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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 $C_6H_6Cl_6$ or γBHC supplies chlorine gas to the flame – commercial grade. The residue after extraction of the γBHC for insecticides was used. White finely powdered material. Analysis results as follows: Cl 70.90% (sodium method). (Theoretical Cl content 73.14%).

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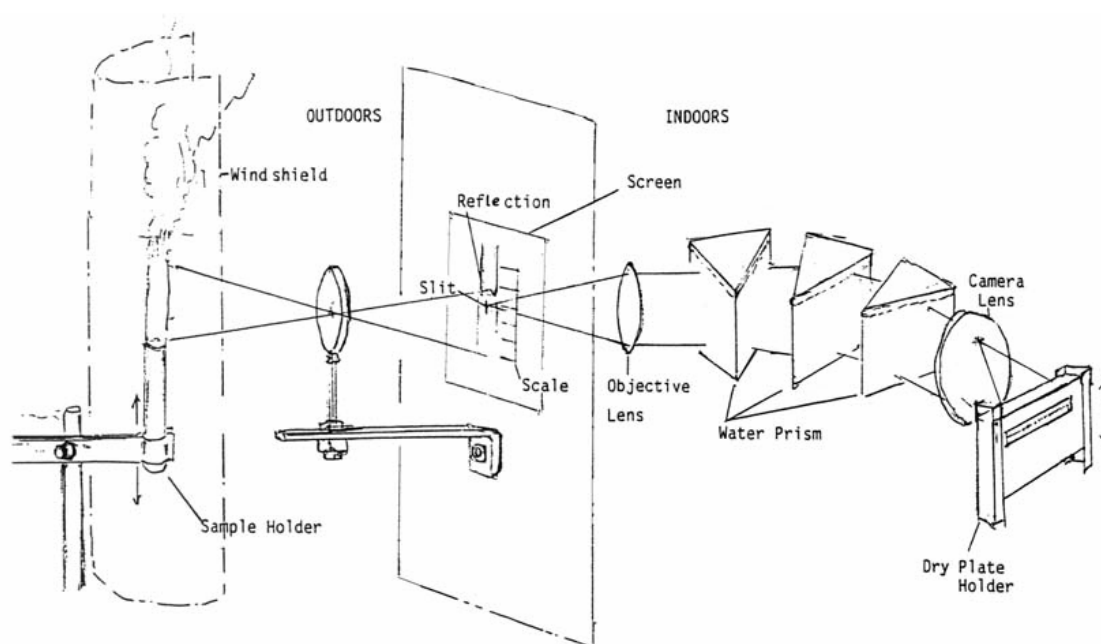
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Figure 1. Sketch of the installation of devices for photographing flame spectra. ***NOTE:*** *There is an error in the illustration. The prisms should be pointing away from not toward the front.*

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 pho-

toelectric cell during the combustion of the sample.

The plates used for taking the photographs were Sakura Panchro-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.
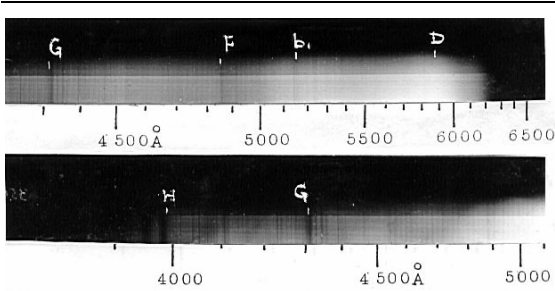

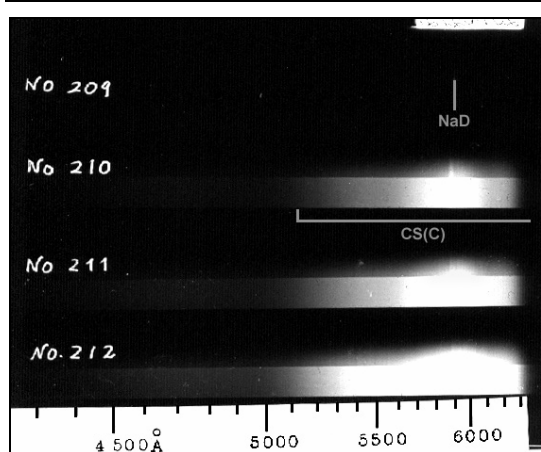*Photo 1. The sun's spectrum in Tokyo, 10 a.m., late in December, 1957.*

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.

a) 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 $i = 4$.

b) 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

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Table 2. Low Temperature Fuels: Background Characteristics.

