which always produces a continuous spectrum, the flame looks reddish. When using ammonium perchlorate, the flame looks pure yellow.

4.3 High Temperature Yellow Flames

(1) *The Effect of Mixing Ratios of Oxidizers and Fuels*

In Table 12, as the ratio of magnesium to oxidizer was decreased, the intensity of Na-D did not change very much; however, the width $\Delta\lambda_1 + \Delta\lambda_2$ changed substantially. This caused a color change of the flame. This effect on the high flame temperature composition is not seen in Table 11, where no continuous spectra appear due to the suppression of HCl in the flame.

Table 12. Effect of Oxidizer and Fuel Mixing Ratios.

Composition (54)	%
Ammonium perchlorate	x
Magnesium	y
Shellac	10
Sodium carbonate	10

No.	x%	y%	Na%	ω	Δ	v	L	E	P	$\Delta\lambda_1$	$\Delta\lambda_2$
167	60	20	4.34	8.7	1.13	1.40	1500	12100	8.0	87	108
168	30	50	4.34	8.2	1.07	?	?	?	7.0	143	207

Table 13. Effect of Color Agents.

Composition (55)	%
Potassium perchlorate	47
Magnesium	35
Polyvinyl chloride	12
Color agent	6

No.	Color agent	Na %	ω	Δ	v	L	E	D	$\Delta\lambda_1$	$\Delta\lambda_2$
177	Sodium carbonate	2.60	9.0	1.22	3.67	2400	6530	7.1	66	260
178	Sodium oxalate	2.06	9.1	1.25	3.96	3200	8080	7.1	66	160
179	Sodium chloride	2.36	9.2	1.27	4.09	3200	7826	7.0	66	125
180	Sodium bicarbonate	1.64	9.0	1.25	4.09	2400	6386	7.0	66	125

Composition (56)	%
Sodium nitrate	20
Magnesium	60
Color agent	20

No.	Color agent	Na%	ω	Δ	v	L	E	D	$\Delta\lambda_1$	$\Delta\lambda_2$
203	Sodium carbonate	8.68	9.0	1.22	12.9	16000	12440	absorbed	141	190
204	Sodium chloride	7.86	8.5	1.14	8.5	16000	18800	absorbed	147	198

(2) The Effect of Various Color Agents

In Table 13, there is hardly any difference between the effects produced with various color agents.

Adding color agents generally makes flame temperatures lower and the width of the flame narrower. Other effects are not notable.

5.0 Flame Spectra with Green Flame Compositions

For making green flame barium salts are used. Boric acid also makes green flame, but the intensity of the green is not as high as the barium effect, and it has been removed from firework use.

5.1 Flame Spectra with Barium Salts

The flame spectra obtained from the burning flame of a composition that contains barium salts:

(1) *Ba line 5535.5 Å*: slightly yellow, always appears clearly, but the intensity is relatively low.

(2) *Ba line 5778 Å*: yellow, hardly visible at high temperatures.

(3) ? 6100 Å: orange, but the intensity is low.

(4) *BaCl band 4995 (blue) ~ 5350 (orange) Å*: has a complex structure as seen Figure 1(a).

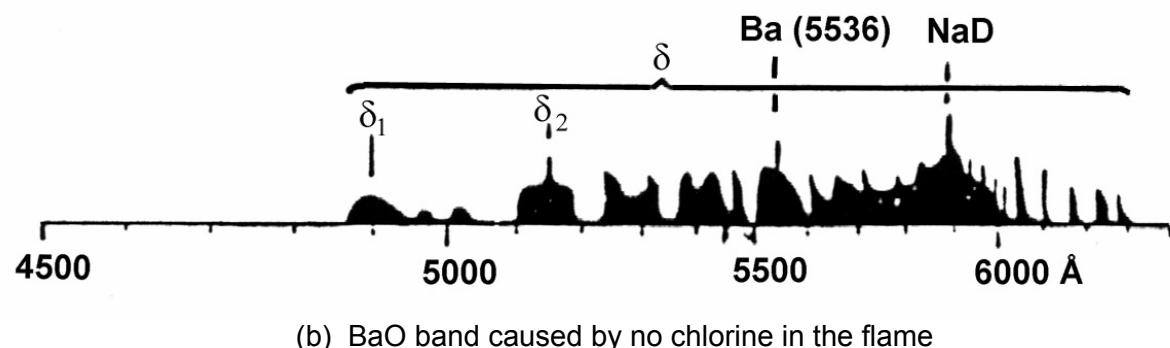
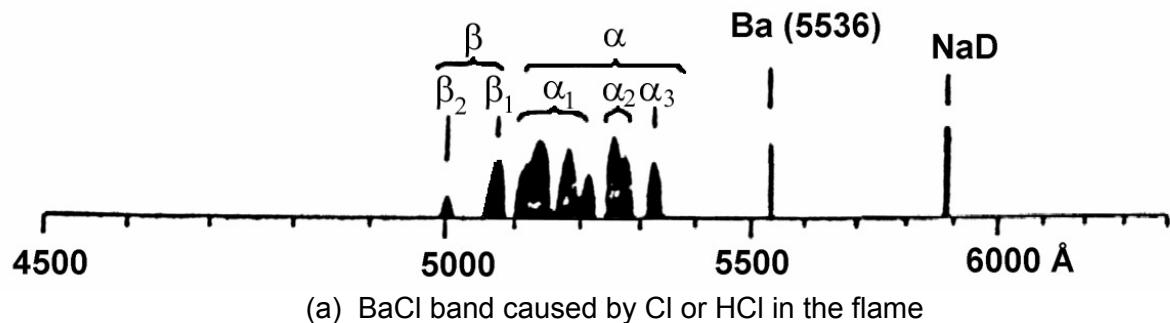


Figure 1. Structure of barium flame spectra.

α band (5097–5341 Å): A group of bands that play the main role in green. They do not appear when the composition does not contain chlorine compounds. Cl or HCl in the flame causes a high emission of this band. As seen in Figure 1(a), it consists of three bands.

α_1 (5097–5209 Å): A group of four bands. The most intense band is at 5122–5150 Å, with the maximum at 5139 Å. The other bands are weaker.

α_2 : (5238–5279 Å): Looks like one above another. One band has the same intensity as that of α_1 .

α_3 : (5303–5341 Å): It looks one band. The intensity is a little lower than α_1 or α_2 bands.

β (4994–5061 Å): It looks like two bands. The intensity of the 5061 Å band is stronger than the other. Comparing the bands, they are weaker than the α bands.

(5) BaO band (4854–6330 Å): In this paper it is named δ band. A group of many sawtooth-shaped bands which severely interfere with green. When no Cl or HCl is present, the intensity is very high, but at high concentrations of Cl or HCl it disappears (see Figure 1(b)). At 4854–4900 Å a dim, small wide band is observed. In this paper the intensity of this band represents the intensity of the BaO band.

(6) Continuous spectrum CS: This comes from high temperature barium oxide particles in the flame and strongly interferes with green. As described later, it is possible to weaken this by adding shellac or a chlorine compound to the composition. In this paper it is noted with the maximum intensity i .

(7) $Na-D$ (5896–5890 Å): These come from impurities in the component chemicals of the composition. Especially intense in high temperature flames, these are also an intense interfering line.

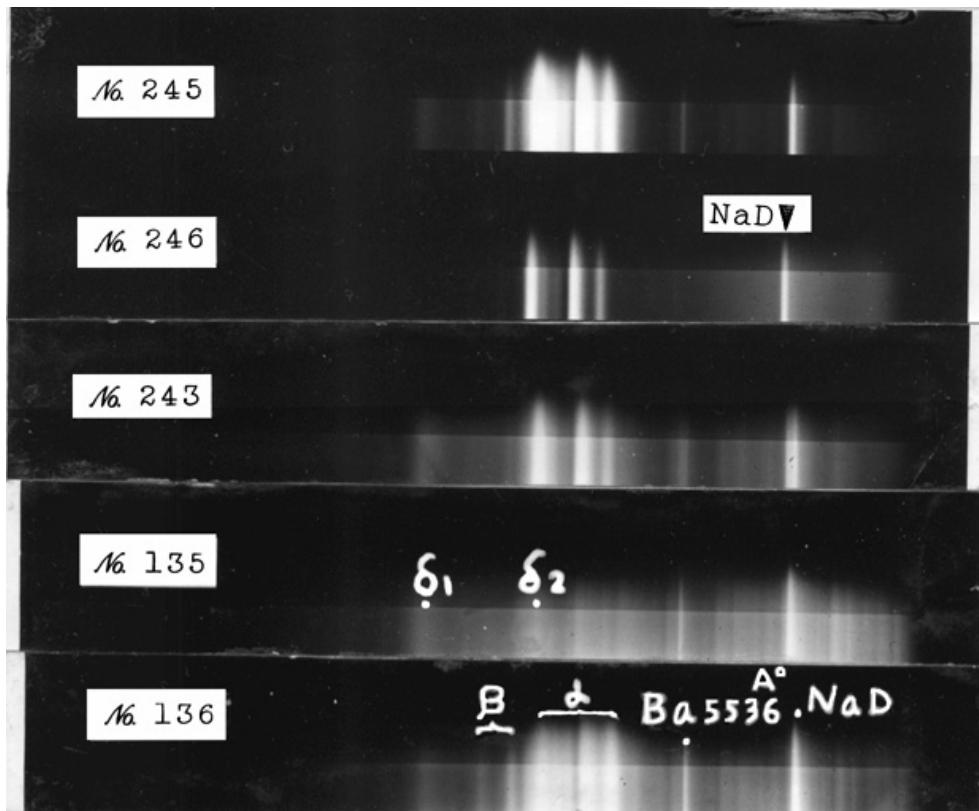


Photo 5. Flame spectra from barium salts.

No. 245: Low flame temperature
80% barium chlorate
20% shellac

No. 246: Low flame temperature
50% ammonium perchlorate
30% barium nitrate
20% shellac

No. 243: Low flame temperature
50% potassium perchlorate
30% barium nitrate
20% colophony

No. 135: High flame temperature
50% barium nitrate
40% magnesium
10% shellac

No. 136: High flame temperature
50% barium nitrate
40% magnesium
10% polyvinyl chloride

Table 14. Effect of Oxidizer and Fuel Mixing Ratios.

Composition (57)		%
Ammonium perchlorate	x	
Shellac	y	
Barium carbonate	10	

No.	x%	y%	Oxygen balance	ω	Δ	v	L	E	α_1	α_2	β	δ	Na-D	CS
225	50	40	-0.674	25.2	1.12	1.73	10	65.9	0.0	0.0	—	—	3.0	3.0
226	60	30	-0.402	25.7	1.16	2.28	15	72.4	weak	weak	—	—	3.8	3.2
227	70	20	-0.130	27.0	1.21	1.90	10	55.6	2.4	3.3	—	—	3.8	2.0
228	80	10	+0.142	30.0	1.33	2.84	1	3.4	4.0	4.5	—	—	3.8	0.0

5.2 Low Temperature Green Flames

(1) The Effect of Mixing Ratios of Oxidizer and Fuel

In Table 14, when the ratio of x/y was 50/40, only the continuous spectrum appeared. When the ratio was 70/20, the continuous spectrum began to diminish and the BaCl band began to appear. At 80/10, only the BaCl band remained, and a green flame was obtained. In this case the α band appeared with a high intensity, and the BaO δ band was very weak.

(2) The Effect of Barium Nitrate or Barium Chlorate as an Oxidizer and Color Agent

Barium nitrate or barium chlorate has been used to produce green for a long time. However, barium nitrate was mixed with other oxidizers, potassium perchlorate or ammonium perchlorate, because it does not burn smoothly when used by itself.

In Table 15, both compositions produced good green flames; however, the green of Composition No. 246 was better than that of Composition No. 247. Perhaps this was because the interfering band did not appear. Namely, when the x/y ratio is less than 30/50, the influence of the δ band becomes larger to make the flame color more whitish.

Table 15. The Influence of Barium Nitrate/Ammonium Perchlorate Oxidizer Mixing Ratios.

Composition (58)		%
Ammonium perchlorate	x	
Barium nitrate	y	
Shellac	20	

No.	x%	y%	HCl%	ω	Δ	v	L	E	α_1	α_2	α_3	NaD	Ba (5536 Å)	δ	CS
246	50	30	15.5	28.3	1.26	0.93	13	142	4.7	5.0	4.2	4.7	0	0	weak
247	30	50	9.3	31.6	1.43	0.80	6	67	5.4	5.9	4.8	4.7	weak	weak	weak

Table 16. The Influence of Barium Nitrate/Potassium Perchlorate Oxidizer Mixing Ratios.

Composition (59)	%
Potassium perchlorate	x
Barium nitrate	y
Colophony	20

No.	x%	y%	ω	Δ	ν	L	E	α_1	α_2	α_3	β	δ	CS
241	30	50	31.6	1.54	?	19	?	6.2	6.2	5.7	0	4.9	weak
242	40	40	31.8	1.52	?	19	?	6.3	6.5	6.0	0	4.4	weak
243	50	30	32.0	1.49	0.67	32	405	6.4	6.8	5.7	0	4.8	stronger
244	60	20	31.6	1.46	1.19	58	424	7.0	7.5	5.8	0	5.4	strong

In Table 16, No. 241 and 242 did not burn well. As the x/y ratio increased, the intensity of the α band increased. In all cases the δ band appeared intense. It was especially large when the x/y ratio was 60/20. Potassium perchlorate as an oxidizer was not as effective in decreasing the intensity of the δ band when compared to the effects of ammonium perchlorate as in Table 15. Namely, it shows that HCl in the flame is effective in decreasing the band. (When the flame of Composition (59) was blown into a beaker of distilled water, Cl or HCl was not detected in the water.) Composition (59) did not contain enough Cl or HCl in the flame to decrease the δ band. Therefore, the flame looked whitish due to the effect of mixing α and δ bands. If Composition (59) is not avoidable, the ratio of x/y should be 40/40 or 50/30.

In this case another continuous spectrum from potassium atoms appears and it interferes with the green.

Next using an oxidizer that produces no HCl was examined, while using a material that produces HCl like polyvinyl chloride.

The flame spectra of Composition (60) is shown in Photo 6. HCl gas in the flame decreased the α band and the β band appeared (compare with Photo 5: No. 243). However, a carbon continuous spectrum CS(C) appeared, which had the highest intensity near the Na-D lines, and the flame looked white with the naked eye. In this case the value of oxygen balance with CO_2 oxidation was -0.08 g per 1 gram of the composition. It could be said that at low temperatures, when a material like polyvinyl chloride is added, the carbon content results in generation of continuous spectra to interfere with green. The type of additives and the composition should be well planned.

Table 17. Effect of Using a Non-HCl Producing Oxidizer, Then Adding PVC to Produce HCl.

Composition (60)	%
Potassium perchlorate	50
Barium nitrate	30
Shellac	15
Polyvinyl chloride	5

No.	HCl%	ω	Δ	ν	L	E	α_1	α_2	α_3	β	δ	CS
248	2.9	30.5	12.8	1.88	51	259	4.7	5.0	4.0	weak	0	4.2

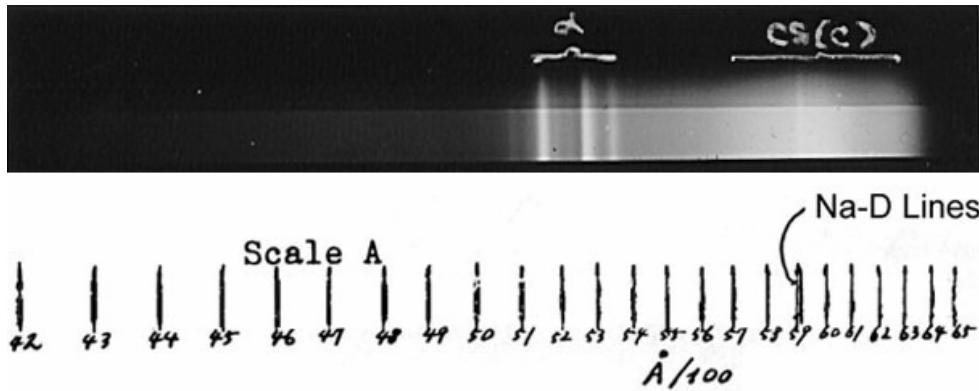


Photo 6. Flame spectra obtained from a low flame temperature composition that contained a HCl producing agent.

From the above descriptions it is difficult, at present, to obtain a good green flame from low temperature compositions using barium nitrate and potassium perchlorate. However, when the flame is observed from a long distance, the flame looks like a fairly good green. Therefore, such compositions have been used for long time.

In Table 18 and Photo 5: No. 245 these spectra resembled the flame spectra when using ammonium perchlorate as the oxidizer (Photo 5: No. 246). Namely, the δ band hardly appeared and the α band was very clear and its intensity was higher than that of ammonium perchlorate. Therefore the flame color was a beautiful clear green. This phenomenon might be due to the HCl producing mechanism from the decomposition of the barium chlorate.

Authors Note: Although barium chlorate gives a very good green flame, it is seldom used in Japan because of accidents from spontaneous ignition of its compositions.

Table 18. Effect of Using Barium Chlorate and Shellac.

Composition (61)	%
Barium chlorate	80
Shellac	20

No.	Ba%	ω	Δ	v	L	E	α_1	α_2	α_3	β	δ	Ba (5536 Å)
245	34.1	31.6	1.84	1.84	45	207	7.0	6.8	6.2	3.8	weak	3.4

Table 19. Effect of Color Agents with Ammonium Perchlorate and Shellac.

Composition (62)	%
Ammonium perchlorate	75
Shellac	15
Color agent	10

No.	Color agent	Ba%	ω	Δ	v	L	E	α_1	α_2	α_3	β	δ
257	Barium carbonate	7.0	28.3	1.27	1.06	3.4	32.3	5.2	5.4	4.2	weak	—
258	Barium oxalate	6.1	27.5	1.27	1.06	3.1	29.2	5.2	5.3	4.2	weak	—
259	Barium chloride	5.6	28.5	1.30	1.19	2.2	18.1	5.2	4.7	3.8	weak	—
260	Barium nitrate	5.3	26.4	1.20	1.36	3.4	26.5	4.8	5.0	4.2	weak	—

(3) Effects of Various Color Agents

In Table 19, the intensities of all the α bands were similar; however, with the naked eye Nos. 257 and 258 produced a good green flame and those of Nos. 259 and 260 were slightly whitish.

In Table 20 the oxidizer was changed from ammonium perchlorate of Composition (62) to potassium perchlorate in Composition (63). The results show that when using barium chloride (No. 279), the β band and the continuous spectra were weaker than the others. However, the burn rate was too slow to have such a result. The flame colors were whitish in all cases of Nos. 277–280.

Table 20. Effect of Color Agents with Potassium Perchlorate and Colophony.

Composition (63)	%
Potassium perchlorate	75
Colophony	15
Color agent	10

No.	Color agent	Ba%	ω	Δ	v	L	E	α_1	α_2	α_3	β	δ	CS
277	Barium carbonate	6.40	31.8	1.53	1.49	83.0	462	6.8	6.4	5.2	4.0	4.0	3.7
278	Barium oxalate	6.10	31.0	1.44	1.43	83.0	514	6.8	6.4	5.5	4.1	4.0	3.7
279	Barium chloride	5.62	31.7	1.55	0.90	45.0	409	6.8	6.3	5.5	3.8	2.0	2.8
280	Barium nitrate	5.26	31.5	1.54	1.40	256	1510	6.4	6.3	5.6	4.8	4.2	3.7

Table 21. Effect of Additives with Barium Nitrate.

Composition (64)	%
Barium nitrate	50
Magnesium	60
Additive	10

No.	Additive	Cl%	HCl%	C%	ω	Δ	v	L	E	α_1	α_2	α_3	β	δ	CS (4500 Å)	Ba (5536 Å)
134	—	—	—	9.0	1.17	32.7	48000	16000	0	0	0	0	5.4	4.8	6.3	
135	Shellac	—	—	6.7	10.5	1.39	4.47	2400	4420	0	0	0	0	5.4	weak	6.0
136	Polyvinyl chloride	—	5.8	3.8	10.0	1.29	6.83	3200	4640	6.4	6.6	6.8	5.2	5.4	weak	6.0
141	BHC	7.3	—	2.5	10.6	1.49	4.78	3700	6590	6.9	7.0	6.8	5.7	5.0	weak	6.0
142	Hexachloroethane	9.0	—	1.0	10.4	1.38	9.05	11200	10240	6.5	6.6	6.2	5.7	5.0	4.0	6.1
143	Ammonium chloride	—	6.7	—	10.1	1.34	5.33	4800	8550	6.5	6.8	6.4	5.7	5.4	3.2	6.0
144	Magnesium chloride	3.5	—	—	10.1	1.35	6.33	6400	9500	6.5	6.6	6.4	5.0	5.4	4.1	6.0
147	Ammonium chloride	—	—	—	10.4	1.41	23.5	32000	12300	0	0	0	5.6	5.3	6.0	
148	Camphor	—	—	7.9	10.0	1.33	21.3	32000	14400	0	0	0	5.5	4.4	6.1	

5.3 High Temperature Green Flames

(1) The Effects of Various Additives

Initially, the flame spectra were examined using barium nitrate in the composition.

