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 (Å). 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 Å 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 effect 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

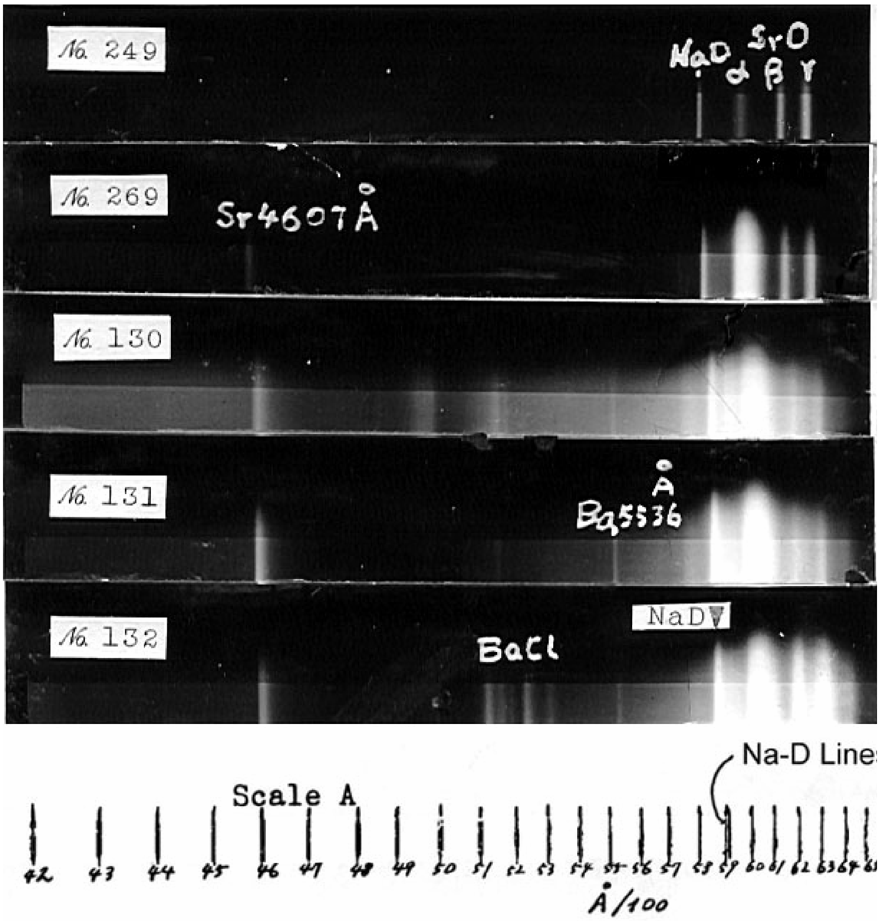


Photo 1. Flame spectra of strontium salts.

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 detect 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	ν	*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)
ν	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 CO_2 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	ν	*L*	*E*	α	β	α–β	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, Δλ, 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 (Δλ = 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	ν	*L*	*E*	α	β	α–β	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	ν	*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	ν	*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.

