Part VII. On Composition Series for Practical Use

ABSTRACT

(1) The spectroscopic studies in the previous Parts are summarized so as to apply the principle of flame color creation for practical use.

(2) According to the results of (1), various samples of red, yellow, green and blue of several composition series are prepared. Their flame colors are examined by the naked eye and good colors are selected. According to these, effective color zones are written as enclosed areas in triangle graphs.

(3) As far as these studies are concerned the important results that seem to be common for each series are as follows:

a) The width of an effective composition zone in a graph is very narrow for low temperature flames and fairly wide for high temperature flames.

b) Ammonium perchlorate is the best oxidizer, for it can produce HCl in a flame and creates deep color.

c) Polyvinyl chloride is also the best additional ingredient that can create a deep color by producing HCl gas in the flame like ammonium perchlorate.

d) It is necessary to completely protect compositions from moisture for high temperature flames to prevent the magnesium and other ingredients from reacting with each other. For practical applications deep and brilliant color flames are obtained only in accord with this consideration.

1. Introduction

The foregoing works provide a guide to developing colored flame compositions, where the characteristics of effective color producing spectra, interfering spectra and the elimination of interfering spectra were explained. Considering the results, in this Part the author describes the fundamental conditions for designing typical colored flame compositions and enumerates representative compositions.

2.0 Summarizing the Results of Foregoing Studies and the Conditions to Obtain Sample Compositions

2.1. Low Flame Temperature Compositions

(l) The highest flame temperature is obtained when the oxygen balance to CO_2 oxidation is nearly fulfilled. From these results the best ratio of the fuel to oxidizer is naturally determined.

(2) The fuel should be selected so that it contains as low a carbon content as possible. This decreases the continuous spectrum from carbon in the flame and produces a reasonable burning velocity.

(3) With reference to the various color agents, it is known that there is a proper value of additive percentages to keep the most effective density of metal vapor in the flame. The excess percentages are not effective. Also negative ions are ineffective for flame color. However, nitrate color agents generally raise the flame temperatures to enlarge the intensity of the flame spectra; however, the interfering spectra also affects the flame color.

Generally, when we select the color agent, purity should be of primary concern (the smaller the quantities of impurity, the better the flame color), especially with Na and sometimes with Ba salts. Additional consideration should be given to moisture absorption, continuation of burning, burn velocity, ignition tendency, toxicity, handling, prices, etc. based on the intended use.

(4) With reference to the selection of the oxidizer, ammonium perchlorate is the best to obtain good flame color without creating interfering spectra; however, the flame temperatures

are somewhat lower than that of potassium perchlorate compositions.

The flame temperatures of potassium perchlorate composition are generally higher than those of ammonium perchlorate compositions and the intensities of the flame spectra are stronger than those of the ammonium perchlorate compositions. However, a continuous spectra and line spectra from potassium atoms appear that interfere with the flame color. However, these compositions have a large advantage with respect to moistureproof characteristics.

Generally, potassium nitrate compositions cannot produce high temperature flames. Therefore, the flame spectra are too weak to use as general firework compositions.

Strontium nitrate or barium nitrate is useable as both the oxidizer and color agent when mixed with another oxidizer even for low flame temperature compositions.

Author's Note: In the past nitrates were used as the main oxidizer, with sulfur or sulfate as the main fuel, which may help to increase flame temperatures. For example, the following compositions were used:

Red flame	Strontium nitrate	45
	Sulfur	13
	Charcoal powder	2
	Potassium chlorate	4
Green flame	Barium nitrate	21
	Sulfur	7
	Potassium chlorate	9

Reference: Franz Sales Meyer, Leipzig, Verlag von Seemann & Co. (1898).

When sulfur was the main fuel, it could produce flame temperatures high enough to create a red or green flame color.

(5) The additive materials that produce Cl or HCl gas in the flame unfortunately also decrease the flame temperature. Therefore, the effect of the addition of such materials to the composition is not as large.

2.2 High Flame Temperature Compositions

(1) Generally, continuous spectra of high intensity appear as the background; however, they are weakened by adding materials that can produce HCl or Cl_2 gas in the flame. It is also effective to add materials that do not contain too much carbon. Excess carbon generates a continuous spectra.

(2) From the above reason, it is always effective to use ammonium perchlorate or potassium perchlorate as the oxidizer. In particular, the addition of a material that can produce HCl gas in the flame is the most effective. Potassium chlorate gives almost the same results as potassium perchlorate.

(3) When using potassium nitrate, barium nitrate, or strontium nitrate that contain no chlorate as the oxidizer, the flame produced is a very clear colored flame. When using CuCl spectra to produce a blue flame, it is necessary to keep HCl gas in the flame to eliminate the green continuous spectra. In such case the addition of ammonium perchlorate, polyvinyl chloride or ammonium chloride is desirable. However, protection from moisture is required except in the case of polyvinyl chloride.