In Table 21, when using additives without chlorine, the α band did not appear, but the δ band appeared. The intensity of the δ band was slightly larger than that of the additives with chlorine. Shellac made the intensity of continuous spectrum CS weak. This might be caused by a lower flame temperature.

Author's Note: It was not due to the lower flame temperature, but to the reduction of MgO molecules (solid) to Mg (vapor) by carbon from shellac.

The additives that contained chlorine produced clear α bands. Also the β band appeared and its intensity was slightly decreased. Polyvinyl chloride and BHC were effective in decreasing the intensity of the continuous spectrum. The Na-D lines from impurities interfered with the green, but it had no relation to chlorine.

Table 22. Effect of Color Agents.

Composition (65)	%
Potassium perchlorate	40
Magnesium	30
Polyvinyl chloride	10
Color agent	20

No.	Color agent	Ba%	ω	Δ	v	L	E	α_1	α_2	α_3	β	δ	CS (K)	Ba (5536 Å)
18 1	Barium carbonate	13.9	10.7	1.45	3.24	2400	7405	6.8	7.0	6.8	5.5	4.5	3.8	6.0
18 2	Barium oxalate	12.2	10.3	1.35	3.03	1600	5280	5.9	6.8	6.8	5.5	4.3	3.2	5.7
18 3	Barium chloride	11.2	10.5	1.39	?	640	?	5.5	5.5	5.2	3.6	weak	weak	3.2
18 4	Barium nitrate	10.5	10.6	1.39	4.08	2880	7054	6.8	6.8	6.7	5.7	4.8	4.6	6.0

(2) The Effect of Various Color Agents

In Table 22, Nos. 181 and 184 burned normally, but Nos. 182 and 183 burned with difficulty. No. 183 burned half and then went out; so the data are not comparable to the others. Each flame looked white: this came from the strong potassium continuous spectrum CS(K). The intensities of the α bands did not differ from one another. The interfering δ band was largest when using barium nitrate. This might come from the higher flame temperatures than others (See Part II).

Next, an experiment was conducted with a non-chlorine oxidizer (i.e., potassium nitrate) and, as the color agent, barium carbonate or barium chloride.

In Table 23, No. 205 had no chlorine, and the α and β bands did not appear. No. 206 produced an α band. This may be caused by the chlorine from barium chloride. The intensity of the δ band did not differ very much. Therefore even No. 206 did not produce a clear green.

Table 23. The Effect of Additives with Non-Chlorine Oxidizer.

Composition (66)	%
Potassium nitrate	20
Magnesium	60
Additive	20

No.	Additive	Ba%	ω	Δ	v	L	E	α_1	α_2	α_3	β	δ	CS (K)	Ba (5536 Å)
205	Barium carbonate	13.9	9.8	1.33	7.23	8000	9950	—	—	—	—	5.6	4.7	6.1
206	Barium chloride	11.2	9.6	1.32	7.15	8000	9950	6.0	6.4	6.2	5.0	5.4	4.0	5.5

Table 24. The Effect of Various Oxidizers.

Composition (67)	%
Oxidizer	30
Magnesium	40
Barium carbonate	20
Additive	10

No.	Oxidizer	Additive	Ba%	Cl% (HCl%)	ω	Δ	v	L	E	α_1	α_2	α_3	β	δ	CS	Ba (5536)
157	NH_4ClO_4	—	14.22	(6.69)	9.5	1.25	5.10	2400	4750	—	—	—	—	5.2	4.3	6.1
158	NH_4ClO_4	Polyvinyl chloride	12.80	(12.15)	9.1	1.18	5.03	600	3430	6.9	6.4	6.6	5.5	3.2	2.3	5.4
159	KClO_4	—	14.22	0.00	9.5	1.26	5.65	17600	31500	6.0	5.9	6.4	5.5	5.4	5.0	5.9
160	KClO_4	Polyvinyl chloride	12.80	(5.83)	9.3	1.34	4.45	2080	4440	6.5	6.3	6.5	5.3	4.9	3.2	5.6
161	KNO_3	—	14.22	0.00	9.5	1.27	9.50	8000	8420	—	—	—	—	5.3	4.6	6.4
162	KNO_3	Polyvinyl chloride	12.80	(5.83)	9.8	1.27	4.26	1600	3760	6.0	5.8	5.8	4.4	4.4	3.7	6.0
163	KNO_3	Ammonium chloride	12.80	(6.69)	10.2	1.33	3.63	1600	4230	6.4	6.2	6.2	5.5	5.1	3.9	5.3
164	KNO_3	Shellac	12.80	0.00	9.5	1.25	2.85	800	2860	—	—	—	—	3.8	3.0	—

(3) The Effect of Various Oxidizers

Using barium carbonate as the color agent, the flame spectra were compared to each other.

Photo 7 shows the spectra in Table 24.

When using no additives: Oxidizers that contain chlorine, potassium perchlorate or ammonium perchlorate, produced a very clear α band of high intensity. In this case, the intensity of the α band with ammonium perchlorate was higher than with potassium perchlorate. The intensity of the δ band and of the continuous spectrum were lower with ammonium perchlorate than with potassium perchlorate. These phenomena are explained by the following: the intensity of the α band depends on the status of Cl atoms with respect to others. When the chlorine atoms are in an isolated state in the flame, the α band appears the most intense. With the δ band it is just the opposite. The continuous spectrum caused by potassium atoms interferes quite a lot with green flames.

With non-chlorine Compositions Nos. 161 and 164, using potassium nitrate as oxidizer, no α band appeared. Comparing these effects with those of flames from non-chloride compositions, the effects of chlorine are clearly understood.

When using additives: Polyvinyl chloride or ammonium chloride increased the intensity of the α band and diminished both the δ band and the continuous spectrum. Especially when using ammonium perchlorate, the δ band and continuous spectrum were almost completely extinguished. When potassium perchlorate or potassium nitrate was used, only the continuous spectrum from potassium atoms remains ineffective.

An example of a completely non-chlorine composition, using potassium nitrate as the oxidizer and shellac as the additive, was also shown in Table 24 to demonstrate the effect of no chlorine. It was observed that the continuous spectrum became weak, the α band did not appear,

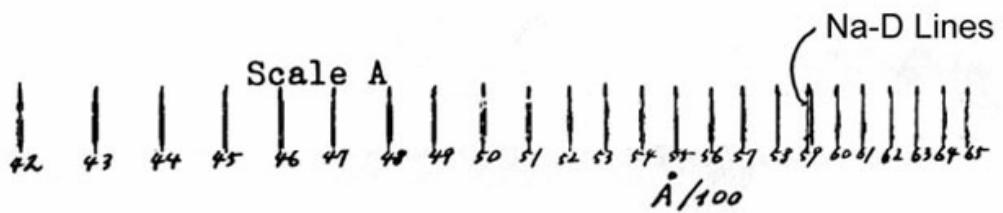
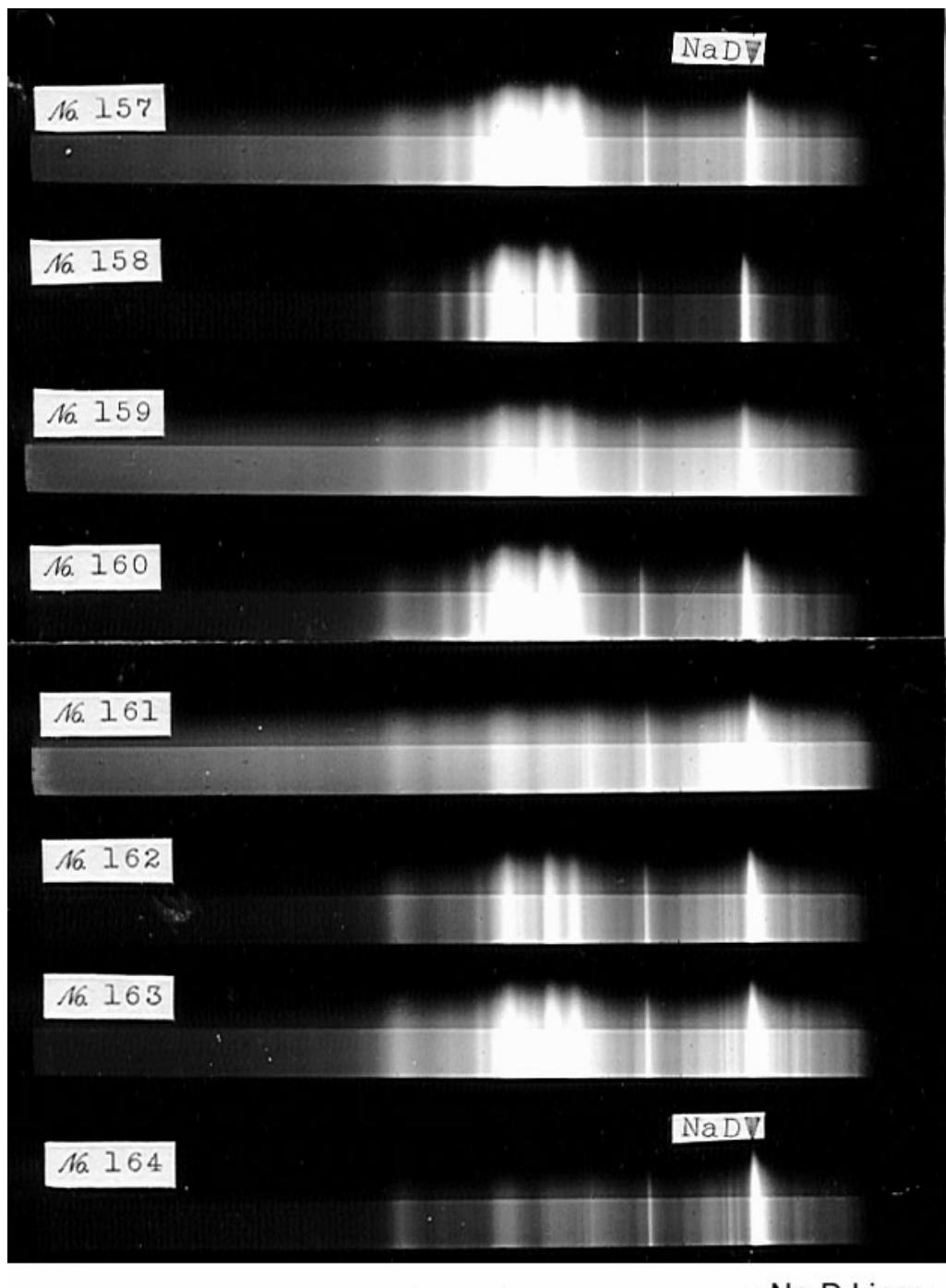


Photo 7. The effects of various oxidizers and additives on green flame spectra (See Table 24).

Table 25. The Effect of Changing the Magnesium to Barium Nitrate Ratio.

Composition (68)		%
Barium nitrate		x
Magnesium		y

No.	x%	y%	Ba%	ω	Δ	v	L	E	α	β	δ	CS	Ba (5536 Å)
133	50	40	26.3	9.2	1.46	26.7	32000	10400	—	—	6.2	5.7	6.4
134	30	60	15.8	9.0	1.17	32.7	48000	16000	—	—	5.4	4.8	6.3

and the distribution of the intensity and the shape of the δ band does not change from those with no additive.

(4) The Effect of Mixing Ratio of Oxidizer and Magnesium

In Table 25, the larger the ratio of barium nitrate to magnesium x/y produced a larger δ band and continuous spectrum. However, it is necessary to examine what happens when the ratio x/y is further increased. (Perhaps, an opposite effect occurs with larger x/y ratios.) The composition is non-chlorine, and the α band does not appear.

With Table 26, the values of i (the length of the spectral line in mm on the photograph obtained by passing the light through the light wedge) versus the values of x (%) are graphically shown in Figure 2.

Table 26. The Effect of Varying the Ammonium Perchlorate to Magnesium Ratio.

Composition (69)		%
Ammonium perchlorate		x
Magnesium		y
		10
		Shellac

No.	x%	y%	HCl%	ω	Δ	v	L	E	α_1	α_2	α_3	β	δ	CS	Ba (5536 Å)
89	30	50	9.3	8.4	1.16	3.00	1920	12170	8.4	8.3	7.7	6.0	5.7	4.8	5.7
90	40	40	12.4	8.5	1.22	2.88	1280	4630	7.3	7.6	6.7	4.8	4.4	4.6	5.1
91	50	30	15.5	8.6	1.29	2.16	320	1470	6.7	7.1	6.4	4.4	3.8	3.8	4.3
92	60	20	18.6	9.1	1.29	1.50	160	1060	6.1	6.7	5.7	3.5	3.2	3.6	4.0
169	60	20	18.6	9.2	1.21	1.54	250	1712	5.6	5.4	4.6	3.7	weak	—	3.0
170	30	50	12.4	8.6	1.12	2.45	?	—	5.3	5.0	4.8	2.5	weak	—	3.0

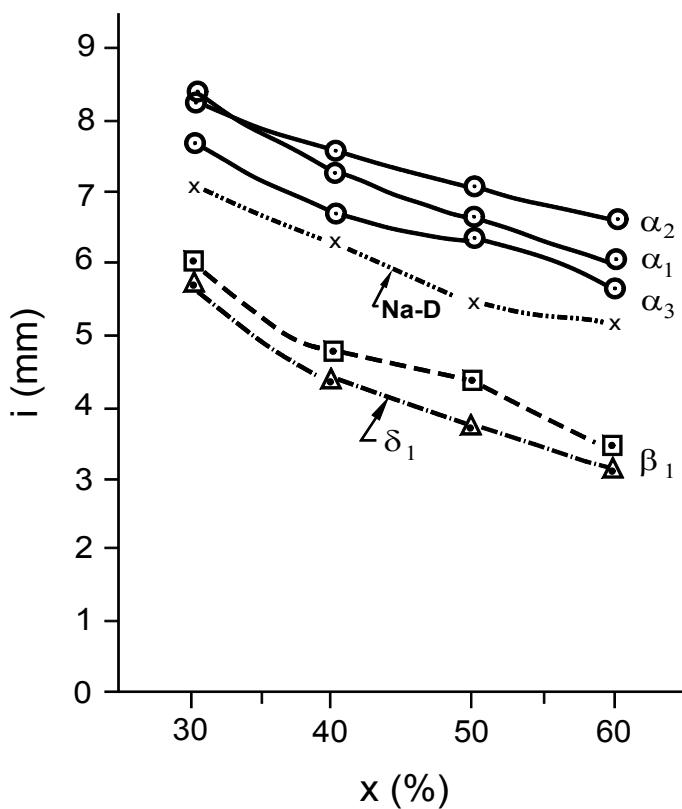


Figure 2. The intensity (i) of spectral line versus $x\%$.

In Figure 2, when the ratio of ammonium perchlorate to magnesium, x/y , was increased, the values of i decreased proportionately with each other.

6. Conclusion

Using spectrographs, various compositions that can produce red, yellow or green flames were examined under various conditions. The most important effects came from Cl or HCl atoms or molecules in the flames.

- (1) *Red:* When using a strontium compound, it is not always necessary for the flame to contain Cl or HCl to obtain red color. Without these molecules or atoms it is possible to obtain a red flame with the presence of the α band. However, when Cl or HCl is contained in the flame, the band spectra of the longer wavelengths appear and the continuous spectrum is diminished to obtain a clear, deep red flame. The effects of Ca salts resembled those of Sr salts.
- (2) *Yellow:* Na-D lines and their supplemental continuous spectrum have no relationship to Cl or HCl atoms or molecules in the flame with respect to the production of yellow flame. However Cl or HCl in the flame is

- effective in decreasing the continuous spectrum, which makes the yellow more pure.
- (3) *Green*: It is absolutely necessary for the flame to contain Cl or HCl to produce green flames. Without it no green flame appears.

For assistance in this study, the author thanks Professor S. Yamamoto of Tokyo University, who always encouraged me. And also many thanks to Professor S. Makishima of Tokyo University, who introduced me to spectral analysis.

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- 2) *ibid.*, Vol. V, p 11.

Part V: Flame Spectra of Blue Color Compositions

ABSTRACT

We can see three different flame colors (i.e., blue, light green and reddish orange) when we insert a small copper piece into a flame of a burner. The blue color is caused by CuCl bands with the strongest lines between 4269–4560 Å. Our goal is to use this color for fireworks. Blue is produced by some copper salts or copper metal powder in the presence of chlorine or hydrogen chloride gas, but if the concentration of gas is small, the blue color is interfered with by the light green color, which seems to be caused by a continuous spectrum of other copper chloride bands (5263–5531 Å).

The flame spectra are examined under various conditions. For low temperature flames, ammonium perchlorate is the best oxidizer and produces an excellent bright blue. For high temperature flames it is necessary to decrease the percentage of magnesium powder, because the CuCl bands seem to dissociate with increasing magnesium.

1. Introduction

The purpose of this Part is to examine the spectra of the blue flames produced by fundamental compositions to explain the principle of making blue flames, considering the effects of various ingredients and ratios of the compositions, etc. This study will greatly help in developing good blue compositions.

2. Materials and Instruments for Experiments

Materials other than color agents were described in earlier Parts.

Blue color agents:

Copper sulfate, CuSO₄: commercial reagent grade.

Cupric chloride, CuCl₂·2H₂O: basic copper carbonate was gradually added to a 12 N hydrochloric acid solution. When the bubbling of CO₂ stopped, the solution was filtered, recrystallized three times, and dried at 60 °C to obtain the cupric chloride.

Cupric oxalate, CuC₂O₄: Ammonium oxalate was added to a water solution of copper sulfate of commercial reagent grade, and the precipitate was separated by natural sedimentation from the liquid. The precipitate was washed four times with distilled water. The precipitate consisted of very fine particles, some of which passed through a filter paper. It was difficult to use ordinary filtrating methods; therefore, it was difficult to completely remove the ammonium salt, which was produced as a by-product.

Basic copper carbonate, CuCO₃·Cu(OH)₂: Ammonium carbonate was added to a water solution of copper sulfate of commercial reagent grade, and the precipitate was washed with distilled water until the reaction of the Nessler reagent did not occur. Then it was dried at 60 °C in an oven. The carbonate produced by this method partially dissolves in the ammonium carbonate solution, which results in a decreased yield.

Paris green, 3CuO·As₂O₃ + Cu(CH₃COO)₂: This was synthesized in the author's laboratory. It was analyzed as Cu=22.5%.^[1]

Copper arsenite, CuHAsO₃: This was synthesized in the author's laboratory.^[2]

Sample specimens and instruments were the same as described in Part III.

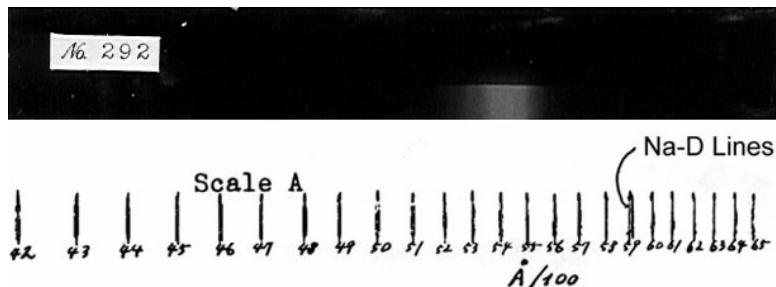


Photo 1. Copper chloride spectrum from a flame of a gasoline burner (2 hour exposure).

3.0 Preliminary Experiment: Observation of Flame Color and Flame Spectra from Copper

As the blue color agent, copper or copper compounds are used. Some formulations show mercury compounds; however, they are not commonly used at present. The color of the flame from copper compounds is fairly complex, and the blue color producing mechanism is quite different from the others, so this preliminary testing is important.

3.1 Observation of Flame Color by Copper and Its Spectra Using Copper Metal Wire

(1) A quantity of sodium chloride (reagent grade) was placed into a conical flask. A quantity of concentrated sulfuric acid was poured onto it and heated. From the flask, well dried HCl gas was produced. The HCl gas was introduced into another conical flask of 1 liter, which was used as a HCl gas reservoir that was closed by a piece of glass plate. Separately, a length of bare electric copper wire of about 2 mm in diameter was prepared. The copper wire was inserted into the HCl reservoir and after a while the surface of the copper wire was chemically covered with a copper chloride film; then the wire was inserted into an almost colorless flame of a gasoline burner. The flame above the wire was colored light green. The spectrum that was photographed is in Photo 1. It was a continuous spectrum of 5170–5510 Å.