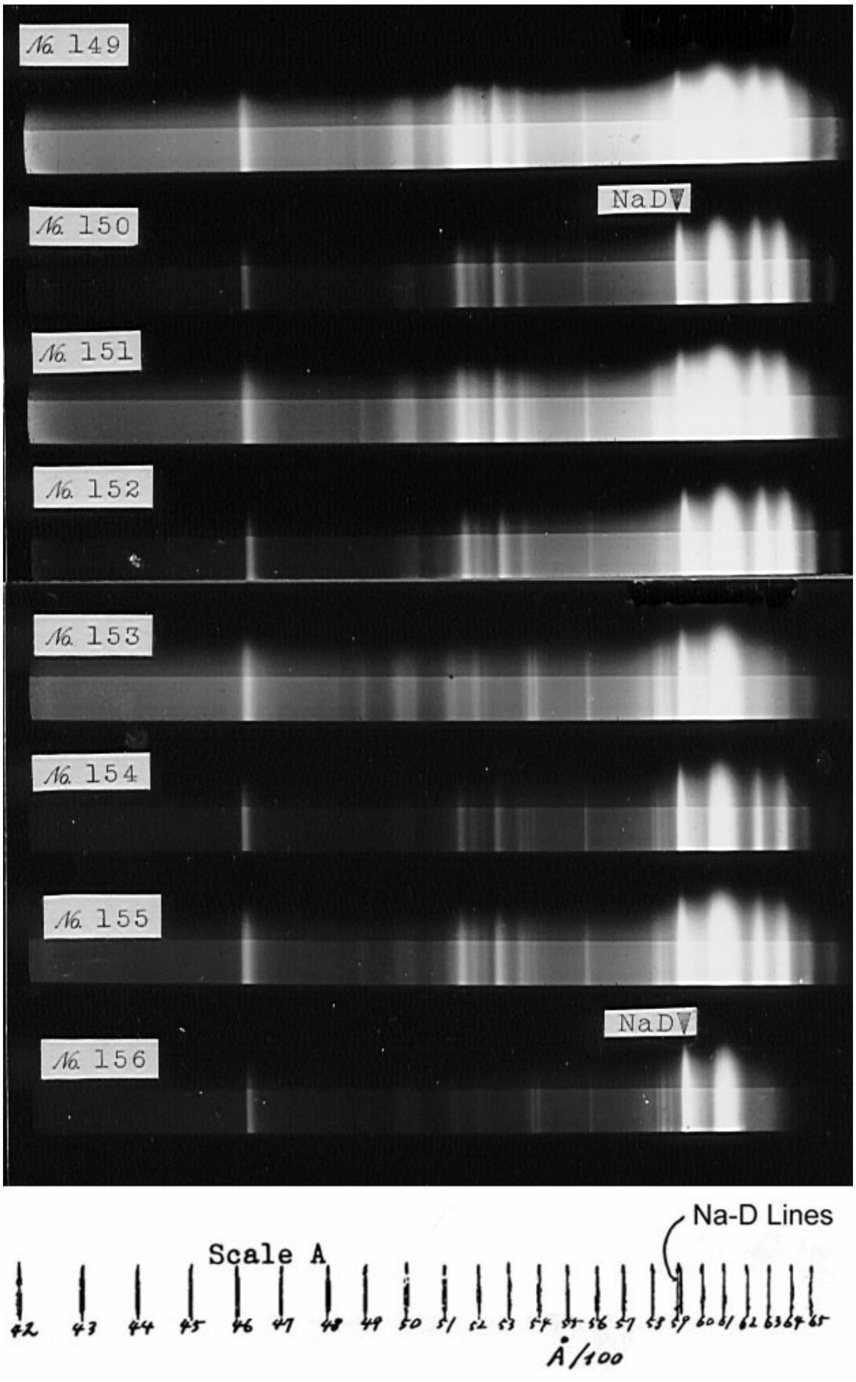


Photo 2. The effect of various oxidizers and additives on red flame spectra at high temperatures.

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

Composition (46)	%
Strontium nitrate	*x*
Magnesium	*y*

No.	*x*%	*y*%	ω	Δ	ν	*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	ν	*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.