	Composition (21)	Ammonium perchlorate		80%		
	Fuel			20%		
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%		
	Fuel			20%		
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.

a) 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 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).

b) 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 K_4 is comparatively strong and the others are quite weak. Since vision sensitivity to K_4 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. (K_4 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,
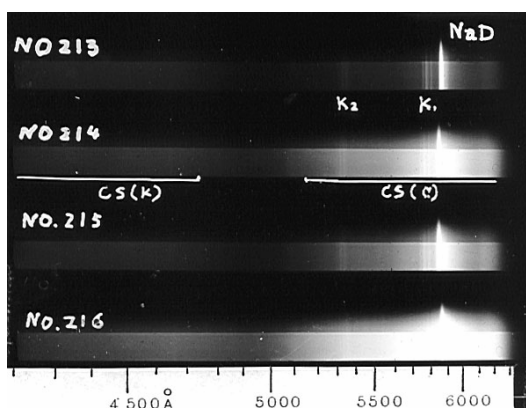

Photo 3. Low flame temperature background using potassium perchlorate as the oxidizer.

Table 3. High Temperature Fuel Background Characteristics.

	Composition (23)		Ammonium perchlorate			x%		
			Fuel			y%		
No.	x%	y%	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

	Composition (24)		Potassium perchlorate			x%		
			Fuel			y%		
No.	x%	y%	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

	Composition (25)		Potassium nitrate			x%		
			Fuel			y%		
No.	x%	y%	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 ultraviolet 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.
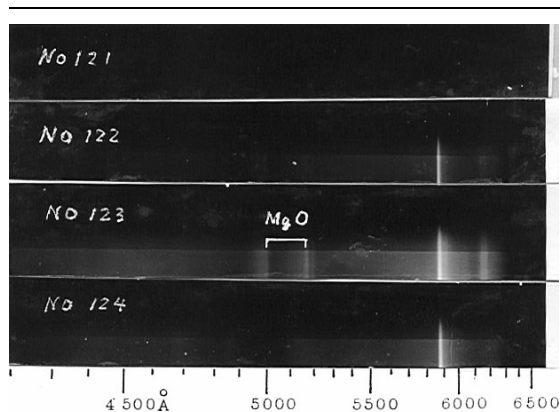
Photo 4. High flame temperature background using ammonium perchlorate as the oxidizer.

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.

a) 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.

b) 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.

c) 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.

d) 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

a) The Na-D lines at 5896 and 5890 Å are due to impurities, and their intensities are fairly high.

b) There is an AlO band at 4648 (1.0), 4842 (0.0), 5079 (0.1) Å with a peak towards the short wave end.

c) 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).
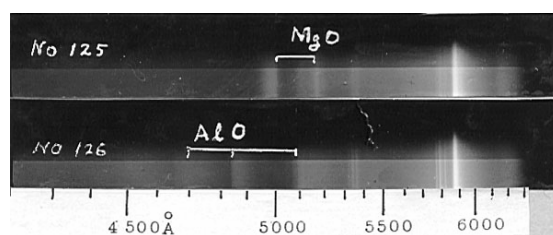

Photo 5. High flame temperature background using potassium perchlorate as the oxidizer.

a) There are added K lines and the continuous spectrum CS (K).

b) The MgCl? band at 6165 and 6196 Å has disappeared.

Table 4. Background from Compositions Using Chlorine Donors.

	Composition (26)	Potassium perchlorate	40%	
		Magnesium	60%	
		Chlorine donor	15%	(additional percent)
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 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.
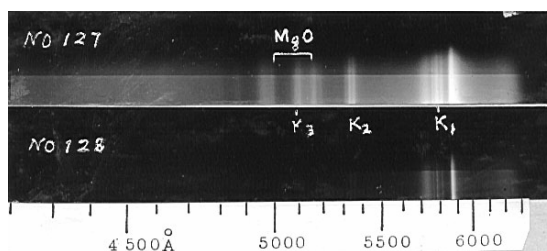

Photo 6. High flame temperature background using potassium nitrate as the oxidizer.

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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)	E (candela·s/g)
353	BHC	9.0	2400	19.0	5067
354	Hexachloroethane	8.8	4000	15.0	6818
348	Polyvinyl chloride	8.0	1600	18.5	3700
355	Ammonium chloride	8.5	1600	22	4141
380	Ammonium chloride	7.6	1280	20	3368

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)	E (candela·s/g)
341	0	8.5	40,000	8.0	14,120
342	5	8.7	32,000	3.5	12,880
343	10	8.5	800	13.5	1,271
344	15	8.7	800	16.0	1,471

	Composition (29)	Potassium nitrate	40%	
		Magnesium	60%	
		Polyvinyl chloride	x%	(additional percent)
No.	x%	ω (g)	L (candela)	t (s)	E (candela·s/g)
345	0	9.0	14,400	5.0	8,000
346	5	8.5	4,000	14.5	6,824
347	10	8.1	2,400	18.0	5,333
348	15	8.0	1,600	18.5	3,700