(2) Initially the spectrum looked green, but a few seconds later it changed to red orange. This change of flame color was due to the va-

porizing of the copper chloride that was fixed on the surface of the copper wire. The spectrum of red orange flame could not be photographed even with two hours of exposure, because it was very weak.

(3) From the above described hydrogen chloride gas generator, HCl gas was blown into the gasoline flame through a nozzle. The partial mixing of the two gases, of the gasoline burner flame and of the hydrogen chloride gas, emitted a faint green light. Then, when a bare copper wire with no preliminary treatment was inserted above the mixing point of the flame, the flame was colored with a pretty blue. This spectrum was photographed as the upper spectrum S6 in Photo 2.

(4) When dried Cl₂ gas, instead of HCl gas, was blown into the flame, yellowish sparks were visible at the mixing point of the gases. When the copper wire was inserted above the mixing point of the flame, the same blue was observed; this spectrum is shown by S7 in Photo 2.

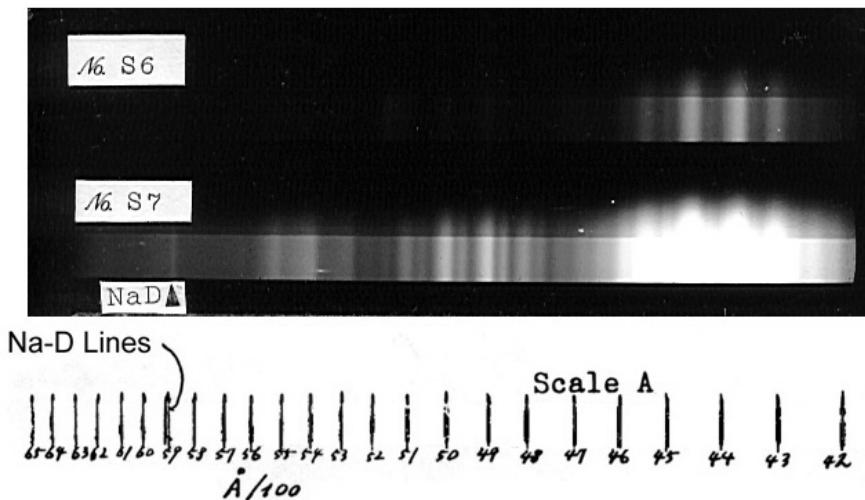


Photo 2. Flame spectra of copper chloride from gasoline burner.
S6: by blowing HCl gas into the flame, 27 minutes exposure,
S7: by blowing Cl₂ gas into the flame, 24 minute exposure.
[Ed. Note: The Scales and Spectra are reversed in this Photo.]

3.2 Experiments with Firework Compositions

(1) A quantity of ammonium perchlorate was mixed with shellac in a weight ratio 5:1. This mixture was burned. A piece of copper wire with no preliminary treatment was inserted into this burning flame. The color was pretty blue; the same as that in (4) of Section 3.1. In this case the tip of the flame was colored with weak red orange. This color was the same as the red orange flame described in (1) of Section 3.1.

(2) A quantity of potassium perchlorate was mixed with shellac in a weight ratio 5:1 to which 10% basic copper carbonate was added. When it was burned, three different flame colors were observed, as shown in Figure 1 with blowing HCl gas into the flame through a nozzle.

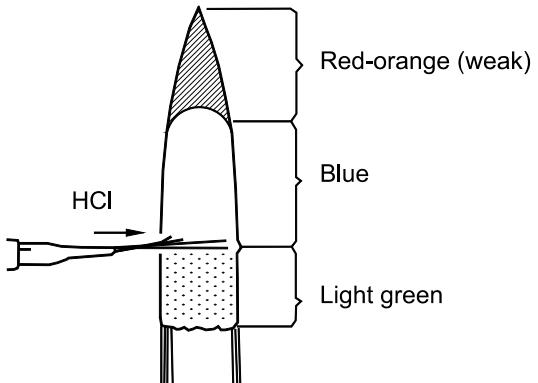


Figure 1. The flame colors observed from the potassium perchlorate composition that contained copper compound blowing into the flame with HCl gas.

3.3 Examination of the Effects

From the above experiments, it is understood that there are three kinds of flame color: blue, light green and red orange. For firework use only the blue is desired. From the above experiments we know that the light green disappears in the presence of HCl gas in the flame, and the blue appears most clearly under the same conditions. Also the red orange does not disappear, however, it is very weak, and from a distance it does not interfere with the blue.

It is well known that blue flames come from CuCl band spectra. However, where does the light green come from? Perhaps the emitter has a different structure from that of the blue. The red orange always appears at the tip of the flame. Therefore it may be caused by CuO due to oxygen in the air.

4. Examination of the CuCl Band Spectra

R. Ritschl already analyzed the CuCl band spectra.^[3] The structures are in Table 1:

Table 1. CuCl Band Spectra Analyzed by R. Ritschl in Å.

1	5380 (0,1)	5262 (0,0)	5152 (1,0)
2	4982 (0,1)	4882 (0,0)	4789 (1,0)
3	4946 (0,1)	4847 (0,0)	4756 (1,0)
4	4434 (0,0)	4354 (0,0)	4281 (1,0)
5	4412 (0,0)	4333 (0,0)	4259 (1,0)

Specifically, five types of transition between electronic states were proposed. However, the values of the wavelengths were somewhat different from the author's. And more intensive bands were omitted. The bands generally appeared with almost the same difference of the wave numbers, and from these results it is thought that there is another way of analyzing than the above.

The CuCl band spectra appeared between 4030–5640 Å. The main blue light source appeared as an intense band: 4210–4589 Å, followed by somewhat weak bands: 4580–5099 Å. The difference in wavelengths between the bands were regular. Thirty one bands were observed in the range of wavelengths shorter than the Na-D lines.

The wavelengths (or wave numbers) and roughly estimated intensities of the bands are shown in Table 2 and Figure 2, using the following symbols:

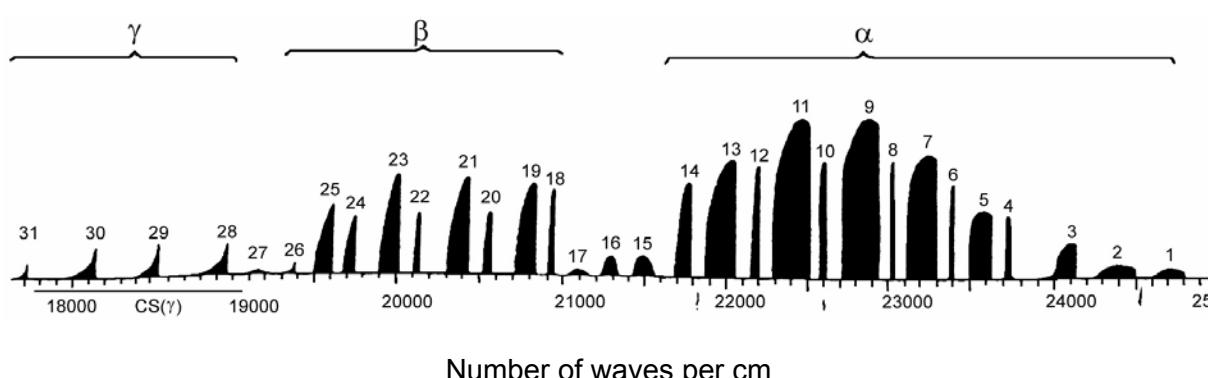


Figure 2. CuCl bands from the author's experiments.

Table 2. CuCl Spectra from the Author's Experiments.

		Bandwidth (Å)				Band width (Å)	
↑	1.	4026–4058		β band	18.	4769–4781* ³	
	2.	4071–4105			19.	4801–4838* ²	◎
	3.	4123–4164			20.	4850–4863* ³	
	4.	4201–4219			21.	4888–4928* ²	◎
	5.	4229–4252			22.	4950–4966* ³	
	6.	4269–4277* ⁵			23.	4989–5037* ²	◎
	7.	4290–4323* ⁴	●		24.	5056–5074	
	8.	4340–4343* ⁵			25.	5092–5120	
	9.	4355–4399* ⁴	●		↓ 26.	5151–5169* ¹	
	10.	4417–4432* ⁵			27.	5190–5225	
	11.	4438–4481* ⁴	●		↑ 28.	5263–5304* ¹	
	12.	4496–4513			29.	5385–5429* ¹	
	13.	4526–4560	●		γ band 30.	5503–5531	
	14.	4590–4608			↓ 31.	5628	
	15.	4630–4658				Continuous spectrum	
	16.	4678–4698				5263–5531	
	17.	4724–4749					

Note: The continuous spectrum 5263–5531 Å appeared when the density of the HCl gas in the flame is low, for example with the flame from a potassium perchlorate composition.

●	strongest
◎	middle class intensity
no symbol	weak and ineffective
*	band corresponding to those of R. Ritschl, (Table 1), with the unit of wavelength as Å

β band: Weaker than the *α* band; however, the band arrangement resembles that of the *α* band. The intensity of band is represented by that of β_{21} .

γ band: weak band elements appear with almost the same intervals. The intensity is represented by that of γ_{29} .

According to the classification in Table 2 and Figure 2, the characteristics of the bands are described as follows:

α band: Strongest band group, which contains four main bands, α_7 , α_9 , α_{11} , α_{13} , with weaker bands that alternately appear between the main bands. These are the main spectra for creating blue. In this paper the intensity of the *α* band is represented by the intensity of the α_9 band.

Table 3. The Effect of Oxidizer-Fuel Mixing Ratio.

Composition (71)	%
Ammonium perchlorate	x
Shellac	y
Basic copper carbonate	10

No.	x%	y%	ω	Δ	v	L	E	α	β	γ	CS(D)	Oxygen Balance
229	50	40	23.6	1.06	1.40	30	257	2.0	weak	0	3.2	-0.674
230	60	30	24.3	1.11	2.20	50	259	2.8	weak	0	3.2	-0.402
231	70	20	25.9	1.15	2.53	50	195	4.7	1.8	weak	weak	-0.130
232	80	10	26.9	1.22	2.93	20	71.4	5.3	2.5	weak	weak	+0.142

Note: The oxygen balance is shown by the excess or lack of oxygen in grams per 1 gram of the composition.

5.0 Low Temperature Blue Flames

5.1 The Effect of Mixing Ratio of Oxidizer and Fuel

For the oxidizer, ammonium perchlorate, which produces HCl gas in the flame, was used.

In Table 3 the intensity of the α band becomes larger and larger with increasing values of x/y , and the intensity of the β or γ bands have

the same tendency as the δ band. On the other hand, the intensity of the continuous spectrum decreases with increasing x/y . Therefore, a clear blue flame can be obtained at a fairly high temperature with excess oxygen.

Table 4. The Effect of Color Agents with Ammonium Perchlorate Oxidizer.

Composition (72)	%
Ammonium perchlorate	75
Shellac	15
Color agent	10

No.	Color agent	Cu %	ω	Δ	v	L	E	α	β	γ	CS
261	Basic copper carbonate	5.75	27.0	1.22	3.35	45	140	5.0	2.4	weak	0
262	Copper oxalate	5.91	27.0	1.23	?	?	—	3.9	weak	0	0
263	Copper chloride	3.73	27.0	1.23	1.16	9.0	80	5.8	3.5	weak	0
264	Copper sulfate	2.55	27.6	1.25	1.16	9.0	79.6	5.7	3.5	weak	0
265	Paris green	2.25	25.5	1.14	1.47	15.0	114	5.7	3.7	2.0	0
266	Copper arsenite	3.39	24.5	1.10	1.46	16.8	134	5.6	3.7	2.0	0
267	5% Copper powder	5.26	30.6	1.16	8.33	33.6	42.7	3.9	weak	0	0
268	10% Copper powder	10.00	26.7	1.19	3.61	44.8	133	5.8	3.9	2.5	0

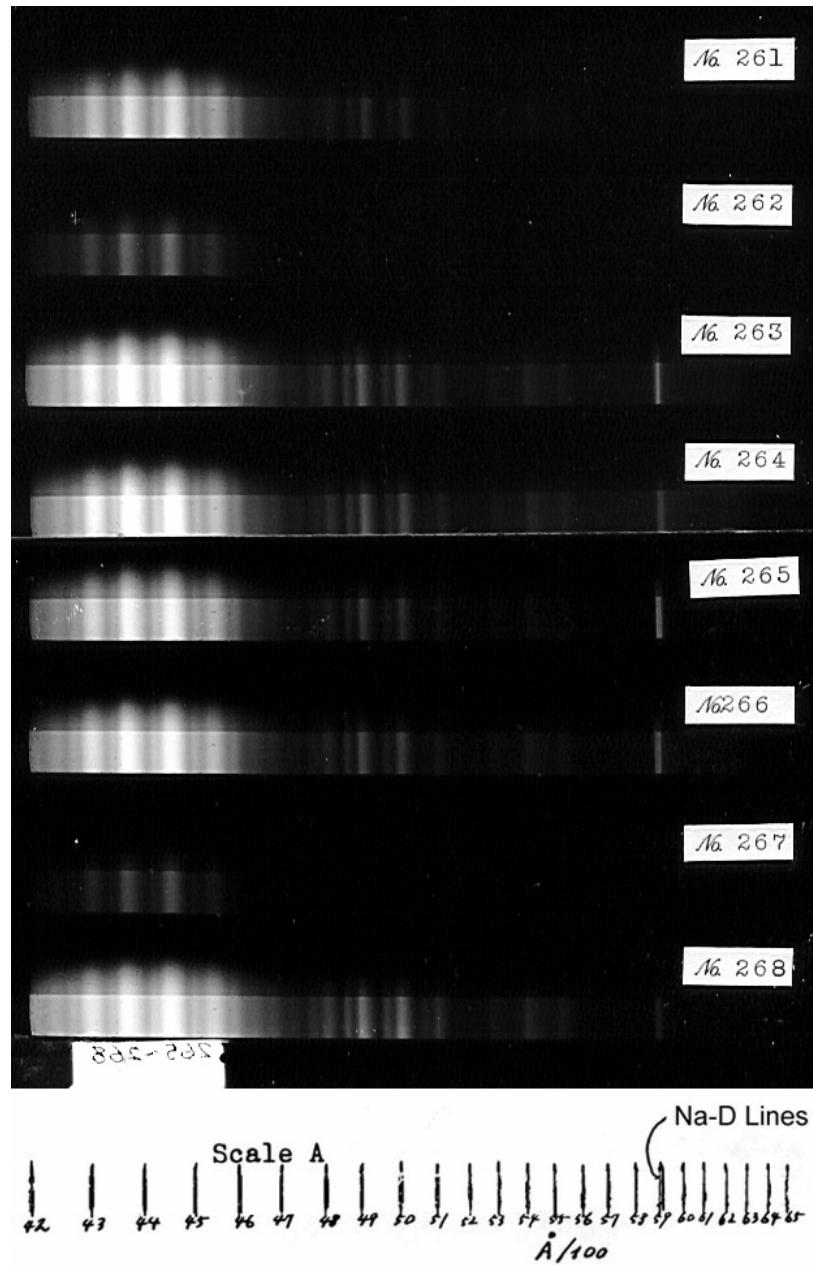


Photo. 3 Flame spectra when using ammonium perchlorate as the oxidizer. (These spectra correspond to the compositions in Table 4.)

5.2 The Effect of Various Color Agents and Oxidizers

The flame color of each composition in Table 4 was a pretty blue. In particular, the flames of Compositions Nos. 263 (copper chloride), 268 (10% copper), 264 (copper sulfate), and 265 (Paris green) were all similar and superior in producing blue. Compositions Nos. 262 (copper oxalate) and 267 (5% copper powder) burned

very irregularly and dangerously fast. All of its light was not introduced into the spectroscope.

As described above, the main part of each flame was colored blue, and only the tip was weak orange red.

Table 5. The Effect of Color Agents with Potassium Perchlorate Oxidizer.

Composition (73)	%
Potassium perchlorate	75
Colophony	15
Color agent	10

No.	Color agent	Cu %	ω	Δ	ν	L	E	α	β_{24}	β_{25}	γ	δ	CS(γ)	CS(K)
281	Basic copper carbonate	5.75	31.0	1.37	2.10	18.0	79.6	5.4	3.0	2.3	0	2.0	3.7	f.s.
282	Copper oxalate	5.91	30.8	1.40	1.29	36.0	254	5.4	2.6	2.6	0	2.4	3.8	f.s.
283	Copper chloride	3.73	29.3	1.30	1.52	23.0	149	4.8	w	w	0	w	3.0	w
284	Copper sulfate	2.55	30.8	1.36	1.70	20.0	110	4.8	w	s	0	w	2.6	w
285	Paris green	2.25	—	—	1.93	72.0	—	5.5	w	3.6	0	2.8	3.6	s
286	Copper arsenite	3.39	30.8	1.36	3.00	58.0	181	6.2	3.4	4.3	0	3.0	4.2	s
287	5% Copper powder	5.26	30.6	1.35	1.76	28.8	154	4.8	0	2.2	0	w	3.8	ss
288	10% Copper powder	10.00	31.2	1.38	1.89	50.4	246	5.0	0	2.8	0	w	3.8	ss

Note: Symbols: w = weak; ss = slightly strong; s = strong.

The flame spectra with potassium perchlorate compositions corresponding to Table 5 are shown in Photo 4.

When using potassium perchlorate as the oxidizer, the compositions with Paris green, copper arsenite and copper powder produced the prettiest blue flames in the range of experiments in Table 5. When comparing the effects of ammonium perchlorate, which produces HCl gas in the flame, and those of potassium perchlorate with no HCl gas, the latter was different from the former in the following points:

(1) The intensity of the α band was similar in both.

(2) New bands appeared at 6070 and 6150 Å, which were longer wavelength than the Na-D lines. In this study these are called the δ bands (Table 5).

(3) The γ band did not appear. In place of this band a green continuous band CS(γ) appeared with a high intensity.

(4) Generally, the bands were not as clear as with ammonium perchlorate and grew somewhat dim.

The above effects make the color of the flame whitish and greenish. From the preliminary experiments in Part III it is clear that this was caused from the lack of HCl in the flame.

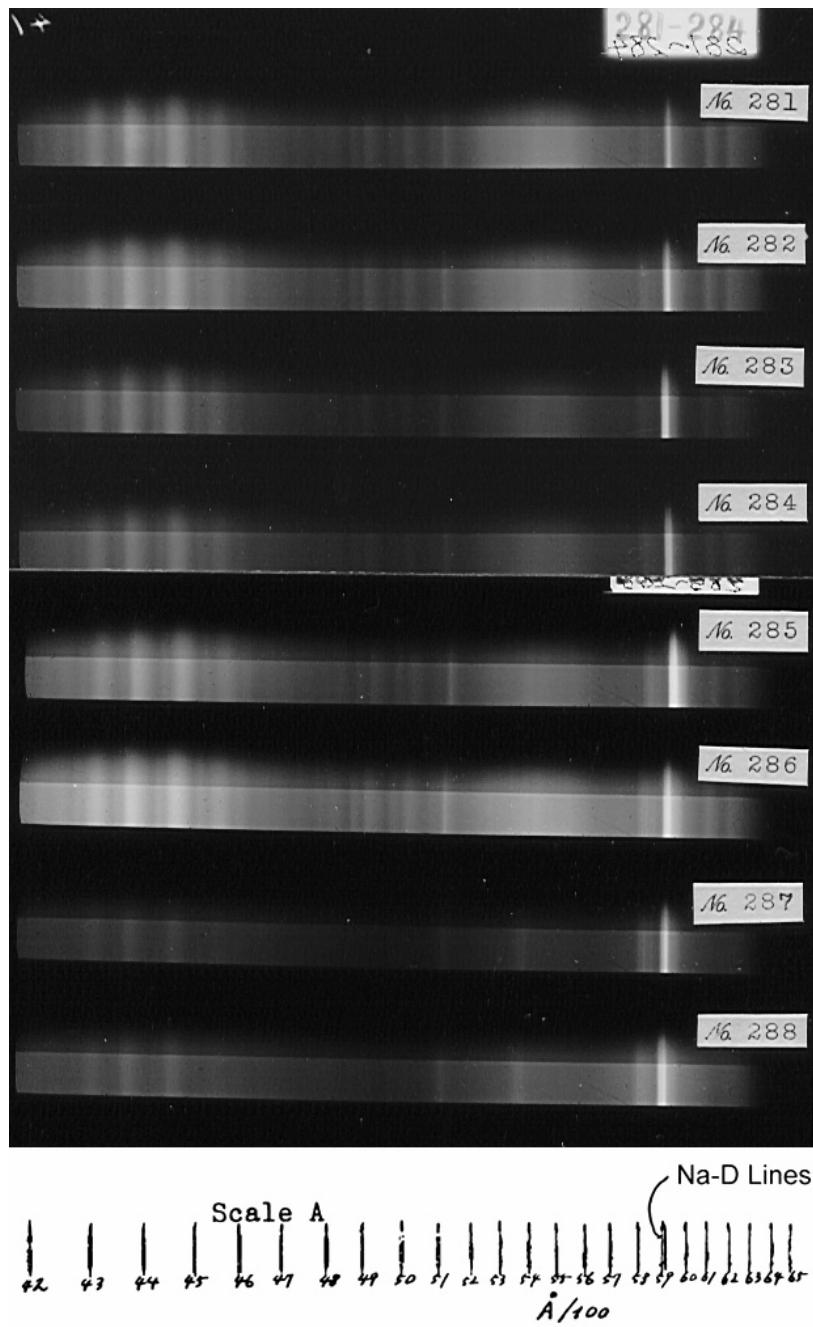


Photo 4. Flame spectra when using potassium perchlorate as the oxidizer. (These spectra correspond to the compositions in Table 5).