When using potassium salts as the oxidizer, continuous spectra from potassium atoms appear as described for low temperature flames. However, such continuous spectra generated from metal atoms cannot be eliminated by having HCl or Cl_2 gas in the flame. There is a large difference between such atomic spectra and band spectra (molecular spectra). Therefore, when using potassium salts, it is not possible to avoid flames that look whitish.

(4) The effective range of the ratio of magnesium to oxidizer becomes greater when using a proper fuel (e.g., shellac) even when the oxygen balance is not good.

3. How To Avoid Interactions between Component Materials

In the foregoing study the interactions between component materials were not discussed. However, we must consider these reactions in practice. These reactions are mainly as follows:

(1) The reaction of magnesium with ammonium perchlorate is likely to occur only in the presence of moisture, producing H_2 and NH_3 gases with heat evolution. The chemical product that remains in the composition is magnesium perchlorate, which is very hygroscopic.

(2) The reaction of magnesium with ammonium chloride resembles that of (1). It is likely to occur only in the presence of moisture, producing H_2 and NH_3 gases with heat evolution. The material that remains after the reaction is magnesium chloride, which is very hygroscopic.

(3) The reaction between potassium nitrate and ammonium perchlorate is the so-called double decomposition. The reaction products are potassium perchlorate and ammonium nitrate. The latter is very hygroscopic.

Another reaction, which resembles the above, is with compositions that contain barium nitrate and ammonium perchlorate. In this composition, the double decomposition did not occur even when unprotected and exposed to the air for 18 months.

The unwanted reactions of (2) and (3) may be avoided by selection of chemicals. Namely, ammonium chloride should be replaced with polyvinyl chloride. This is experimentally confirmed. Polyvinyl chloride is superior to ammonium chloride because it is non-hygroscopic and combustible by nature. The contact of potassium nitrate and ammonium perchlorate often occurs when there is contact between black powder prime and colored flame composition. This can be avoided by using a potassium perchlorate-based prime in such cases.

The cases are not always avoidable; however, with perfect moisture-proof construction one can suppress the reactions. Namely, by selection of binder or by selection of container, one can obtain almost perfect moisture-proof conditions at low cost. It is most important to develop a method of stabilizing magnesium from corrosion. The author shall describe this problem in another study.

4.0 Series of Fundamental Compositions in Practical Use

Described here are some fundamental compositions based on the foregoing spectral studies and other naked eye observations of flames. For the judgment of usability of the composition, the author put the emphasis on flame colors.

When the limit of product use is decided, one can select the most adaptable composition with burning velocity and loading density for one's purpose. And if this allowable range is wide enough, the freedom of the composition selection is also large.

The range of practical use, which is designated by the shaded area in the triangle diagram, is based on two factors: one comes from the distinction of flame color; the other comes from the distinction of the possibility of burning—combustible or incombustible zones. If the composition produces a good flame color but is difficult to burn, it is out of the zone. There is a problem in deciding the range. The sample specimens are as small as that of lance work. Generally when the diameter of the composition increases, the effective zone also increases. Therefore, the compositions of larger diameter items may sometimes fall in an expanded effective zone.

4.1 Method of Deciding the Effective Zone

(l) Compositions of various mixing ratios were burned, and the flames were observed with the naked eye to decide if they were in the effective zone or not. The component ratios were differentiated generally by 10 weight percent, and at important points or important compositions with 5 weight percent. The observation with naked eye of flame color was very sensitive and effective to decide the effective zone. (The spectrometer is useful for investigation of the color flame mechanism, but not for determining good flame color.)

(2) The sample specimens were made by loading a composition into a threefold brown paper tube of 9.5 mm inside diameter by 60 mm long. These were the same dimensions as for the lance of the frame works. The loading densities of a series are shown in Figure 1 as an example. Generally other series show nearly the same tendency. In Figure 1 the values of the loading density refer to the values of the weight ratio of oxidizer to magnesium, and the larger the former, the larger the latter. (The numbers added to the curves show the loading densities in g/cc.)

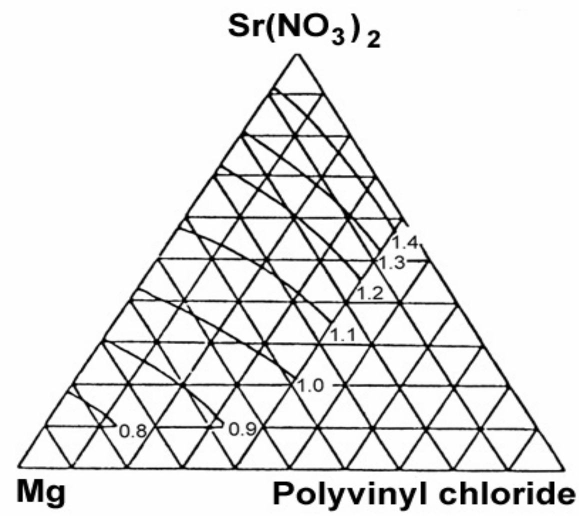

Figure 1 . Distribution of loading densities of a series of composition: $Sr(NO_3)_2$ + Mg + polyvinyl chloride.