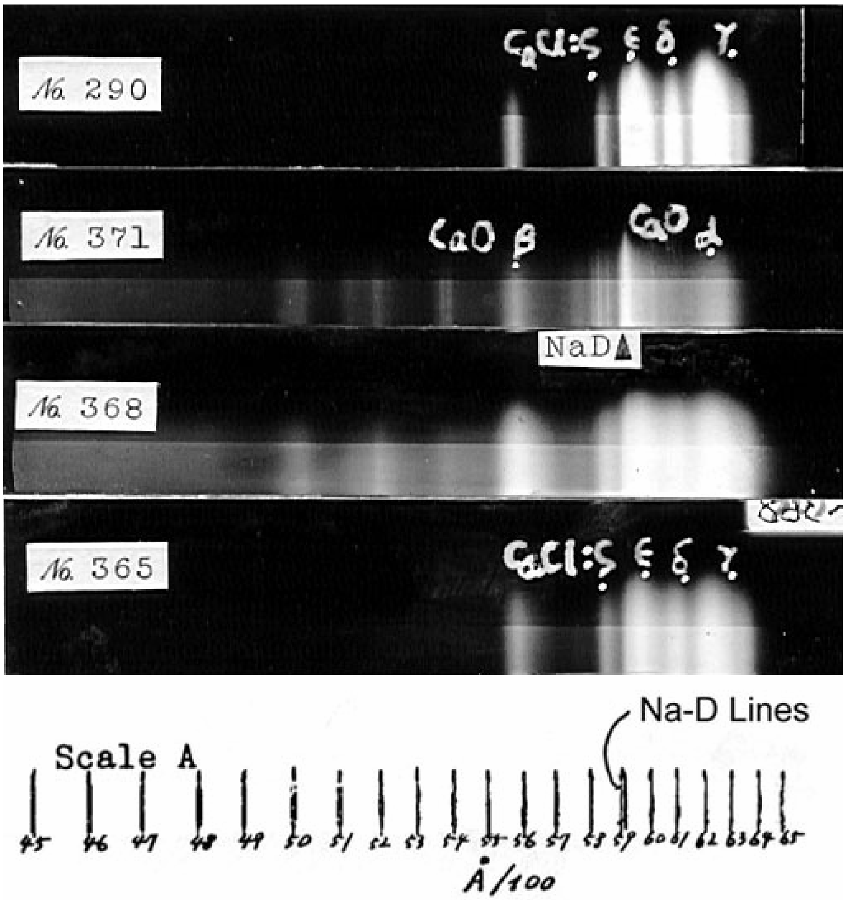


Photo 3. Flame spectra produced by calcium salts.

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*	ν	*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	Δλ = 66 Å
δ	6030–6078 Å (two)	Δλ = 48 Å
ε	5915–5986 Å	Δλ = 71 Å
ζ	5803–5838 Å	Δλ = 35 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	ν	*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	ν	*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

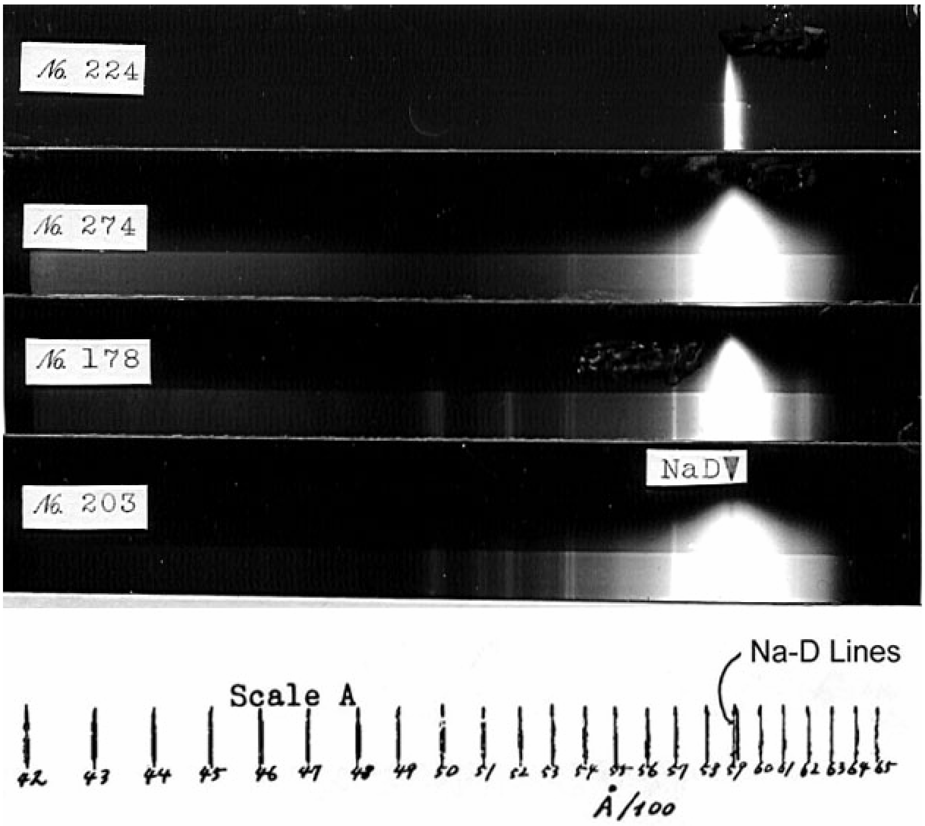


Photo 4. Flame spectra with sodium salts.