Table 6. The Effect of Various Fuels with Ammonium Perchlorate as the Oxidizer.

Composition (74)	%
Ammonium perchlorate	75
Fuel	15
Copper powder	10

No.	Fuel	ω	Δ	v	L	E	α	β	γ	δ	CS(γ)
313	Shellac	30.2	1.34	3.20	72	215	4.9	3.1	weak	—	weak
314	Colophony	28.0	1.24	?	—	—	—	—	—	—	—
315	Pine root pitch	30.3	1.34	?	54	—	5.2	2.7	weak	—	weak
316	Coal pitch	28.8	1.27	?	—	—	—	—	—	—	—

Composition (75)	%
Ammonium perchlorate	80
Fuel	10
Copper powder	10

No.	Fuel	ω	Δ	v	L	E	α	β
321	Shellac	31.5	1.48	4.84	43	76.5	—	—
322	Colophony	30.3	1.39	5.05	54	98.0	—	—
323	Pine root pitch	32.0	1.42	4.78	43	80.6	—	—
324	Coal pitch	31.7	1.44	0.00	—	—	—	—

5.3 The Effect of Various Fuels

It was difficult to obtain precise data from the tests in Table 6 because the samples generally burned in an unstable manner. Nos. 314, 316, and 321–324 burned irregularly and too fast to measure the intensity of the bands photographically. The tendency was enhanced by increasing the percentage of ammonium perchlorate. Shellac or pine root pitch was a relatively good fuel to create stable burning. The spectra in this case were similar to each other.

In Table 7, comparing Composition (76) with (77) the latter produced clearer, but somewhat weaker bands than the former.

The compositions that contained potassium perchlorate generally produced unclear bands. And in this case CS(γ) and δ other than α , β bands made the flame look quite blue green.

5.4 The Effect of Fuels That Contain Chlorine

Too much chlorine containing fuel decreases the flame temperature; so the quantity should be limited. Therefore 5% of this substance was tested.

In Table 8 the effects of the Cl or HCl producing substances was not very effective with such small quantities. However, if more is added, the flame temperatures will be decreased to obtain worthless effects. Therefore, for low temperature compositions, adding Cl or HCl producing substances is not expected to produce very good effects.

Table 7. The Effect of Various Fuels with Potassium Perchlorate as the Oxidizer.

Composition (76)		%
Potassium perchlorate	75	
Fuel	15	
Copper powder	10	

No.	Fuel	ω	Δ	v	L	E	α	β_{24}	β_{25}	γ	δ	CS(K)
317	Shellac	31.8	1.41	1.80	29.0	146	5.7	3.8	5.2	5.2	4.6	strong
318	Colophony	30.2	1.34	1.96	36	175	5.3	3.5	4.3	5.0	3.8	strong
319	Pine root pitch	32.0	1.47	2.24	54	209	5.8	3.4	3.8	4.8	4.4	strong
320	Coal pitch	31.8	1.41	2.03	68	304	5.7	3.2	4.0	4.8	4.8	strong

Composition (77)		%
Potassium perchlorate	80	
Fuel	10	
Copper powder	10	

No.	Fuel	ω	Δ	v	L	E	α	β_{24}	β_{25}	γ	δ	CS(K)
325	Shellac	32.0	1.61	1.71	7	31.7	5.1	weak	weak	3.4	2.1	weak
326	Colophony	31.9	1.49	1.37	18	64.9	4.7	weak	weak	3.4	2.6	weak
327	Pine root pitch	31.5	1.59	2.33	36	123	5.5	2.0	2.0	3.3	3.5	weak
328	Coal pitch	31.7	1.64	1.94	36	144	5.0	weak	2.0	3.9	3.5	weak

Table 8. The Effect of Various Chlorine Donors

Composition (78)		%
Potassium perchlorate	70	
Colophony	10	
Paris green	15	
Cl or HCl producing substance (Cl donor)	5	

No.	Cl donor	Cl %	HCl %	ω	Δ	v	L	E	α	β_{24}	β_{28}	δ	γ	CS(K)
237	—	—	—	30.5	1.53	2.71	77	237	6.7	3.6	3.9	4.5	3.9	strong
238	Polyvinyl chloride	—	2.92	31.6	1.45	2.45	83	296	5.9	3.7	3.7	4.3	3.5	strong
293	BHC	3.66	—	32.0	1.49	2.04	54	226	6.4	4.9	4.2	4.6	4.0	strong
294	Ammonium chloride	—	3.34	32.3	1.43	1.76	18	90	6.4	4.4	4.0	4.1	3.0	strong

Table 9. The Effect of Various Oxidizers to Fuel Mixing Ratios.

Composition (79)	%
Ammonium perchlorate	x
Magnesium	y
Polyvinyl chloride	10
Paris Green	10

No.	x%	y%	ω	Δ	α	β	γ	CS
418	60	20	8.4	5.4	2.7	weak	0	weak
419	40	40	8.3	5.4	2.7	0	0	slightly weak
420	20	60	7.9	4.1	weak	0	0	strong
421	20	60	7.3	0	0	0	0	strong

Composition (80)	%
Potassium perchlorate	x
Magnesium	y
Polyvinyl chloride	10
Paris Green	10

No.	x%	y%	ω	α	β	γ	δ	CS(K)
422	60	20	9.2	6.0	0	0	?	strong
423	40	40	8.8	6.0	0	0	?	strong
424	20	60	7.8	4.9	0	0	?	strong
425	20	60	7.6	0	0	0	?	strong

6.0 High Temperature Blue Flames

The color producing mechanism of the high temperature blue flames using CuCl band spectra is quite different from that of high temperature red flames using strontium bands or green flame using barium bands.

6.1 The Effect of Mixing Ratios of Oxidizers and Fuels

In Table 9 Nos. 421 and 425 were blank tests; they did not contain Paris green. The photographs related to Table 9 are shown in Photo 5.

In Table 9 the intensity of CuCl band spectra was very much decreased when the ratio of oxidizer to magnesium decreased (Photo 5). This is a central characteristics to SrO or BaCl band spectra. The emitter CuCl may be dissociated at

high temperatures to build MgCl molecules consuming Cl atoms in the flame. Therefore, at high flame temperatures, bright blue light can not be obtained when we use the CuCl band.

Using potassium perchlorate as the oxidizer produced a strong continuous spectra CS(K) that interferes with blue light.

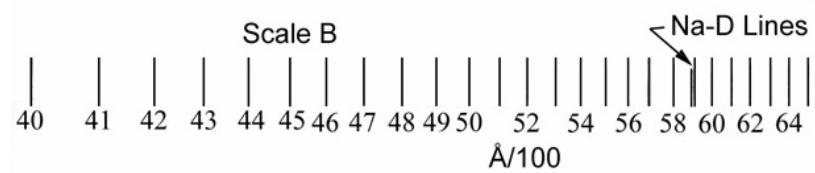
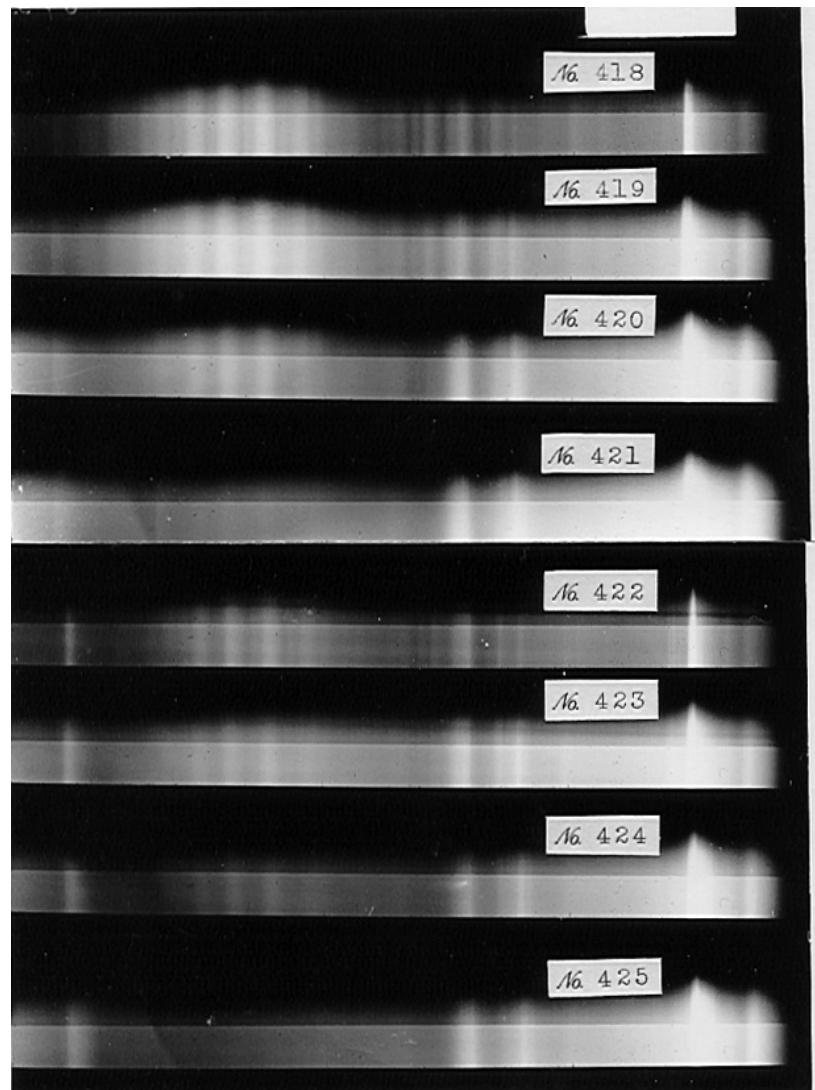


Photo 5. Effects of the mixing ratio of oxidizer to magnesium on the CuCl band spectra.

Table 10. The Effect of Various Copper Salts.

Composition (81)	%
Potassium nitrate	50
Magnesium	30
Copper salt	20

No.	Copper salt	ω	Δ	ν	L	E	α	β	γ	δ	CS(K)
207	Basic copper carbonate	10.2	1.49	2.91	800	2740	0	0	0	0	4.1
208	Copper chloride	9.7	1.30	4.04	800	1980	0	0	0	0	3.4

In Table 10, Composition No. 207 did not contain chlorine and no band related to chlorine appeared. This, as a matter of course, confirms the already described fact that the Cu bands came from copper chloride. The fact that no Cl band appeared, even when using copper chloride, may be due to the Cl being consumed to form MgCl.

6.2 The Effect of Various Color Agents

In Table 11, Composition (82), 10% copper powder was the most effective in producing color, followed by Paris green and copper arsenite.

Table 11. The Effect of Various Color Agents.

Composition (82)	%
Potassium perchlorate	60
Magnesium	10
Polyvinyl chloride	10
Color agent	20

No.	Color agent	Cu %	ω	Δ	ν	L	E	α	β	γ	δ	CS(K)
185	Basic copper carbonate	11.49	10.2	1.55	1.28	300	2532	weak	0	0	0	0
186	Copper oxalate	11.82	10.6	1.57	1.22	30	246	weak	0	0	0	0
187	Copper chloride	7.45	9.8	1.29	1.07	10	93	slight	0	0	0	0
188	Copper sulfate	5.09	10.3	1.38	1.03	10	97	0	0	0	0	0
189	Paris green	4.50	10.5	1.52	2.26	150	663	3.6	0	0	0	0
190	Copper arsenite	6.78	10.5	1.39	2.04	100	490	3.4	slight	0	0	0
191	5% Copper powder	5.88	9.0	1.45	2.65	200	765	2.9	slight	0	0	0
192	10% Copper powder	11.11	9.5	1.32	3.65	320	876	4.0	weak	0	0	0

6.3 The Effect of Using a Non-Chlorine Oxidizer with a Chlorine Producing Agent (Chlorine Donor)

Table 12. The Effect of Using a Chlorine Donor with a Non-Chlorine Containing Oxidizer.

Composition (83)	%
Potassium nitrate	40
Magnesium	60
Copper powder	additional 10
Polyvinyl chloride	additional x

When Composition (83) was tested with values for PVC of $x=20$ and 30, the CuCl band did not appear. Perhaps this might be caused by the chlorine being consumed by magnesium to produce MgCl gas as in the case of No. 187.

7. Conclusion

To obtain good blue flames it is important to consider the following conditions.

(1) For low temperature flames: the existence of HCl (or Cl₂) gas in the flame is important to create the CuCl- α band, which is the main factor in blue light. When using an oxidizer that cannot produce HCl (or Cl₂) gas in the flame, the intensity of the δ band decreases. Ammonium perchlorate works well to produce blue flame compositions. Potassium perchlorate does not work well. It produces green continuous spectra CS(γ), and the flame becomes green white.

(2) For high temperature flames: it is difficult to obtain good blue flames at high temperatures. When the weight ratio of magnesium to oxidizer increases, the blue of the flame gradually decreases with the increasing consumption of HCl or Cl₂ gas by magnesium vapor to produce MgCl compound in the flame.

Literature cited

- 1) T. Shimizu, *Fireworks* (in Japanese) (1957) p 35.
- 2) Ditto, p 37.
- 3) V. Nishizawa, *Studies on Fireworks* (in Japanese) (1938) p 157.
- 4) J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry III* (1923) p 48.
- 5) Borenstein, *Physikalische Chemische Tabellen II*, p 862.

Autobiography of a Pyrotechnist — Dr. Takeo Shimizu

(Continued from page 56)

In November 1934 all officers of Artillery and Engineers of my contemporary came back from the regiments and entered the Military Artillery and Engineer Academy. We were taught mathematics, physics, chemistry, metallurgy, electrical engineering, ballistics, etc. So many things were stuffed into our heads by the cramming system of the Academy. After the regular course of one year and the higher course of one year, I was selected to learn more at Tokyo University.

In April 1937 I entered the School of Explosives at Tokyo University. In my class five other students from regular high schools gathered. Professor Nishimatsu, who was the highest authority of the day on manufacturing explosives, was chief. Professor Dr. N. Yamaga, who was a rear admiral in the Navy, lectured on interior ballistics. Assistant Professor S. Yamamoto lectured on manufacturing explosives. Their speaking was terrible and the students suffered to note their lectures. I felt most of the lectures in the School of Explosives were not of much interest. Therefore, I often visited the School of Chemistry, where Assistant Dr. Morino was studying the Raman Effect. I learned quantum mechanics with the help of Professor Dr. K. Higashi, who was an authority in the chemical structure of molecules. Dr. Higashi gave me a book, *FUYU NO HANA* which means "Winter Flowers" in English, by Professor Nakaya (1902-1962). It gave me a deep impression that I knew how to do experiments without any noble instruments of high cost, but using only the human head with excellent success. I named such a method "Terada's Style". The late Dr. Terada (1875-1935) was a famous professor in the Faculty of Physics at Tokyo University. Dr. Nakaya was a student under Dr. Terada and had most faithfully succeeded Terada's school.

rada's school. Although I had no personal acquaintance with Dr. Nakaya nor Dr. Terada, I decided to succeed Terada's school in my future life. Therefore I thank Dr. Higashi who gave me such a direction until today.

In April 1940 I graduated from Tokyo University and arrived at my post at Ohji Factory of Explosives of the Tokyo Second Military Ordnance. I worked there as the section chief of manufacturing nitric and sulfuric acids. There stood a nitric acid plant producing 20 tons per day. Large absorption towers of 18-8 nickel-chrome steel were in use at that time. There were other sections for manufacturing TNT, picric acid, nitrocellulose, and tetryl and about a thousand people worked at the factory. I learned the controlling method of a chemical plant that moves continuously—day and night—with few people. Lieutenant Abe and Mr. Kojima, who had a special sense on chemical plants, helped me. Thus I started with this very interesting work as a chemical engineer. I feel it was the most happy days of my life.

After the daytime duty in the factory was over, I studied in my home at Saginomiya in the western part of Tokyo. I read papers of philosophy by professors Dr. Nishida and Dr. Tanabe of Kyoto University. They founded what was called the "Kyoto School". I learned the dialectics. I also learned Buddhism and the Old and New Testaments by translations in Japanese. I intended further to read them in originals and began to study Sanskrit, Pall, Hebrew, and Greek. I thought the principle of Buddhism might be:

"All things change with time and go in the worse direction when making no human effort."

(Continued on page 106)

Part VI. Flame Spectra of Metal Aluminum Composition

ABSTRACT

The previous Parts showed the effect of magnesium powder as a fuel in high temperature compositions. In this Part the effect of aluminum powder is examined. In general aluminum melts and is sprayed as sparks out of the flame. It is not as easily vaporized because of its high boiling point. With aluminum the intensity of the spectrum of color-producing bands is not as high as with magnesium.

1. Introduction

In the foregoing Parts the author reported on the flame spectra of high flame temperature compositions using magnesium as the fuel. In this paper the author tried to examine the flame spectra using aluminum metal powder as the fuel in a few experiments. The method of experiments and the construction of the sample specimens were the same as before.

The flame using aluminum was quite different from that using magnesium. In the aluminum flame, many small liquid particles were generated in the flame and dispersed in the air as fine sparks. This might be due to the fact that aluminum has a much higher boiling point (2767 °C) than magnesium (1110 °C), and the vaporization of aluminum in the flame is not complete. Therefore, when a color agent is mixed into the composition, its effect is not clearly observed.

Table 1. Effect of Adding Color Agent to an Aluminum Fuel Composition.