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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-
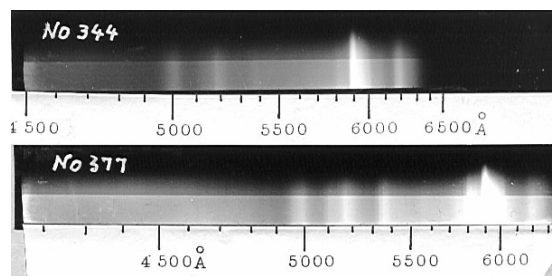

Photo 7. Comparison of effect with polyvinyl chloride and shellac.

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]

$$2\,MgO + 2\,Cl_2 \rightleftarrows 2\,MgCl_2 + O_2$$

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

$$MgO + 2\,HCl \rightleftarrows MgCl_2 + H_2O$$

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_2O	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 (MgCl$_2$) 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-
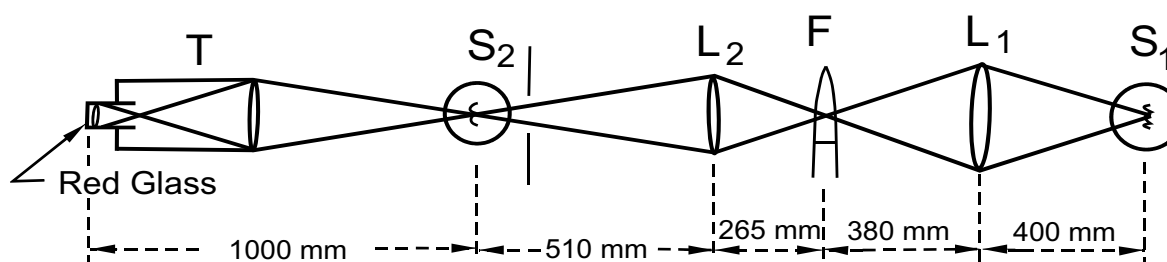
Figure 2. Light path through the measuring apparatus for black body temperatures of flames.

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

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

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

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:

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

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

$$\frac{1}{\tau_F} = \frac{1}{\tau'_F} + 2.303 \frac{0.0000626}{1.438} \log 0.916^3$$

$$= \frac{1}{\tau'_F} - 0.0000115$$

$$(8)$$

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 $\tau_F(\lambda_e = 6260 \text{ Å})$; 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

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Table 7. Black Body Temperature of the Flame $\tau_F(\lambda_e = 6260$ Å$)$; 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	ν (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	ν (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	ν (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	ν (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	ν (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 $\tau_F(\lambda_e = 6260$ Å); 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 l 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.

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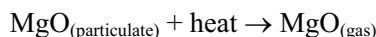
In concluding this report I would like to thank Mr. Yamamoto of Tokyo University, Technology Department for general guidance, and Mr. Makishima for great help in analysis of the spectra. Also for analysis of the raw materials I thank Mr. Takada and Mr. Hosotani.
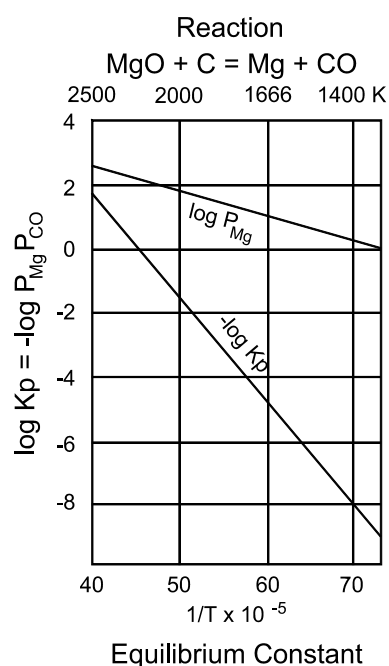
Literature

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:

$$MgO_{(particulate)} + heat \rightarrow MgO_{(gas)}$$

$$MgO_{(gas)} + C_{(particulate)} \rightarrow Mg_{(gas)} + CO_{(gas)}$$
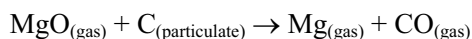
at high temperatures.

Reaction
MgO + C = Mg + CO

Equilibrium Constant

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

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.

Autobiography of a Pyrotechnist — Dr. Takeo Shimizu

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."

Autobiography of a Pyrotechnist — Dr. Takeo Shimizu

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.

Autobiography of a Pyrotechnist — Dr. Takeo Shimizu

In November 1951 I obtained a position at Hosoyo 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, Matsumoto 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 Kawagoeshi, 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.