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	ν	*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	ν	*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	ν	*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	ν	*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	ν	*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

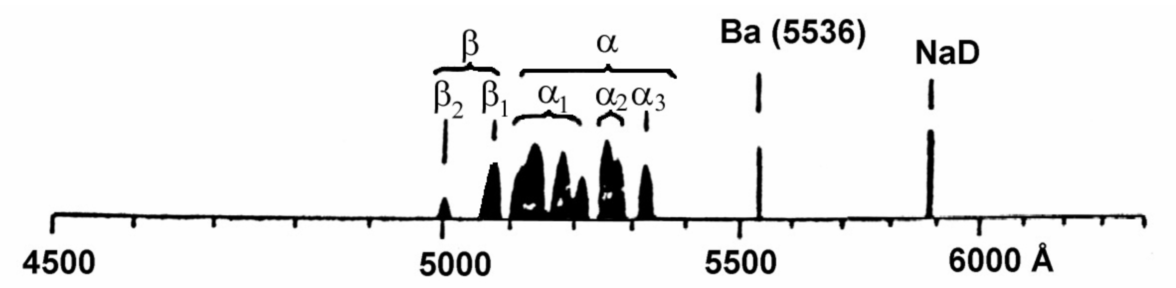
The flame spectra obtained from the burning flame of a composition that contains barium salts:

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

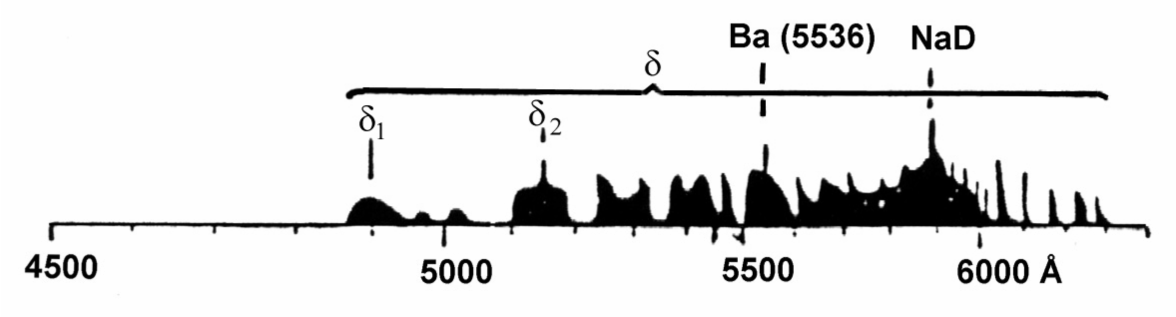
(2) *Ba line 5778 Å*: yellow, hardly visible at high temperatures.

(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).



(a) BaCl band caused by Cl or HCl in the flame



(b) BaO band caused by no chlorine in the flame

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.