Composition (84)	%
Ammonium perchlorate	x
Aluminum	y
Shellac	10
Color agent	10

No.	Color Agent	x%	y%	ω	Δ	v	L	E	SrO _α	SrO _β
193	Strontium carbonate	60	20	9.0	1.18	1.84	160	871	3.0	4.0
194	Strontium carbonate	30	50	8.0	1.05	1.82	160	880	0.0	weak
									Na-D	
195	Sodium carbonate	60	20	9.3	1.22	1.62	160	1032	8.4	
196	Sodium carbonate	30	50	8.3	1.09	2.16	320	1735	5.8	
									BaCl _{α1}	BaCl _{α2}
197	Barium carbonate	60	20	9.3	1.18	1.80	160	960	4.2	4.2
198	Barium carbonate	30	50	8.3	1.09	2.85	160	656	3.9	3.8
									CuCl _α	CuCl _β
199	Basic copper carbonate	60	20	9.1	1.20	2.69	320	1270	5.1	3.4
200	Basic copper carbonate	30	50	8.0	1.06	2.91	160	1320	4.0	weak

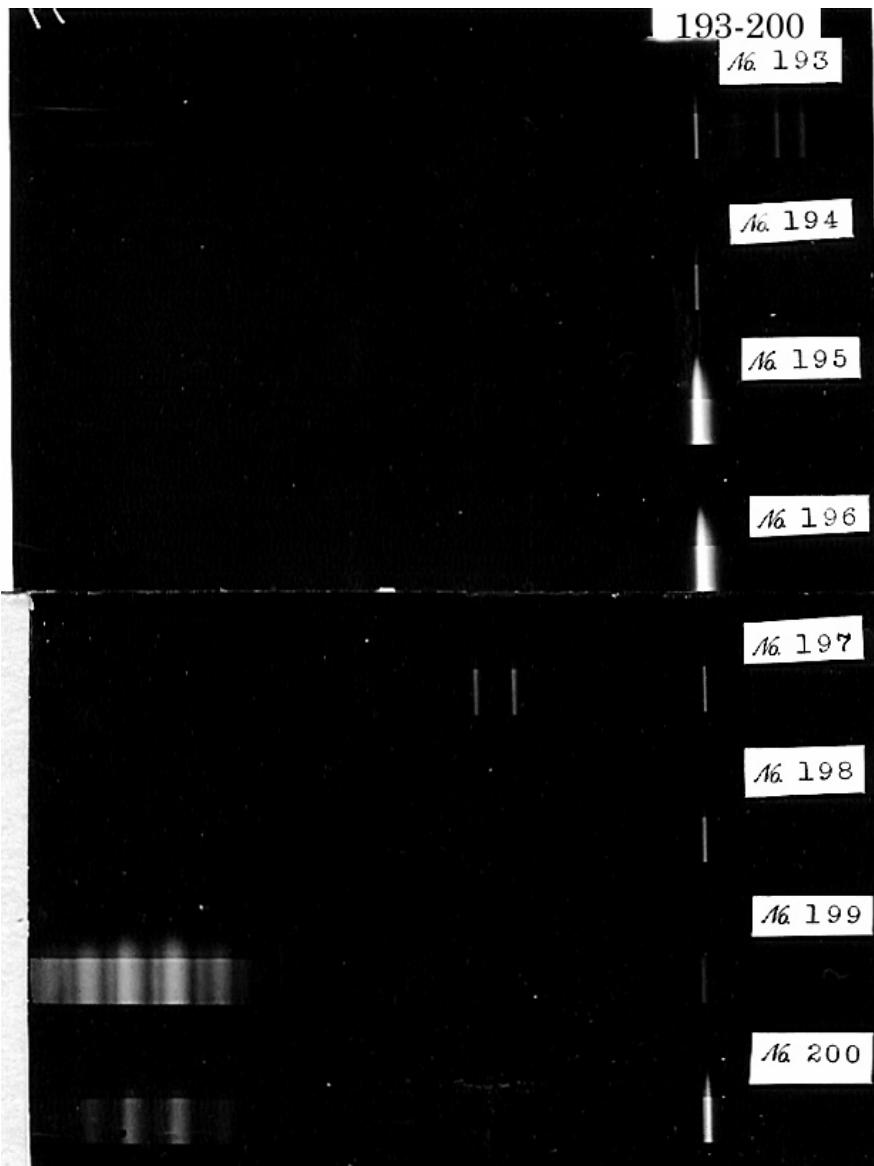


Photo 1. Flame spectra obtained from Composition No. 84 that contained aluminum as fuel.

2. Experimental Results and Examination of the Effects

An experiment was carried out with Composition (84). The results are shown in Table 1. The flame spectra corresponding to Table 1 are shown in Photo 1.

The following effects in the flame were observed with the naked eye. The flame of No. 193 was slightly reddish at the base of the flame. With No. 194 no red appeared, but pretty sparks were produced. In Nos. 195 and 196, the flame produced sparks; the sparks of No. 196 were very beautiful. In No. 198 the flame went out. The sparks from No. 199 were also very pretty.

When we examine Photo 1 of the flame spectra, we can understand that the lower aluminum percentage compositions produced a relatively stronger spectral band, which produces a better color effect than the higher aluminum percentage. Therefore, the lower aluminum percentage gives a better effect when seen with the naked eye. However the effects are much less than when magnesium is used in the compositions. The 20% aluminum sample is near the low flame temperature, and the effect of shellac in this experiment, like in general cases, appeared to aid in the deoxidation of the metal oxide.

3. Conclusion

The effective band spectra are very weak. The larger the percentage of aluminum, the weaker the band. Therefore it is difficult to obtain good colored flame when using aluminum as the fuel.

Autobiography of a Pyrotechnist — Dr. Takeo Shimizu

(Continued from page 102)

In 1941 World War II broke out. I was in the ballistic section of the Institute of Explosives of the Second Tokyo Ordnance. All the officers in the ordnance felt uneasy because Japan was already fatigued by the long war in China. However, our work proceeded with no confusion. Everyone knew that battle is very foolish work for human beings, which are not different from animals. Men made many inventions in the war; however, there had been no invention that decreased the pain in their lives.

In 1942 I had an additional post as teacher at the Artillery and Engineer Academy, where I gave lectures on interior ballistics to the young officers in the higher course. My students returned from the battlefields. I completely rewrote the textbook, which had been a direct translation from a French one. I discovered a similarity rule to obtain velocity, pressure, and time, as functions of four parameters. When the war was over in 1945, I was a lieutenant colonel and the leader of the ballistic section of the Institute of Explosives. My military life was over with the defeat of Japan.

I had lost my spirit to survive; however, I had to live to support my wife and two children. I decided not to make explosives any more and selected to live in my birthplace, the village of Takamata. My parents were already dead and my junior brother was killed in battle in the Philippines. Few relatives supported me. I bought farm fields of two and a half acres from which I could obtain rice and vegetables for one years living. I built a small house of my own, a shack, without any help of a carpenter.

The house faced the south. There was a hill of Japanese Cedar behind the house. After a walk of ten minutes going up through cedars I would see a vast wild field. Before my house there were rice fields and eleven houses. The village was surrounded by copse hills through which a road and a stream passed outside. In

the daytime my wife and I labored in the rice and vegetable fields and at night I read sutras of Buddha under the light of an oil lamp while my wife and children where sleeping in bed. In spring and summer I enjoyed the twitters of birds. In the autumn my garden was full of flowers of cosmos. In winter it snowed deeply, and I heard the voices of hunted rabbits while I was weaving charcoal containers around the fire. I became very idle in writing letters and I acted rudely to people in acquaintance against my will. No radio or newspaper was in the house, and I could escape from troubles among people. The most terrible times were the rain storms and blizzards in the night. When attacking, I protected my family against the rain or snow by binding the doors and pushing them from the inside, however, it came into the rooms and fell onto the beds through the roof of cryptmeria barks. At last I fell into financial difficulties and had to sell books from my library with the help of my friend, Professor Namba of Tokyo University. One day I suddenly lost my eyesight. I thought I could not work anymore, fortunately I recovered in about a month. My wife fell ill, perhaps it came from an unbalanced diet. She had to go to her father living in Osaka, so I had to bring up my children by myself.

One day in the autumn of 1951, when the sun was shining in the blue sky, I received a letter from Professor S. Yamamoto of the School of Explosives at Tokyo University. Dr. Yamamoto recommended Hanabi, fireworks, to me. I did not know anything about fireworks, but felt it might be very interesting, and I accepted Dr. Yamamoto's request. Dr. Yamamoto was the only one who was concerned with fireworks at that time as a scholar in Japan. Dr. Yamamoto asked me to suppress accidents in this field and to make the traditional technique more scientific.

(Continued on page 120)

Part VII. On Composition Series for Practical Use

ABSTRACT

(1) The spectroscopic studies in the previous Parts are summarized so as to apply the principle of flame color creation for practical use.

(2) According to the results of (1), various samples of red, yellow, green and blue of several composition series are prepared. Their flame colors are examined by the naked eye and good colors are selected. According to these, effective color zones are written as enclosed areas in triangle graphs.

(3) As far as these studies are concerned the important results that seem to be common for each series are as follows:

a) The width of an effective composition zone in a graph is very narrow for low temperature flames and fairly wide for high temperature flames.

b) Ammonium perchlorate is the best oxidizer, for it can produce HCl in a flame and creates deep color.

c) Polyvinyl chloride is also the best additional ingredient that can create a deep color by producing HCl gas in the flame like ammonium perchlorate.

d) It is necessary to completely protect compositions from moisture for high temperature flames to prevent the magnesium and other ingredients from reacting with each other. For practical applications deep and brilliant color flames are obtained only in accord with this consideration.

1. Introduction

The foregoing works provide a guide to developing colored flame compositions, where the characteristics of effective color producing spectra, interfering spectra and the elimination of interfering spectra were explained. Considering the results, in this Part the author describes the fundamental conditions for designing typical

colored flame compositions and enumerates representative compositions.

2.0 Summarizing the Results of Foregoing Studies and the Conditions to Obtain Sample Compositions

2.1. Low Flame Temperature Compositions

(1) The highest flame temperature is obtained when the oxygen balance to CO₂ oxidation is nearly fulfilled. From these results the best ratio of the fuel to oxidizer is naturally determined.

(2) The fuel should be selected so that it contains as low a carbon content as possible. This decreases the continuous spectrum from carbon in the flame and produces a reasonable burning velocity.

(3) With reference to the various color agents, it is known that there is a proper value of additive percentages to keep the most effective density of metal vapor in the flame. The excess percentages are not effective. Also negative ions are ineffective for flame color. However, nitrate color agents generally raise the flame temperatures to enlarge the intensity of the flame spectra; however, the interfering spectra also affects the flame color.

Generally, when we select the color agent, purity should be of primary concern (the smaller the quantities of impurity, the better the flame color), especially with Na and sometimes with Ba salts. Additional consideration should be given to moisture absorption, continuation of burning, burn velocity, ignition tendency, toxicity, handling, prices, etc. based on the intended use.

(4) With reference to the selection of the oxidizer, ammonium perchlorate is the best to obtain good flame color without creating interfering spectra; however, the flame temperatures

are somewhat lower than that of potassium perchlorate compositions.

The flame temperatures of potassium perchlorate composition are generally higher than those of ammonium perchlorate compositions and the intensities of the flame spectra are stronger than those of the ammonium perchlorate compositions. However, a continuous spectra and line spectra from potassium atoms appear that interfere with the flame color. However, these compositions have a large advantage with respect to moistureproof characteristics.

Generally, potassium nitrate compositions cannot produce high temperature flames. Therefore, the flame spectra are too weak to use as general firework compositions.

Strontium nitrate or barium nitrate is useable as both the oxidizer and color agent when mixed with another oxidizer even for low flame temperature compositions.

Author's Note: In the past nitrates were used as the main oxidizer, with sulfur or sulfate as the main fuel, which may help to increase flame temperatures. For example, the following compositions were used:

Red flame	Strontium nitrate	45
	Sulfur	13
	Charcoal powder	2
	Potassium chlorate	4
Green flame	Barium nitrate	21
	Sulfur	7
	Potassium chlorate	9

Reference: Franz Sales Meyer, Leipzig, Verlag von Seemann & Co. (1898).

When sulfur was the main fuel, it could produce flame temperatures high enough to create a red or green flame color.

(5) The additive materials that produce Cl or HCl gas in the flame unfortunately also decrease the flame temperature. Therefore, the effect of the addition of such materials to the composition is not as large.

2.2 High Flame Temperature Compositions

(1) Generally, continuous spectra of high intensity appear as the background; however, they are weakened by adding materials that can produce HCl or Cl₂ gas in the flame. It is also effective to add materials that do not contain too much carbon. Excess carbon generates a continuous spectra.

(2) From the above reason, it is always effective to use ammonium perchlorate or potassium perchlorate as the oxidizer. In particular, the addition of a material that can produce HCl gas in the flame is the most effective. Potassium chlorate gives almost the same results as potassium perchlorate.

(3) When using potassium nitrate, barium nitrate, or strontium nitrate that contain no chloride as the oxidizer, the flame produced is a very clear colored flame. When using CuCl spectra to produce a blue flame, it is necessary to keep HCl gas in the flame to eliminate the green continuous spectra. In such case the addition of ammonium perchlorate, polyvinyl chloride or ammonium chloride is desirable. However, protection from moisture is required except in the case of polyvinyl chloride.

When using potassium salts as the oxidizer, continuous spectra from potassium atoms appear as described for low temperature flames. However, such continuous spectra generated from metal atoms cannot be eliminated by having HCl or Cl₂ gas in the flame. There is a large difference between such atomic spectra and band spectra (molecular spectra). Therefore, when using potassium salts, it is not possible to avoid flames that look whitish.

(4) The effective range of the ratio of magnesium to oxidizer becomes greater when using a proper fuel (e.g., shellac) even when the oxygen balance is not good.

3. How To Avoid Interactions between Component Materials

In the foregoing study the interactions between component materials were not discussed. However, we must consider these reactions in practice. These reactions are mainly as follows:

(1) The reaction of magnesium with ammonium perchlorate is likely to occur only in the presence of moisture, producing H₂ and NH₃ gases with heat evolution. The chemical product that remains in the composition is magnesium perchlorate, which is very hygroscopic.

(2) The reaction of magnesium with ammonium chloride resembles that of (1). It is likely to occur only in the presence of moisture, producing H₂ and NH₃ gases with heat evolution. The material that remains after the reaction is magnesium chloride, which is very hygroscopic.

(3) The reaction between potassium nitrate and ammonium perchlorate is the so-called double decomposition. The reaction products are potassium perchlorate and ammonium nitrate. The latter is very hygroscopic.

Another reaction, which resembles the above, is with compositions that contain barium nitrate and ammonium perchlorate. In this composition, the double decomposition did not occur even when unprotected and exposed to the air for 18 months.

The unwanted reactions of (2) and (3) may be avoided by selection of chemicals. Namely, ammonium chloride should be replaced with polyvinyl chloride. This is experimentally confirmed. Polyvinyl chloride is superior to ammonium chloride because it is non-hygroscopic and combustible by nature. The contact of potassium nitrate and ammonium perchlorate often occurs when there is contact between black powder prime and colored flame composition. This can be avoided by using a potassium perchlorate-based prime in such cases.

The cases are not always avoidable; however, with perfect moisture-proof construction one can suppress the reactions. Namely, by selection of binder or by selection of container, one can obtain almost perfect moisture-proof conditions at low cost. It is most important to develop a

method of stabilizing magnesium from corrosion. The author shall describe this problem in another study.

4.0 Series of Fundamental Compositions in Practical Use

Described here are some fundamental compositions based on the foregoing spectral studies and other naked eye observations of flames. For the judgment of usability of the composition, the author put the emphasis on flame colors.

When the limit of product use is decided, one can select the most adaptable composition with burning velocity and loading density for one's purpose. And if this allowable range is wide enough, the freedom of the composition selection is also large.

The range of practical use, which is designated by the shaded area in the triangle diagram, is based on two factors: one comes from the distinction of flame color; the other comes from the distinction of the possibility of burning—combustible or incombustible zones. If the composition produces a good flame color but is difficult to burn, it is out of the zone. There is a problem in deciding the range. The sample specimens are as small as that of lance work. Generally when the diameter of the composition increases, the effective zone also increases. Therefore, the compositions of larger diameter items may sometimes fall in an expanded effective zone.

4.1 Method of Deciding the Effective Zone

(1) Compositions of various mixing ratios were burned, and the flames were observed with the naked eye to decide if they were in the effective zone or not. The component ratios were differentiated generally by 10 weight percent, and at important points or important compositions with 5 weight percent. The observation with naked eye of flame color was very sensitive and effective to decide the effective zone. (The spectrometer is useful for investigation of the color flame mechanism, but not for determining good flame color.)

(2) The sample specimens were made by loading a composition into a threefold brown paper tube of 9.5 mm inside diameter by 60 mm long. These were the same dimensions as for the lance of the frame works. The loading densities of a series are shown in Figure 1 as an example. Generally other series show nearly the same tendency. In Figure 1 the values of the loading density refer to the values of the weight ratio of oxidizer to magnesium, and the larger the former, the larger the latter. (The numbers added to the curves show the loading densities in g/cc.)

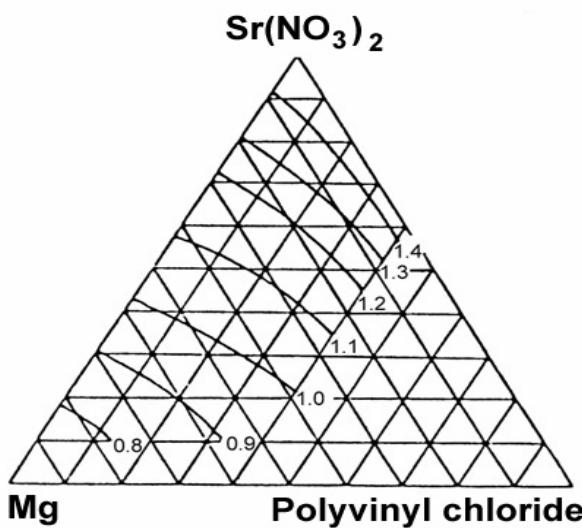


Figure 1. Distribution of loading densities of a series of composition: $\text{Sr}(\text{NO}_3)_2 + \text{Mg} + \text{polyvinyl chloride}$.

(3) The chemicals used were of commercial industrial grade. Therefore, the flame color might be interfered with by Na-D lines and $\text{BaCl-}\alpha$ bands to some degree.

(4) The flames were observed from a distance of 1 m for low temperature flames and 50 m for high temperature flames.

4.2 Series of Low Temperature Flames

It is already known from Parts IV and V that the effective zone is very narrow. Namely, the influence of the oxygen balance on the effective zone related to flame color is very large. A balanced or excess of oxygen condition is the most effective for good color. Therefore, it is almost

impossible to regulate the burning velocity by regulating the fuel to oxidizer ratio under good flame color conditions.

The flame color of the low temperature flame series was greatly affected by the type of fuel. Moreover the state of the spectral band and the flame temperature also affect the flame color.

Examples of low flame temperature compositions were listed in Parts IV and V and in author's book.^[3] Here only blue flame compositions using copper powder are additionally described. When using ammonium perchlorate as the oxidizer and copper powder as the color agent, only shellac, pine root pitch or colophony were effective as the fuel. The quantity of fuel was the most effective at 10%; that of copper powder was effective from 5–30%, but the intensity of the blue colored light was not proportional to the percentage, but practically 5–10% may be useful. Therefore, the next standard may be recommended:

Blue flame composition with ammonium perchlorate as oxidizer:

Ingredient	%
Ammonium perchlorate	80–85
Fuel (shellac, pine root pitch, or colophony)	10
Copper powder	10–15

When using copper powder and potassium perchlorate, only shellac is recommended as the fuel. The quantity of the copper powder was effective with 5–30%, but practically 5–10% may be useful:

Ingredient	%
Potassium perchlorate	80–85
Fuel (shellac)	10
Copper powder	5–10

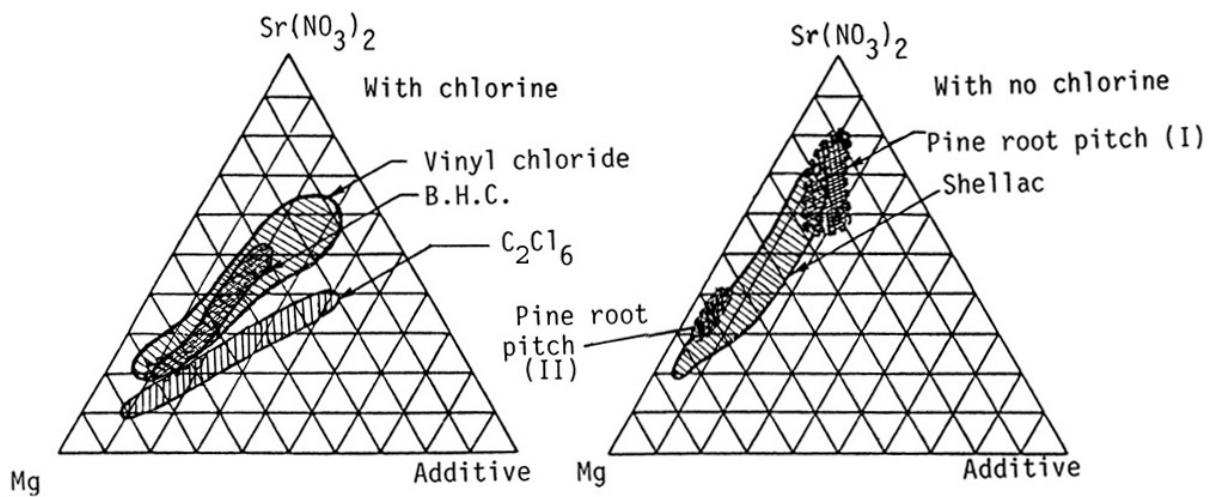


Figure 2. Effective zone of $\text{Sr}(\text{NO}_3)_2 + \text{Mg} + \text{additive}$ series.

4.3 Series of High Temperature Flames

4.3.1 Red flame series

(1) Strontium nitrate series (Figures 2 and 3)

In this series, strontium nitrate contains no chlorine. Therefore, the continuous spectrum is very strong, and it is necessary to add something to suppress it. When BHC, polyvinyl chloride, hexachloroethane, shellac, or pine root pitch was added, the color producing ranges are shown in Figure 2.

When using materials that contain chlorine as an additive, the shapes of effective zone of flame color resembles well that of BHC. However, the former is wider than the latter. Namely, polyvinyl chloride gives more flexible selections of burning velocity or loading density than BHC. With reference to the flame color in the effective zones, polyvinyl chloride gave clearer and prettier red flames than the others. The effect of BHC was next and that of hexachloroethane followed last. Hexachloroethane has the largest chlorine content of all, but the effect was contradicted with the result of the experiment. (See Parts IV and V.)

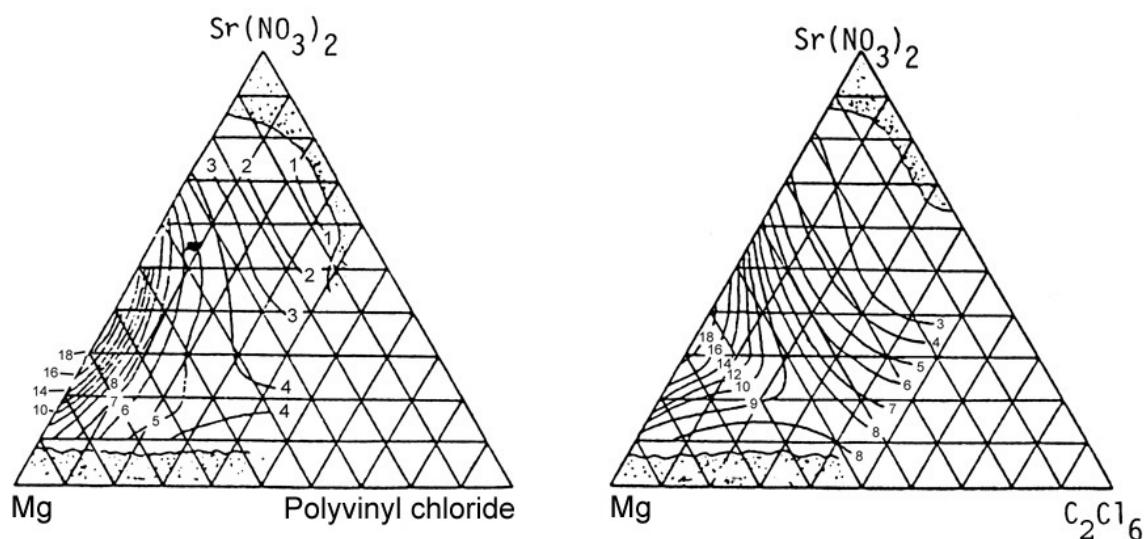


Figure 3. Burn rate (mm/sec) of a part of the above series.

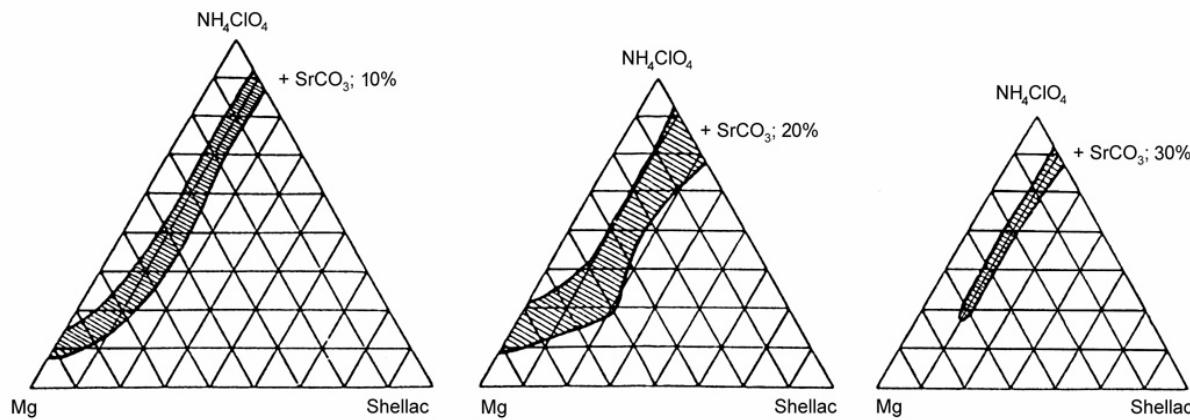


Figure 4. Effective zone of $\text{NH}_4\text{ClO}_4 + \text{Mg} + \text{shellac} + \text{SrCO}_3$ series

When using materials with no chlorine additive, the shapes of the effective zone are quite different from that described above. Also the effective zone of shellac is different from that of pine root pitch. Namely, shellac produces the best flame color at 10–15%. When using pine root pitch, the effective zone is divided into two areas. The color of the no chlorine flame is slightly different from that of the chlorine containing flame, and it looks slightly yellowish red. This is caused by the strong SrO band with very weak bands of β , γ , and δ .

Examples of burn rate are shown in Figure 3. The numbers on the curves show the values of burn rate in mm/sec. The curves in both figures resemble each other and represent general conditions of such compositions. Namely, in the zone of effective color production the burn rate increases with the increase of the ratio of magnesium to oxidizer.

As in the examples in Figure 2, the effective color producing zone is a long bandlike area parallel to the oxidizer-Mg line. In the area where the weight ratio of Mg to oxidizer is small, the composition does not burn easily and produces many sparks. When the ratio becomes larger, it is easier to burn and has fewer sparks. However, when the ratio becomes too large, the sparks are too numerous, and they interfere with the flame.

(2) Ammonium perchlorate series

The results using shellac as an additive are shown in Figure 4. The numbers indicate that the quantity of 10–15% shellac in weight ratio is the most effective regardless of the quantity of strontium carbonate. The quantity of strontium carbonate has the largest width of the effective zone at a weight ratio of 20% as indicated in Figure 4.

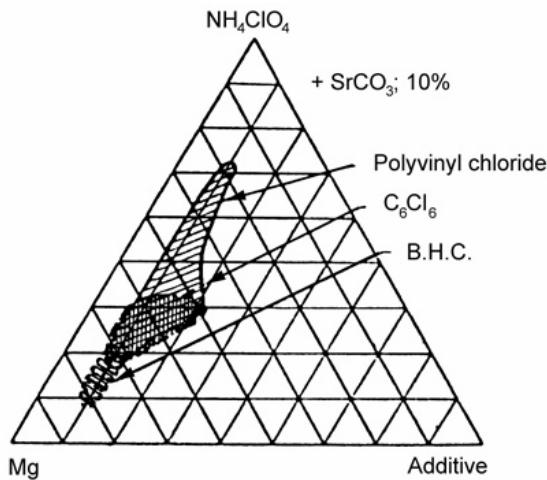


Figure 5. Effective zone of $\text{NH}_4\text{ClO}_4 + \text{Mg} + \text{additive} + \text{SrCO}_3$ series.

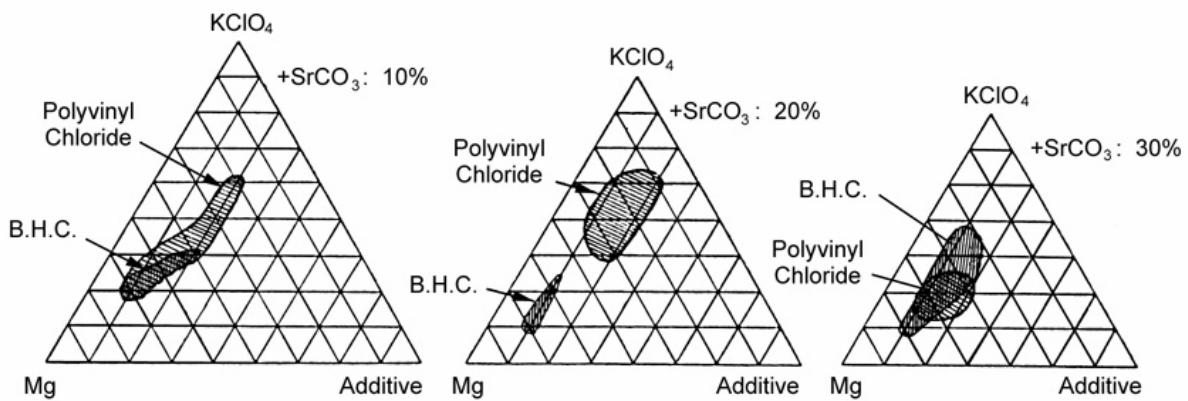


Figure 6. Effective zone of $KClO_4 + Mg + \text{additive} + SrCO_3$ series.

In the ammonium perchlorate series, HCl gas is produced in the flame, which is favorable for color creation. Therefore, it seems unnecessary to add some additives for color production. When polyvinyl chloride, BHC or hexachloroethane was added to the composition, the effective color producing zone was narrower than that when shellac was added to the composition; compare Figure 5 with Figure 4.

(3) Potassium perchlorate series

i. When additives contain chlorine:

The quantity of color agent needs to be fairly large (i.e., 20–30% of the composition) to obtain a good effective zone. The results of the experiment are shown in Figure 6.

Strontium carbonate is useful until the quantity increases to 30%. This is the case with am-

monium perchlorate. The additives are most effective in the 10–20% range. The flame color is somewhat pinkish. The effective zone for polyvinyl chloride is somewhat wider than that for shellac, and for hexachloroethane (10% addition) the flame color is not good even when the strontium carbonate is increased to a higher percentage.

ii. When additives contain no chlorine:

When using shellac as the additive, the flame color is more clear and beautiful than with the chlorine-containing additive. The effective color producing zone is shown in Figure 7.

(4) Potassium nitrate series

It can be predicted that some additives that contain chlorine may be effective because potassium nitrate does not contain chlorine. An

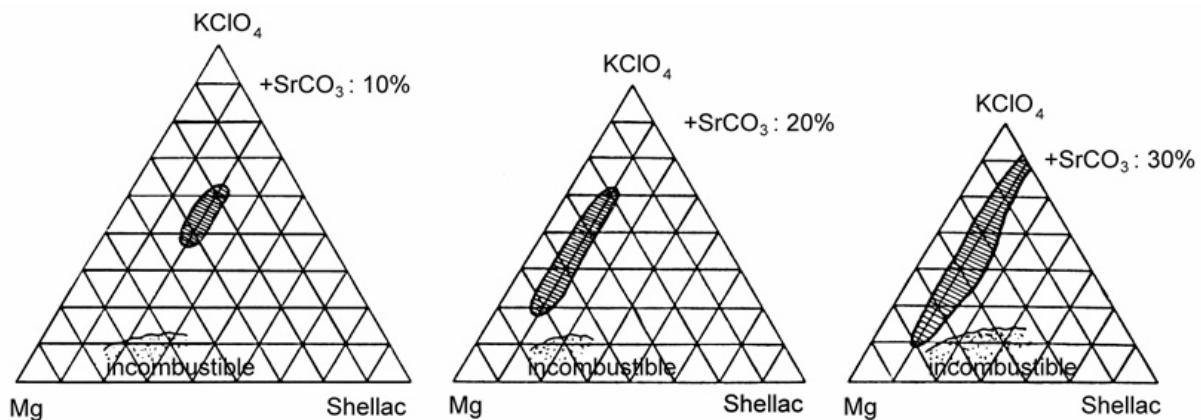


Figure 7. Effective zone of $KClO_4 + Mg + \text{shellac} + SrCO_3$ Series.

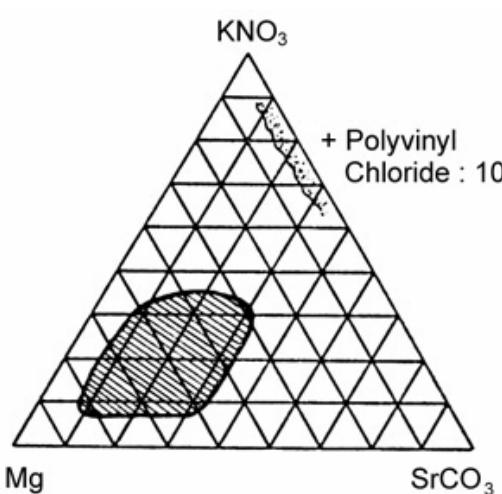


Figure 8. Effective zone of $KNO_3 + Mg + SrCO_3$ + polyvinyl chloride series.

experimental result when using polyvinyl chloride is shown in Figure 8.

The experiment with 20% potassium nitrate and 20% strontium carbonate produced the most effective flame color. Using potassium nitrate for color production is limited only in high flame temperature compositions.

With the above experiments it was shown that polyvinyl chloride or shellac gave the widest effective zone of color production. However, shellac gave slightly orange red flames due to the strong α band and Na spectra from impurities.

4.3.2 Yellow flame series

Na-D lines appear very easily and the effective zone is very wide; so there are no problems except when a pure yellow flame is required. Generally in high temperature flames, a large width of continuous spectrum CS(Na) accompanies the Na-D lines. Therefore, the flame color is slightly reddish yellow, so-called golden yellow.

The effective zones for ammonium perchlorate and potassium perchlorate are shown in Figure 9.

However, when ammonium perchlorate is used as the oxidizer, the zone in the graph is surrounded by an incombustible area. Fortunately, the combustible part produces a good flame color when it burns.

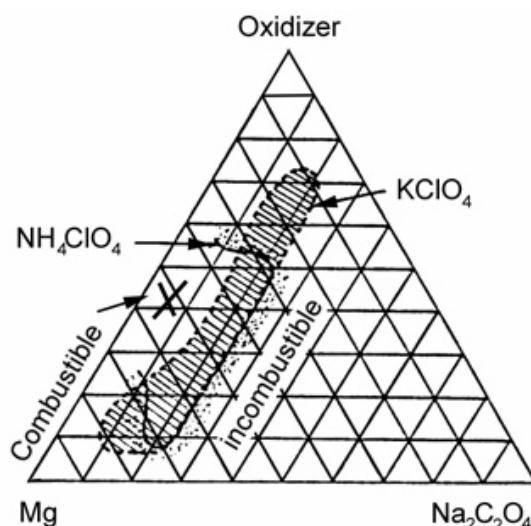


Figure 9. Effective zone of oxidizer + Mg + $Na_2C_2O_4$ series.

When potassium perchlorate is used as the oxidizer, 10% sodium oxalate gives the best flame color zone.

When potassium nitrate is used as oxidizer, the effect of adding 10% polyvinyl chloride is shown in Figure 10. Polyvinyl chloride has a role to suppress the continuous spectra. The effective zone is very wide and with no problems.

4.3.3 Green flame series

(1) Barium nitrate series

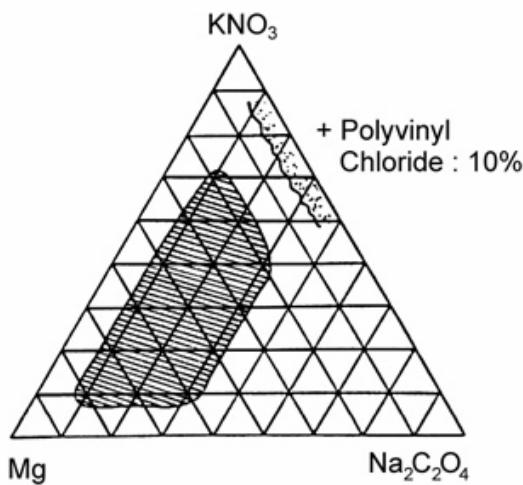


Figure 10. Effective zone of $KNO_3 + Mg + Na_2C_2O_4$ + polyvinyl chloride series.

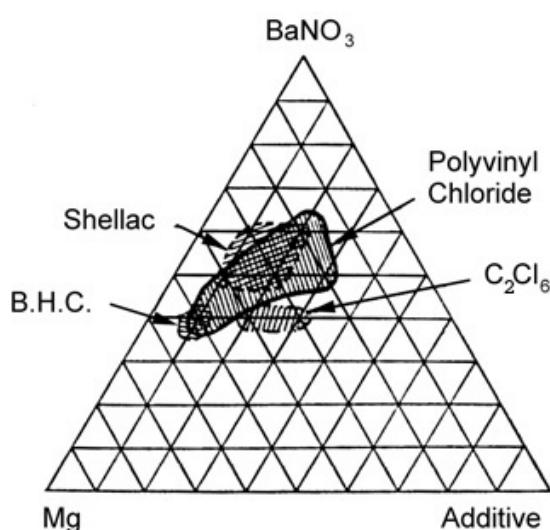


Figure 11. Effective zone of $\text{BaNO}_3 + \text{Mg} + \text{additive}$ series.

This oxidizer has no chlorine; therefore, it is necessary to add chlorine donors to intensify the BaCl band and suppress the continuous spectra. The experimental results are shown in Figure 11.

Figure 11 shows that polyvinyl chloride gives the widest effective zone of color production zone, and 20% polyvinyl chloride produces the

best green flame. BHC and hexachloroethane give very narrow effective zones and the color is not as good as with polyvinyl chloride.

When shellac is used as the additive, the color of the flame appears faint and not very clear. This is due to the fact that shellac does not increase the intensity of the BaCl band.

(2) Ammonium perchlorate series

This oxidizer produces HCl in the flame. In this study additives that contain chlorine were added to further suppress the continuous spectrum. The effects are shown in Figure 12.

Polyvinyl chloride as an additive gave the widest effective zone. The flame color for the hexachloroethane is not good.

(3) Potassium perchlorate series

The three component compositions of potassium perchlorate, magnesium and barium carbonate produce a weak green flame (only producing visible color at 20% potassium perchlorate). This defect comes from the very strong continuous spectrum caused by heated metal oxide particles, which at high temperatures emit white light. Additives result in better flame color. The results are shown in Figure 13.

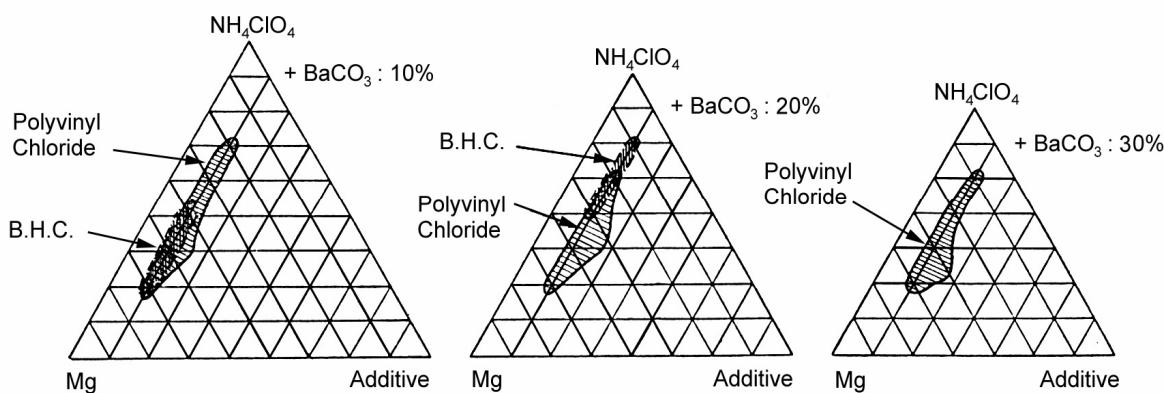


Figure 12. Effective zone of $\text{NH}_4\text{ClO}_4 + \text{Mg} + \text{additive} + \text{BaCO}_3$ series.

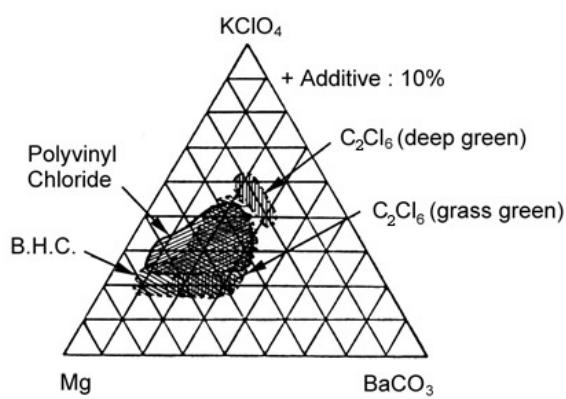


Figure 13. Effective zone of $KClO_4$ + Mg + $BaCO_3$ + additive series.

With polyvinyl chloride as an additive, the flame color is good and the effective zone is wide. BHC is not good for color production. Hexachloroethane makes two effective zones producing special effects (i.e., as the percentage of magnesium increases, first the flame is colored deep green, becomes white, then changes to a pretty grass green).

(4) Potassium nitrate series

Three component compositions of potassium nitrate, magnesium and barium carbonate were tested, the effects are shown in Figure 14.

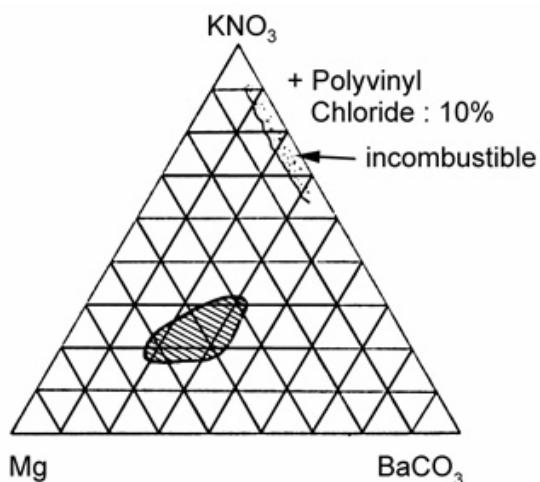


Figure 14. Effective zone of KNO_3 + Mg + $BaCO_3$ series.