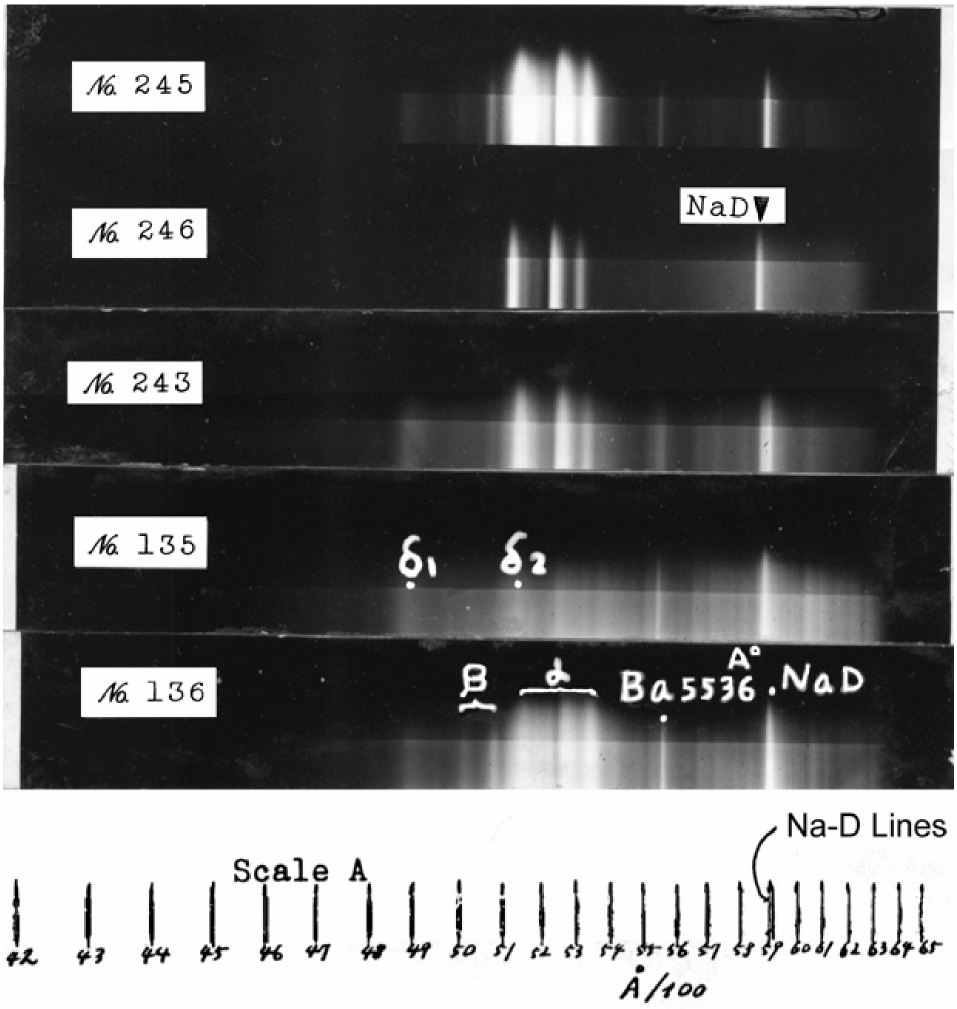


Photo 5. Flame spectra from barium salts.

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	ν	*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	ν	*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

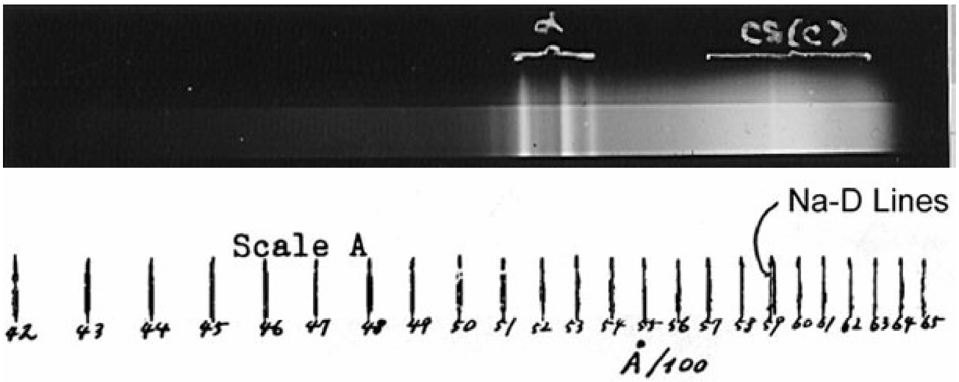


Photo 6. Flame spectra obtained from a low flame temperature composition that contained a HCl producing agent.

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	ν	*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	ν	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	ν	*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	ν	*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	Hexachloro-ethane	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	0	5.6	5.3	6.0
148	Camphor	—	—	7.9	10.0	1.33	21.3	32000	14400	0	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	ν	*L*	*E*	α_1	α_2	α_3	β	δ	CS (K)	Ba (5536 Å)
181	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
182	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
183	Barium chloride	11.2	10.5	1.39	?	640	?	5.5	5.5	5.2	3.6	weak	weak	3.2
184	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	ν	*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	ν	*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,