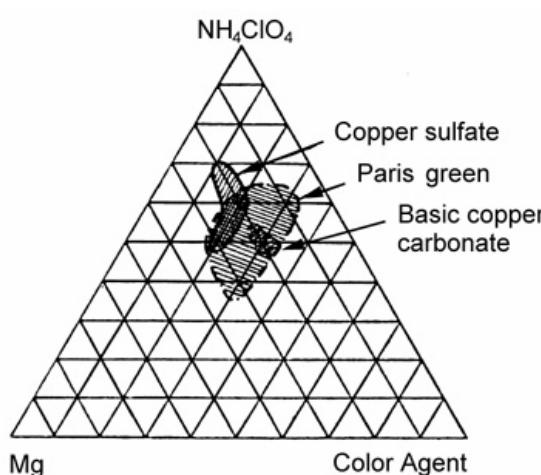


Figure 15. Effective zone of NH_4ClO_4 + Mg + color producing agent series.

The color in the effective zone was grass green.

4.3.4 Blue flame series

Producing blue colored flame is difficult when using the CuCl band at high temperatures (See Part V).

(1) Ammonium perchlorate series

i. No fuel additive:

The effect of the three component composition of ammonium perchlorate, magnesium and color agents is shown in Figure 15.

Paris green gives the prettiest blue flame and the widest effective zone of all.

ii. With 10% polyvinyl chloride additive:

Ten percent polyvinyl chloride was added to the above composition and tested. The effect is shown in Figure 16.

Basic copper carbonate gives the prettiest blue flame and the widest effective zone; next is Paris green. From other spectral studies the author did not notice much difference among the various color agents; however, in this case fairly large differences appear. This might be due to the Na impurity due to using industrial grade chemicals.

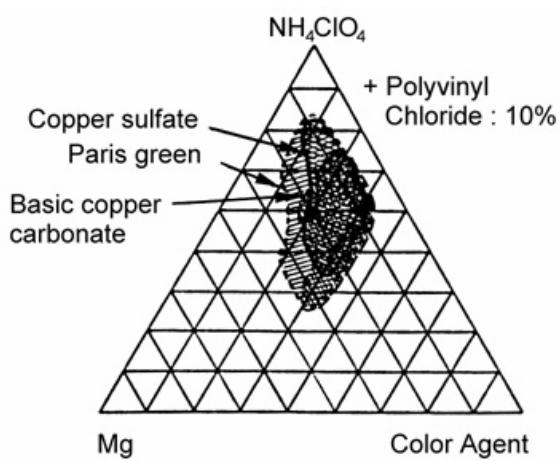


Figure 16. Effective zone of $\text{NH}_4\text{ClO}_4 + \text{Mg} + \text{color agent} + \text{polyvinyl chloride}$ series.

Compositions using copper powder as the color agent that give good blue flame color are as follows:

Polyvinyl chloride %	NH_4ClO_4 %	Mg %	Cu (additional %)
10	70	20	2
10	80	10	2
10	70	20	4
10	80	10	4
10	60	30	6
10	70	20	6
10	80	10	8

The result of the experiment using BHC in place of polyvinyl chloride is shown in Figure 17.

Using BHC as an additive and copper powder as the color agent did not produce good flame color. The flame was whitish and not a clear blue. Hexachloroethane did not give good color to the flame. Shellac was tested as an additive fuel and the result is shown in Figure 18.

(2) Potassium perchlorate series

The continuous spectrum of potassium interferes with the flame color and the color is not as good as when using ammonium perchlorate.

i. Three component compositions that consisted of potassium perchlorate, magnesium and color agent were tested. As the color agent, Paris green, copper sulfate and basic copper carbon-

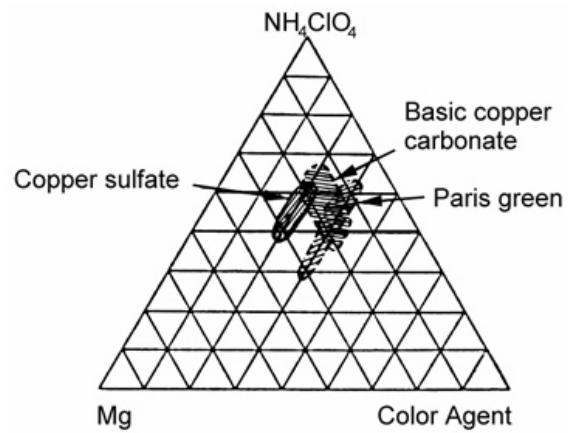


Figure 17. Effective zone of $\text{NH}_4\text{ClO}_4 + \text{Mg} + \text{color agent} + \text{BHC}$ series.

ate were used. None produced good flame color; however, a composition of 60% potassium perchlorate, 10% magnesium and 30% Paris green gave a slightly blue flame.

ii. An experiment was carried out that added 10% polyvinyl chloride to the above compositions. Paris green gave the best flame color. Copper powder made the flame whitish and is not practical. The above results are shown in Figure 19.

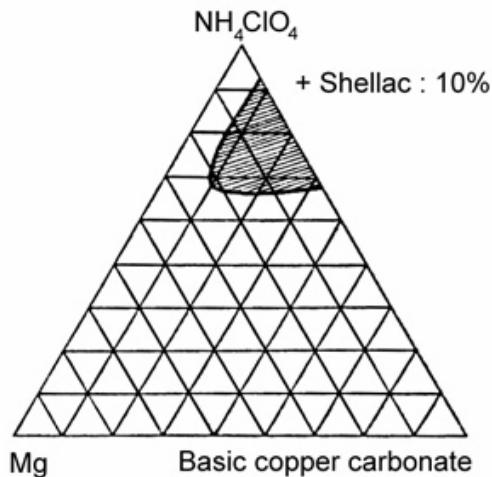


Figure 18. Effective zone of $\text{NH}_4\text{ClO}_4 + \text{Mg} + \text{basic copper carbonate} + \text{shellac}$ series.

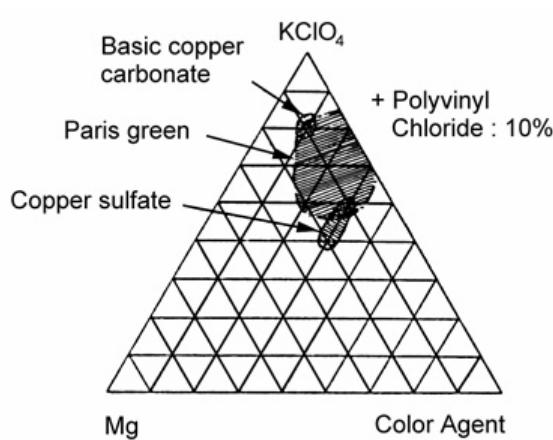


Figure 19. Effective zone of $KClO_4 + Mg +$ color agent + polyvinyl chloride series.

5. Conclusion

On the basis of the former spectrometric study the author investigated practical, useful effective zones of various compositions from the standpoint of producing good colored flames. In the practical case, we could easily select the composition for our purpose, considering the color producing conditions. However, it will be more useful, when we prepare the data of burn rate, light intensity, or loading density, etc. for the effective zones. This remains as a future problem.

The common important factors in Part VII are as follows:

(1) Effective color producing zone:

The low temperature series is mostly affected by oxygen balance; the effective color producing zone is very narrow and the selection is difficult. On the other hand, the high temperature series is not as much affected by the oxygen balance, and the selection of flame color, burn rate or light intensity is far easier than for the low temperature series.

(2) Storage problem:

The high temperature flame series generally contains magnesium as a fuel. Therefore, for storage the compositions should be completely waterproof or moistureproof, or the magnesium should be coated to protect it from corrosion.

When using the low temperature series of compositions, generally there is no need for such processes.

(3) At present the most pretty and deep flame color is obtained by using an additive that produces HCl gas in the flame like ammonium perchlorate or polyvinyl chloride. However, ammonium perchlorate is only useful when it is protected from effects due to water or moisture.

(4) In the high temperature series potassium perchlorate is useful for red or yellow flame without ammonium perchlorate.

(5) Potassium nitrate is practical for use only in the high temperature series of red, yellow and green (grass green) for special purpose. The low temperature series are useful only for red, yellow, and green (grass green) but not for blue.

(6) Of the chlorine or hydrogen chloride containing material, polyvinyl chloride, hexachloroethane, etc., polyvinyl chloride is the most effective for producing good colored flame; BHC follows the next, and third is hexachloroethane, which is not as good for color production.

(7) Shellac has no chlorine but is effective for producing red or yellow flames.

As described earlier, the sample specimens were of small diameter. The compositions that did not burn with such a small diameter would often burn when the diameter is larger than the samples used. For example, a superior blue composition is here given. This composition burns producing a beautiful blue when the diameter is more than 20 mm.

Ingredient	Percentage
Barium nitrate	50
Magnesium	20
Hexachloroethane	30
Copper powder	5 (additional)

Literature Cited

- 1) T. Shimizu, *Hanabi* (1957) p 151.
 - 2) Ibid., p 277.
 - 3) Ibid., p 129.
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Acknowledgement

The author is very grateful to Professor Dr. S. Yamamoto, my teacher at the Tokyo University, who always encouraged this author to do firework studies. Further I am also grateful to Mr. Takada, Hosoya, Kinsei, Kizaki and Endo who kindly helped the author in doing experiments.

Autobiography of a Pyrotechnist — Dr. Takeo Shimizu

(Continued from page 106)

In November 1951 I obtained a position at Hosoya Fireworks Co. in Tokyo through the introduction of Dr. Yamamoto. I had two duties there; to learn the manufacturing of fireworks from the President, Masao Hosoya, and to modernize the factory in business and technique. Mr. Hosoya very kindly taught his secrets in the technique called the "Machida School". I analyzed the technique of Japanese chrysanthemum shells, and Dr. Yamamoto recommended that I submit the paper as a thesis for a degree. In 1958 I was granted the degree of Doctor of Engineering with the paper "The Design Conditions of Chrysanthemum Shells".

My senior, A. Kawai, who was a friend of Dr. Yamamoto, asked me to help with his work, the manufacturing of rocket propellants at the plant of Dainippon Celluloid Co. in Kochi village in Hyogo-ken. Therefore, I often visited the plant and helped Mr. Kawai in designing rocket propellant. In the plant there were not many people, but two very superior assistants, Matsunoto and Matsuda.

In 1963 I changed my position to the Perfect Liberty Religion Order in Osaka, accepting the offer from the founder, T. Mild, who planned to build a new factory and an institute of fireworks. However, the plan was not realized because of financial reasons. I was very disappointed. Dr. Yamamoto had passed away that same year, and I lost my largest prop and stay in fireworks. I had plenty of time every day and decided to learn languages from the NHK Broadcasting. I had a secret desire to live in some foreign country and to build a fireworks factory. I learned English, German, French, Spanish, Russian, Chinese,

and by books, Italian and Arabic. I used to walk from my house to the PL fireworks office memorizing Arabic letters. I was often interrupted by the kind PL teachers who offered to bring me by car.

In 1967 I got my present position in the factory of Koa Fireworks. The factory was built by my old friend, the late N. Mizogami, who built a small laboratory for me. The factory was mainly producing maritime distress signals. I continued the study of fireworks finding time intervals at the work until today following the request of my old teacher Dr. Yamamoto. Therefore, very often, even on holidays, I am not working at home, but in my laboratory at the factory, which is fifteen kilometers distant from my house.

In the past some friends from overseas countries stayed overnight in my home in Kawagoe-shi, which is thirty five kilometers northwest of Tokyo: Miss Sigrid Wied, Dr. F-W Wasmann, W. Zink from Germany, Pierre-Alain Hubert from France, and Mrs. Pettit from the USA. Recently my wife fractured a vertebra and I can not invite guests to my home any more. My work room has been recently confused. The bookshelves are full of books and the residual books are scattered on the tables and floor. On the shelves there stand the complete works of philosophy by the late Dr. Nishida, and the same of the late Dr. Tanabe and of the late Kenji Miyazawa on his poets, the Testaments in various languages, books concerning Buddhism plus technical books, etc. They are covered in dust and will sleep until I have more time.

Selected Pyrotechnic Publications of Dr. Takeo Shimizu

Part 1 (1985 to 1994) from the International Pyrotechnic Seminars

This is a collection of previously published technical papers that appeared in the *Proceedings of the International Pyrotechnics Seminars* from 1985 to 1994. [ISBN 1-889526-08-8]

Cover Price is \$ \$25

Discounted Price is \$18*

Hypothesis on the Cause of Serious Accidents Related to Salutes Charges

Proceedings of the 10th International Pyrotechnic Seminar, July, 1985

Abstract: First, we hypothesize that a serious accident related to the use of salutes may be caused by the simultaneous explosion of several salutes or salute components, resulting in an unexpected, abnormally strong shock wave. To prove our theory, we conducted three experiments. In Experiment 1, we examined the transfer of the explosion between salutes with one donor to shed light on the properties of the charges. Experiment 2, which we conducted to examine the transfer in the case of two donors, revealed a localized effect of the transfer. In Experiment 3, we measured the pressure during explosion using a pressure-sensing film, which was used to create pressure contour lines. Our experiments reveal that there is an area of abnormally high pressure, a finding which supports our hypothesis.

A Concept and the Use of Negative Explosives

Proceedings of the 11th International Pyrotechnics Seminar, July 1986

Abstract: In general, a pyrotechnic composition consists of an oxygen donor such as KNO₃, KClO₃, or KClO₄, etc., an oxygen donee such as organic resin and some other inert substances. When substances, CaCO₃, Al₂O₃, SiO or CaSO₄, etc. are contained in it, they are regarded as an inert substance, because they are full of oxygen and cannot be more oxidized. This type of explosive deflagrates with oxidation reaction and could be called "positive explosives". However, with some substances, Mg, Al or Si, etc., which have a very large reduction capacity, the inert substances change to active ones. This type of explosives, which consist of Mg, Al or Si, etc., plus a substance that is thought to be inert in conventional explosives, is defined here as "negative explosives". With the oxygen donee, Mg was concerned as a representative case, because it is very popular and has the largest reduction capacity; it burns even sand or earth. About 50 types of negative mixtures were listed as samples. Their characteristics were examined by several tests. Ignition and burning properties were tested on the ground by using black match. Ignition temperatures were obtained from a heating test in a glass tube. Illuminating capacities were measured by burning consolidated mixtures as a flare. Ballistic characteristics were examined by firing a projectile with a small mortar by using granulated mixtures for the propellant charge. The results were discussed and a proposal for use of negative explosives was made.

Ballistics of Firework Shells

Proceedings of the 13th International Pyrotechnics Seminar, July 1988

Abstract: Heretofore we have had four important problems with calculations in this field, i.e., with the interior ballistics when using Black Powder as the propellant: (1) to obtain a suitable form function of the propellant which consists of irregular grains, (2) to obtain solutions when the burning rate of the propellant grains is proportional to P (where P is an internal pressure of the mortar barrel and the pressure exponent, (3) to obtain suitable solutions when the propellant gas escapes from the burning room through the clearance between the wall and the shell in the mortar, and with the exterior ballistics (4) to obtain simply the drag coefficient for various shapes of shells. For (1) a treatment to calculate the surface areas and volumes of grains assuming the propellant grains consist of a mixture of cubes and spheres is proposed. For (2) a method to solve a third order differential equation derived from three basic interior ballistic equations step by step with proper time intervals is proposed. For (3) the nozzle theory used for rocket engines is introduced. For (4) the fact that the maximum height of the projectile in the air is almost the same as that of vacuum when the flying times of the both are equal is applied. These methods are applied to 6-inch shells and examined if they are suitable in practice.

An Example of Negative Explosives: Magnesium Sulfate/Magnesium Mixture

Proceedings of the 15th International Pyrotechnics Seminar, July 1990

Abstract: At the Eleventh International Pyrotechnics Seminar, 1986, in Vail, Colorado, I reported on a study of pyrotechnic mixtures with a theme, "A Concept and the Use of Negative Explosives". A further study has been continued on the same subject as before. In the former report it was known that magnesium sulfate/magnesium mixture detonates on heating. I studied if it is suitable for the noise mixture of fireworks in place of the ordinary one which contains aluminum and potassium perchlorate and which has long been a cause of serious accidents in the firework industry. The chemical reaction of the magnesium sulfate/magnesium mixture on detonation is thought to be: MgSO₄ + 4 Mg → MgS + 4 MgO + 353 kcal. From several experiments the following results were obtained: (1) The intensity of the explosive noise from the magnesium sulfate/magnesium mixture is almost the same as that from the ordinary aluminum mixture when the weight of the charge of the former is two or two and a half times as large as that of the latter. (2) The magnesium sulfate/magnesium mixture is far more safe on handling than the ordinary aluminum mixture. It was proved by an iron ball drop test and a fire propagation test. (3) The tone quality of the noise from the magnesium sulfate/magnesium mixture is mild and superior to that from the ordinary

aluminum mixture. (4) In practical use it is necessary to protect the noise unit which contains the magnesium sulfate/magnesium mixture from moisture.

The Effect of Hot Spots on Burning Surface and Its Application to Strobe Light Formation with Mixtures Which Contain No Ammonium Perchlorate

Proceedings of the 16th International Pyrotechnic Seminar, June, 1991

Abstract: The objective of this work was to make clear the effect of hot spots or hot spot materials on burning pyrotechnic compositions and to find practicable strobe light compositions without ammonium perchlorate which is not always popular in the firework field, using the effect of hot spot materials. As the hot spot materials, four types, Japanese oak charcoal, red iron, red lead, and potassium dichromate were selected from many substances. The effect of each was examined by burning tests of compositions which contained rosin, usual oxidizers (ammonium perchlorate, potassium perchlorate, and potassium nitrate), and a small quantity of each hot spot material. In this case, the effects did not clearly appear except that of potassium dichromate, which promoted the burn rate of compositions in fairly large extent. Secondly, the effect of red lead and potassium dichromate was examined with compositions which consisted of magnesium, guanidine nitrate, and metal sulfates, which had been thought to be suitable for strobe lights. From the results of experiments, examples of four colored light compositions are shown for practical use. It is concluded that the effects of hot spots are not so clear, when using with compositions which contain usual oxidizers. However, when using with the compositions for strobe light, which do not burn so easily, the hot spot materials are very effective in adjusting the strobe reaction and to obtain the compositions in practical use.

The Surface Explosion of Pyrotechnic Mixtures

Proceedings of the 18th International Pyrotechnics Seminar, July 1992

Abstract: In the past we sometimes observed a fairly large burning star caused an explosion with a loud noise at the very moment when it fell onto the ground. The star did not explode totally, but only with the thin surface layer. The burning surface layer of the star may be very sensitive to shock because of the high temperature. This phenomenon is here called the "surface explosion". The objective of this paper is to investigate the surface explosion by experiments. It may be very important to make clear the mechanism of the transition from burning to explosion or detonation not only with pyrotechnic mixtures, but also with general explosives, especially to avoid accidents. The mechanical sensitivity of the burning surface layer was examined by dropping an iron ball onto it with consolidated mixtures of ordinary stars and illuminants, etc. Most of them showed a higher sensitivity than that of a standard mixture called red explosive at ordinary temperatures. Using small rocket engines, propellant of potassium chlorate and potassium perchlorate comparing with that of ammonium perchlorate were examined. The former two caused the surface explosion or a perfect detonation when ignited and the rocket engines were broken, and only the propellant of ammonium perchlorate worked well. The phenomenon of the surface explosion was discussed in combination with a past accident.

Stabilizing Firework Compositions I. Minimum Solubility Law to Foresee the Degeneration II. A New Chemical Method of Magnesium Coating

Proceedings of the 19th International Pyrotechnics Seminar, February, 1994

Abstract: These studies concern two important problems at present: one is how to select the component materials of a mixture not to cause degeneration, and another is to find a more effective method of magnesium coating than those at present. A firework mixture generally consists of several solid materials which are closely in contact with each other. The state is not so much natural as artificial. Therefore, the mixture often causes chemical degeneration to remove into a more stable state which is opposite to the purpose. The direction of the change has been unknown without experiences. It has been a great difficulty on selecting materials. I have found a rule to foresee the direction: the component materials in a mixture gradually decomposes with each other to create the most water insoluble material. This tendency should be called the "minimum solubility law". A table was prepared to foresee the direction of the degeneration reactions arranging materials in the order of their solubilities. When a magnesium flake is soaked in a solution of dichromate and sulfate, the flake is gradually coated with a thin black film. It may be CrO₂ and have a high corrosion resistance. The effect was tested with several dichromates and sulfates against mainly ammonium perchlorate using magnesium ribbon and powder. In addition an effect of guanidine nitrate on the coating was observed because it gave a good result of corrosion resistance when it was used as a blinker (strobes) in the past.