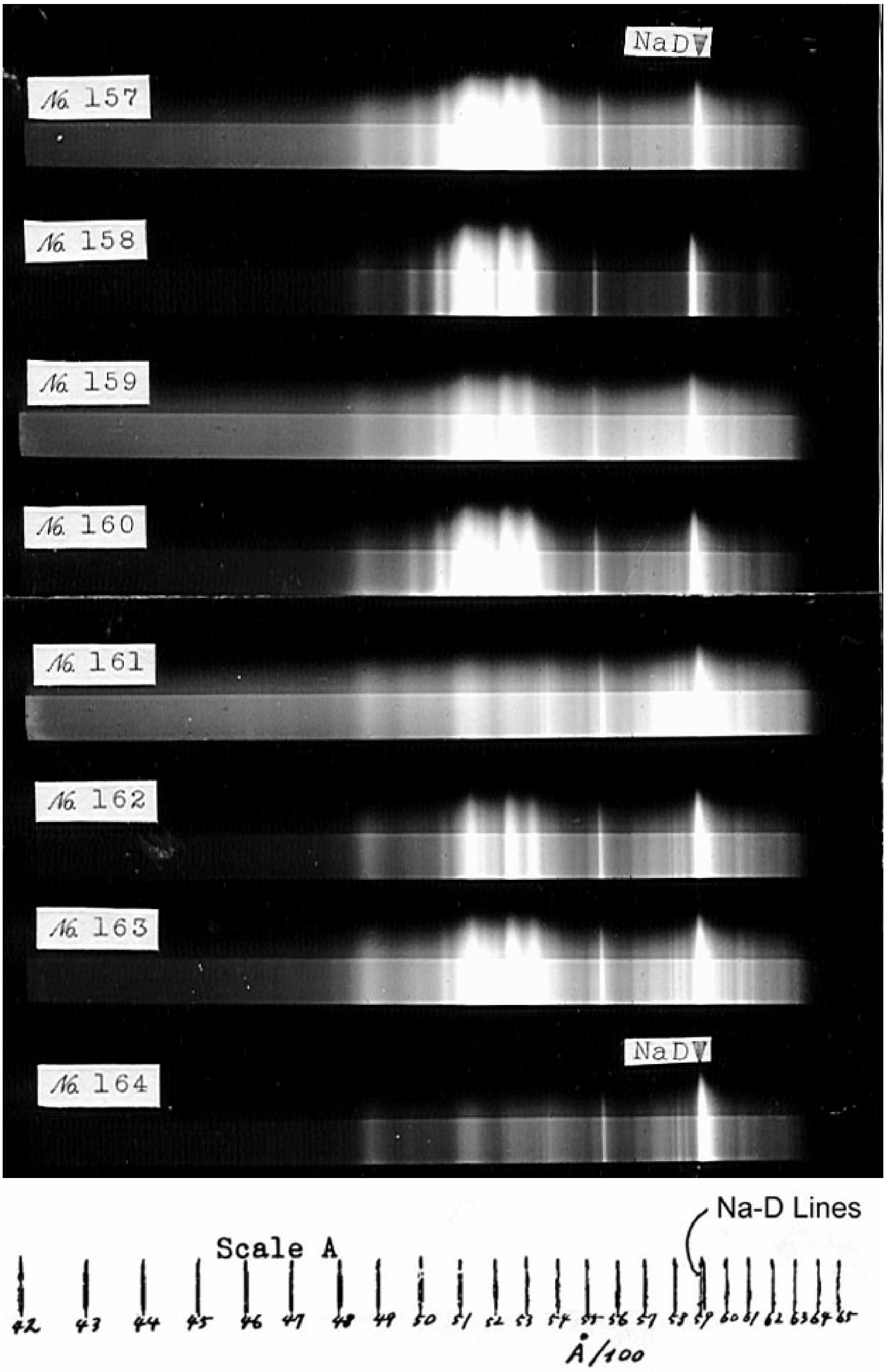


Photo 7. The effects of various oxidizers and additives on green flame spectra (See Table 24).

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	ν	*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*
Barium carbonate	10
Shellac	10

No.	*x*%	*y*%	HCl%	ω	Δ	ν	*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

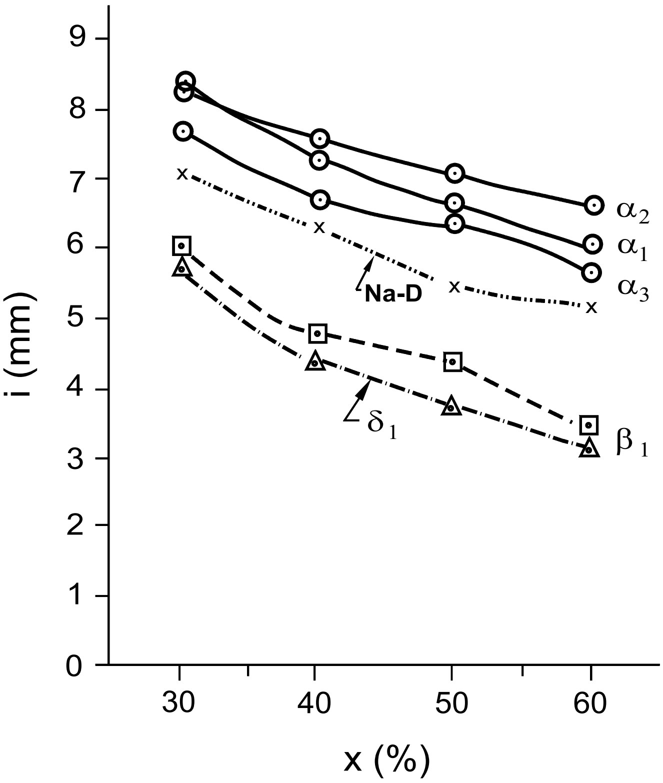


Figure 2. The intensity (i) of spectral line versus x%.

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.

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References

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