Burning Rate and Grain Size of Component Materials of Pyrotechnic Mixtures

Proceedings of the 20th International Pyrotechnics Seminar, July 1994

Abstract: It has been generally believed that the finer the grain size, the faster the burning when we select the component materials of a pyrotechnic mixture. It is not always true because a small explosion occurred in the past when we tested a smoke mixture, although it contained a dye of very coarse grains. The purpose of this paper is to make clear the general mechanism of the burning rate of pyrotechnic mixtures on the standpoint of the grain size of component materials of pyrotechnic mixtures. Experiments on burning rate were carried out with four types of mixtures changing the grain size of the component materials: (a) base mixtures of oxidizer (conventional materials as potassium chlorate, potassium perchlorate or ammonium perchlorate) and fuel (accroides resin), (b) mixtures of the base and an inert material (clay), (c) mixtures of the base and a semi-inert material (barium nitrate), (d) mixtures of an explosive of synthesized simple substance (potassium picrate) and an inert material (clay). All the materials except potassium picrate were sieved to obtain grains of six class

sizes. With decreasing the grain size of the component materials, some mixtures increased and some decreased the burning rate. In other cases there were grain sizes which gave the smallest burning rate: the burning rate at first decreased and then increased. In general, the burning reaction seemed to be stabilized as the grain size decreased. These effects will help the designing of pyrotechnic mixtures for various purposes.

Selected Pyrotechnic Publications of Dr. Takeo Shimizu

Part 2. Translated Articles

A collection of previously published technical papers that appeared in various publications between 1978 and 1995. These articles were translated into English. [ISBN 1-889526-10-X]

Cover Price is \$ \$25

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The Critical Burning of Pyrotechnic Compositions

From *Pyroteknikdagen*, 1983

Introduction: The author attempts to establish a general theory summarizing the phenomena related to the chemical reactions occurring inside pyrotechnic compositions.

There are three types of reactions: smoldering, burning and detonation. In addition, there are several interesting variations like sparking, flashing [strobing] and pyrotechnic whistling. These phenomena fall between smoldering and burning or between burning and explosion and should be referred to as "critical burning". The theory must include these phenomena.

Some Techniques for Manufacturing Fireworks (1) Dark Delay Compositions

(2) The Use of Metal Powders

From *XVth Internat'l Pyrotechnics Congress* 8 – 11 Nov. 1989

Introduction: In recent years I have studied the oxidation and reduction taking place between various substances in a mixture. I reported on some of these studies in a paper titled "A Concept of Negative Explosives" presented in 1986 at the Eleventh International Pyrotechnics Seminar in Vail, Colorado, USA. In the present paper, I will be presenting the follow-up work, which I have performed under the above title.

The work was carried out using the oxygen value of the mixture to clarify the burning effects. The oxygen value denotes the excess (positive) or inadequate (negative) amount of oxygen generated in grams per 100 grams of mixture during the burn.

The term "dark delay composition" refers to a mixture which does not form a flame or spark that is visible from a distance. The effect can be used to prevent the formation of the trail from a flying firework. It is referred to for short in the following as "dark composition".

When a metal is used as the component of a mixture, a special effect is generated. A report is given here on metal sparks, red lead explosive charges and water flares. The metals in question are magnesium, magnalium, aluminum, ferrotitanium and zirconium, whose effects are explained as a function of the properties of the metal, those of the oxygen carrier and the oxygen value of the mixture.

Research on the Most Appropriate Method for the Pyrotechnic Industry To Determine the Sensitivity of Compositions

From *EuroPyro 93, 5^e Congrès International de Pyrotechnie du Groupe de Travail*, 6–11 June, 1993

SUMMARY: Those of us who work in the pyrotechnic industry have three requirements to obtain data concerning the sensitivity of mixtures: establish the starting point of no-ignition; understand the possibility of propagation of the ignition to combustion or explosion; clarify the variation of the sensitivity, which is dependent on the materials that we have used for tools. The methods used up to now have not satisfied our requirements.

The sensitivity was determined with a drop test using a steel ball onto a sample placed on an anvil. The sample used was molded as a thin round disk. This method was used to establish the propagation of ignition.

Initially, the experiment was conducted using the up-and-down method so as to compare with that described below. The data obtained on a salute composition did not indicate a normal probability distribution. This method does not give an exact result, without having some prior test data.

The experiment was then conducted using the descending-method, which I use regularly at the factory. The height of no-ignition was determined on 50 trials with the salute composition and with the composition CuO-Al.

It was possible determine the influence of the material of the anvil on the sensitivity of the mixture and substituting aluminum for the steel.

Study on the Reaction Mechanism of Black Powder And Its Applications

From *26th International Annual Conference on Pyrotechnics*, 1995

ABSTRACT: Black Powder is said to be the oldest explosive. At present, it is one of the most important explosives. However, the burning reaction mechanism of materials in the mixture is still obscure. The purpose of this study is to clarify this mechanism and illustrate some applications of Black Powder.

The burning reaction of Black Powder has been denoted for a long time by various formulae that include potassium carbonate or sulfate, which is found in the ash. The author has endeavored to clarify the formation of such materials during burning, in an effort to shed light on the burning reaction mechanism.

Through his experiments, the author found that potassium carbonate or sulfate is formed not only in the case of Black Powder, but also in the case of mixtures of potassium nitrate and charcoal or potassium nitrate and sulfur. It is clear that the formation of potassium carbonate or sulfate is not peculiar to Black Powder, but to nitrate.

The ash contains both of these substances. The formation reaction takes place not in a gaseous, but rather in a solid or liquid state. Such a reaction would explain the excellent ignition characteristics of Black Powder.

Other applications of the burning reaction mechanism of Black Powder could be found to make ignition of other compounds more effective.

Detection of Underwater Blasting Using Electrical Noise

From *Jour. Indust. Explosives Society, Japan*, Vol. 39 (1), 1978

Abstract: We conducted a small-scale experiment on soil simulating underwater blasting and studied the shape of waves as well as properties of electrical noises generated during blasting. From these noise waves, we wanted to detect any failure in initiation of the charge or blasting conditions, etc. It was observed that the main source of noise is the residual electricity in the exploder; the shape of noise waves is typical of blasting conditions of the charge. It enables us to detect blasting failure, or blasting of detonator touching the water, or detonation of charge, etc. from these noise waveforms. It was also confirmed that this method of detection can also be applied in double-hole or multi-hole blasting which follows stage explosion.

Selected Pyrotechnic Publications of K.L. & B.J. Kosanke

A collection of previously published technical papers on a variety of pyrotechnic topics. Only those articles which continue to be of interest and use to pyrotechnicians have been included.

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[ISBN 1-889526-05-3]

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Illustrated Dictionary of Pyrotechnics

Cover \$40	Discounted Price \$24.00*
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Many areas of applied pyrotechnics, fireworks in particular, suffer from a lexicon that contains many specialized terms, is poorly documented, and about which there is much disagreement. For example, what you call *glitter*, others still call *flitter*, and vice-versa; your *separation distance* may be someone else's *setback*. As a result, effective communication is made more difficult than necessary. Having an extensive dictionary of terms will not instantly solve such communication problems, but it can help, especially over time. Unfortunately, until now such a dictionary has not been available.

The *Illustrated Dictionary of Pyrotechnics* [ISBN-1-889526-01-0] is 130 pages in length, with a durable binding. There are more than 1200 entries, 130 figures and illustrations, and 50 short tables. It includes scientific and craft terms from fireworks, explosives, rocketry and pyrotechnic special effects.

In addition to the principal authors, eight individuals with expertise from each of the technical areas addressed, reviewed and contributed to the development of the dictionary. Most entries go well beyond merely defining a term; many terms are explained using examples, data, and/or illustration. Accordingly, the dictionary should be both authoritative and easy to comprehend.

Excerpts from review by L. Homan for the *Western Pyrotechnic Association Newsletter*, March, 1995.

“A dictionary is undoubtedly the most daunting of literary tasks, only for the most motivated and knowledgeable. In this case the selection of terms is somewhat eccentric, as any beginning project must be, including technical terms of little value to the average pyrotechnician. The content might form the basis for a game of knowledge amongst a group of fireworks enthusiasts, see who can find a term which someone else in the group does not know. The dictionary is very readable, being clearly laid out and not too specific or complicated, giving good meanings yet stopping short of excessive explanations... The individual reader will have to gauge his own level of need, the less you understand it, the more useful it is, I suggest a sneak preview... This new dictionary is very well done, worth the reasonable price for most, but I wouldn’t steal it.”

Excerpts from review by R. Winokur for *American Fireworks News*, No. 163, April, 1995.

"The content of this volume is eclectic in the extreme. It contains entries on all aspects of fireworks, from regulatory definitions to Italian and Japanese shell making. It also contains a large variety of terms used in rocketry which are not normally seen in the fireworks literature. In addition there are many terms taken from high explosive science and technology, and some from stage and movie special effects. To illustrate the eclectic nature of this volume one only has to open the pages at random. For example, on pages 74 and 75 we find "M-80" defined: "One type of small but powerful exploding device...". In the next entry we find "Mach Diamonds: Diamond shaped features exhibited by the exhaust plume of rocket motors and engines"... Several entries later we find "Magnesium, Magnalium, Magnesium carbonate and Magnus Force". Terms are sometimes grouped together based on their being closely related in definition rather than strictly alphabetically. For example, the terms "Color Purity, Color Species and Color Spectrum come before Colored Heart and Colored Smoke". Although this is unusual in a dictionary, it is an extremely functional aspect of the volume."

The entries are usually considerably more than brief definitions. On average an entry is composed of a short paragraph or more, and often includes one or more illustrations in the form of diagrams, drawings and graphs. In some instances a series of closely related entries may take up several pages. For example, if one searches for the term Mortar, the following entries are found Mortar (fireworks), Mortar (special effects), Mortar Burst, Mortar Length, Mortar Organization, Mortar Placement, Mortar Plug, Mortar Rack, Mortar Racks - Dense-Pack, Mortar Strength, and Mortar Trough. These eleven entries take about 2½ pages and contain a wealth of information on structure, physical properties, composition, safety, and function of mortars..."

Lecture Notes for Pyrotechnic Chemistry

Cover \$90

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Lecture Notes for Pyrotechnic Chemistry [ISBN-1-889526-09-6] are the class notes for a three-day course on Pyrotechnic Chemistry. The Course Notes assume only minimal levels of understanding of Chemistry and Pyrotechnics. Each 8½×11" page contains a pair of viewgraphs from the course lectures. The over 400 viewgraphs include many illustrations and tables. Each viewgraph of text is complete enough for the reader to be able to understand the subject being discussed. Following is the outline of topics:

I Basic Chemical Principles

- Atomic Structure
- Chemical Bonds
- Chemical Names
- Chemical Formulas and Equations
- Common Pyrotechnic Materials

II Pyrotechnic Chemistry, Ignition and Propagation

- Oxidation–Reduction Reactions
- Reaction Energy Considerations
- Pyrotechnic Ignition

III Pyrotechnic Primes and Priming

- Ignition and Propagation Energy Considerations
- Functions Performed by Primes
- Prime Formulations
- Application Techniques
- Alternatives to Priming

IV Factors Affecting Burn Rate

- Choice of Fuel / Oxidizer and Ratio
- Degree of Mixing
- Particle Size and Shape
- Additives and Catalysts
- Temperature, Pressure and Confinement

Physical Form and Incorporation
Geometry, Crystal and Environmental
Effects

V Aspects of Pyrotechnic Burning

- Pyrotechnic Delays
- Progressive vs. Propagative Burning
- Black Match / Quick Match Mechanism
- Rocket Performance / Malfunctions
- Burning / Deflagration / Detonation

VI Physical Basis for Colored Light Production

- Nature of Light
- Basic Quantum Theory
- Line, Band and Continuous Emissions
- Chromaticity Diagram
- Laws of Additive Color Mixing
- Color Theory Applied

VII Chemistry of Colored Flame

- Mechanism of Colored Light Production
- Colored Light Chemistry
- Control of Color Chemistry
- Color Enhancers
- Use of Metal Fuels
- Special Topics

VIII Chemistry of Sparks, Glitter and Strobe	Mix Compositions Triangle Diagrams Stoichiometric Approach Other Approaches
Light Emission from Sparks Control of Spark Chemistry Mechanism of Glitter Influence of Metal Fuels on Glitter Control of Glitter Delay Mechanism of Strobe Control of Strobe Rate	
IX Pyrotechnic Smoke and Noise	
Physical Smoke Chemical Smoke Whistles Salutes / Reports	
X Approaches to Formulation Development	
Approaches to Formulation Development Add a Component	
	XI Pyrotechnic Sensitivity
	Water Sensitivity Auto-Ignition Temperature Friction Sensitivity Impact Sensitivity Electrostatic Sensitivity
	XII Pyrotechnic Hazard Management
	Elements of Hazard Management Chemical Toxicity Hazards Pyrotechnic Hazards Hazardous Chemical Combinations Control of Hazards
	XII Pyrotechnic Hazard Management

Lecture Notes for Fireworks Display Practices

Cover \$90	Discounted Price \$54.00*
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The *Lecture Notes for Fireworks Display Practices* [ISBN-1-889526-03-7] are the set of class notes from a week-long course on practical and safety aspects of performing fireworks displays. Each $8\frac{1}{2} \times 11$ " page contains a pair of viewgraphs from the course lectures. The 385 viewgraphs include many photographs and tables. Each viewgraph of text is complete enough for the reader to understand the subject being discussed.

Course Outline:

I. Elements of Hazard Management for Fireworks <ul style="list-style-type: none"> A. Safety Defined B. Hazard Management <ul style="list-style-type: none"> 1. Recognition 2. Evaluation 3. Control 	<ul style="list-style-type: none"> d) Flowerpot e) Shell "Detonation" f) Muzzle Break g) Low Break h) Dud
II. Fireworks Construction, Operation, and Characteristics <ul style="list-style-type: none"> A. Aerial Shells <ul style="list-style-type: none"> 1. Basic Aerial Shell Components and Their Manner of Functioning <ul style="list-style-type: none"> a) Shapes and Sizes b) Basic Manner of Functioning c) Quickmatch Shell Leader d) Lift Charge e) Time Fuse f) Stars g) Burst Charge 2. Aerial Shell Malfunctions, Causes and Safety Considerations <ul style="list-style-type: none"> a) Premature Ignition b) Hang-fire c) Mis-fire 	<ul style="list-style-type: none"> 3. Variations in Aerial Shell Construction <ul style="list-style-type: none"> a) Top vs. Bottom Fusing b) Redundant Fusing c) Spolette Fuses d) Multi-break Shells e) Component Shells f) Salutes / Report Shells g) Spherical Shell Star Configurations h) Star Types 4. Typical Performance Characteristics and Safety <ul style="list-style-type: none"> a) Typical Aerial Shell Performance <ul style="list-style-type: none"> (1) Effect of Mortar Length (2) Burst Delay Times (3) Burst Spreads (4) Effect of Mortar Tilt Angle (5) Drift distance b) Measures for Safety c) Aerial Shell Safety Inspection

- B. Other Fireworks Types
 - 1. Low-level Aerial
 - a) Mines
 - b) Comets
 - c) Roman Candles
 - d) Cakes and Multi-shots
 - 2. Rockets
 - 3. Wheels
 - 4. Fountains, Gerbs, Waterfalls
 - 5. Lancework

III. Fireworks and Fireworks Display Safety

- A. Fireworks Display Practices
 - 1. Fireworks as an Art Form
 - 2. Manual Firing Styles
 - a) European / US
 - b) Asian
 - 3. Electrically Fired Displays
- B. Display Site Requirements
 - 1. Display Site Size
 - 2. Site Security
 - 3. Other Requirements
 - 4. Site Plan
 - 5. Display Permit
 - 6. Check List
- C. Fireworks Display Equipment
 - 1. Fireworks Mortar Types
 - 2. Fireworks Mortar Requirements
 - 3. Mortar Inspections
 - 4. Mortar Racks and Similar Equipment
 - 5. Ready Boxes
 - 6. Display Equipment
 - 7. Personal Safety Equipment
 - 8. Emergency Equipment
 - 9. Mortar Placement
 - a) Mortar Location within Secured Area
 - (1) Required when Reloading
 - (2) Optional for Preloaded Displays
 - b) Organization of Mortars
 - c) Burial of Mortars
 - d) Mortar Angling
 - e) Placement of Mortar Racks
 - 10. Chain-fusing Techniques
 - a) Chain-fusing Method 1
 - b) Chain-fusing Method 2
 - c) Preparation of Finale Chain Fuses
 - d) Methods for Slowing Quickmatch Burn Time
 - e) Short Fusing
 - f) Re-ignition Points
 - 11. Making Repairs to Fireworks
 - a) Aerial Shells
 - (1) Missing Shell Leader Safety Cap
 - (2) Short or Damaged Blackmatch End
 - (3) Short or Damaged Shell Leader
 - (4) Tear in Shell Leader
 - (5) Fuse Loop Torn or Missing
 - (6) Leaking Lift Powder
 - (7) Damaged Casing
 - (8) Wet Shell
 - b) Repairs to Other Fireworks
 - 12. Set-up of Ground and Low-level Aerial Fireworks

- a) Minimum Separation Distances
- b) Set-up of Fireworks on Poles
- c) Guy Wire Safety Tips
- d) Set-up of Low-Level Aerial Fireworks
- e) Accidental Ignition Considerations
- 13. Operator Responsibilities
- 14. Personnel Assignments
- 15. Loading Technique
- 16. Firing Technique
- 17. Ready Box Tending
- 18. Spotting
- 19. Monitors
- 20. Operator
- 21. Shot Interruptions
- 22. After the Show
- 23. The Next Day
- D. Electrical Display Procedures
 - 1. Basic Electricity
 - a) Ohms Law
 - b) Wire Resistance
 - c) Electric Circuit Symbols
 - d) Series Circuits
 - e) Parallel Circuits
 - f) Battery Internal Resistance
 - 2. Set-up and Safety of Electrically Fired Displays
 - a) Basic Electrically Fired Display Set-up
 - b) Public and Crew Safety
 - c) Requirements for Electrically Fired Displays
 - d) Earth as a Source of Firing Current
 - e) Electric Match Sensitivity
 - f) Mortar Inspection After Malfunctions
 - g) Short Wiring
 - h) Exceptions to Inspection after Malfunctions
 - 3. Techniques for Electric Firing
 - a) Basic Firing Circuit
 - b) Electric Matches
 - c) Characteristics of Electric Matches
 - d) Installation of Electric Matches
 - e) Parallel Firing Circuit
 - f) Comparison of Series and Parallel Firing Circuits
 - g) Testing Firing Circuits
 - h) Electric Firing Equipment
 - i) Covering Electrically Fired Mortars

IV. Fireworks Transportation and Storage Requirements

- A. Fireworks Sensitivity to Accidental Ignition
 - 1. Pyrotechnic Combustion
 - 2. Sensitivity Indicators
 - 3. Fireworks Sensitivity
 - 4. Fireworks with Electric Igniters
 - 5. Storage Considerations
- B. Blast and Thermal Effects from Fireworks
 - 1. Background Information
 - a) Classes of Combustion Reactions
 - b) Hazards of Burning, Deflagrations and Detonations
 - 2. Output from Fireworks
 - 3. Mass Storage Considerations

V. Fireworks Display Design

- A. Basic Display Design
- B. Fireworks Plus Music
- C. Evoking Emotion with Music and Fireworks
 - 1. Music Examples
 - 2. Firing Styles / Shell Types

D. Mechanics of Choreography

- 1. Music Selection
- 2. Music Charting
- 3. Design of Display
- 4. Logistical Considerations

Journal of Pyrotechnics

Issues of the Journal of Pyrotechnics appear twice a year and now contain approximately 75 pages. Areas of pyrotechnics addressed include fireworks, pyrotechnic special effects, propellants & rocketry, and civilian pyrotechnics. The Journal is “dedicated to the advancement of pyrotechnics through the sharing of information”. This is accomplished with a mix of different types of articles; however, most will fall into two areas. One area is reports on research conducted by both professional scientists and individual experimenters. The other area is reviews of various technical and craft areas of pyrotechnics, some at an advanced level and others at a tutorial level. [ISSN 1082-3999]

Abstracts for all issues are available on the Journal of Pyrotechnics Web Site:

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