(3) The chemicals used were of commercial industrial grade. Therefore, the flame color might be interfered with by Na-D lines and BaCl-α bands to some degree.

(4) The flames were observed from a distance of 1 m for low temperature flames and 50 m for high temperature flames.

4.2 Series of Low Temperature Flames

It is already known from Parts IV and V that the effective zone is very narrow. Namely, the influence of the oxygen balance on the effective zone related to flame color is very large. A balanced or excess of oxygen condition is the most effective for good color. Therefore, it is almost impossible to regulate the burning velocity by regulating the fuel to oxidizer ratio under good flame color conditions.

The flame color of the low temperature flame series was greatly affected by the type of fuel. Moreover the state of the spectral band and the flame temperature also affect the flame color.

Examples of low flame temperature compositions were listed in Parts IV and V and in author's book.[3] Here only blue flame compositions using copper powder are additionally described. When using ammonium perchlorate as the oxidizer and copper powder as the color agent, only shellac, pine root pitch or colophony were effective as the fuel. The quantity of fuel was the most effective at 10%; that of copper powder was effective from 5–30%, but the intensity of the blue colored light was not proportional to the percentage, but practically 5–10% may be useful. Therefore, the next standard may be recommended:

Blue flame composition with ammonium perchlorate as oxidizer:

Ingredient	%
Ammonium perchlorate	80–85
Fuel (shellac, pine root pitch, or colophony)	10
Copper powder	10–15

When using copper powder and potassium perchlorate, only shellac is recommended as the fuel. The quantity of the copper powder was effective with 5–30%, but practically 5–10% may be useful:

Ingredient	%
Potassium perchlorate	80-85
Fuel (shellac)	10
Copper powder	5–10

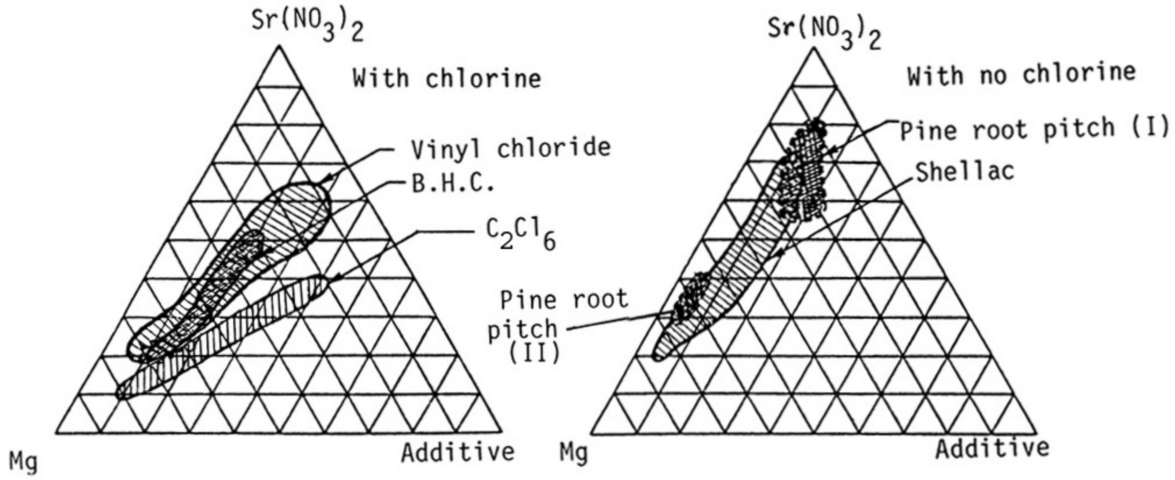

Figure 2. Effective zone of $Sr(N0_3)_2$ + Mg + additive series.

4.3 Series of High Temperature Flames

4.3.1 Red flame series

(1) Strontium nitrate series (Figures 2 and 3)

In this series, strontium nitrate contains no chlorine. Therefore, the continuous spectrum is very strong, and it is necessary to add something to suppress it. When BHC, polyvinyl chloride, hexachloroethane, shellac, or pine root pitch was added, the color producing ranges are shown in Figure 2.

When using materials that contain chlorine as an additive, the shapes of effective zone of flame color resembles well that of BHC. However, the former is wider than the latter. Namely, polyvinyl chloride gives more flexible selections of burning velocity or loading density than BHC. With reference to the flame color in the effective zones, polyvinyl chloride gave clearer and prettier red flames than the others. The effect of BHC was next and that of hexachloroethane followed last. Hexachloroethane has the largest chlorine content of all, but the effect was contradicted with the result of the experiment. (See Parts IV and V.)

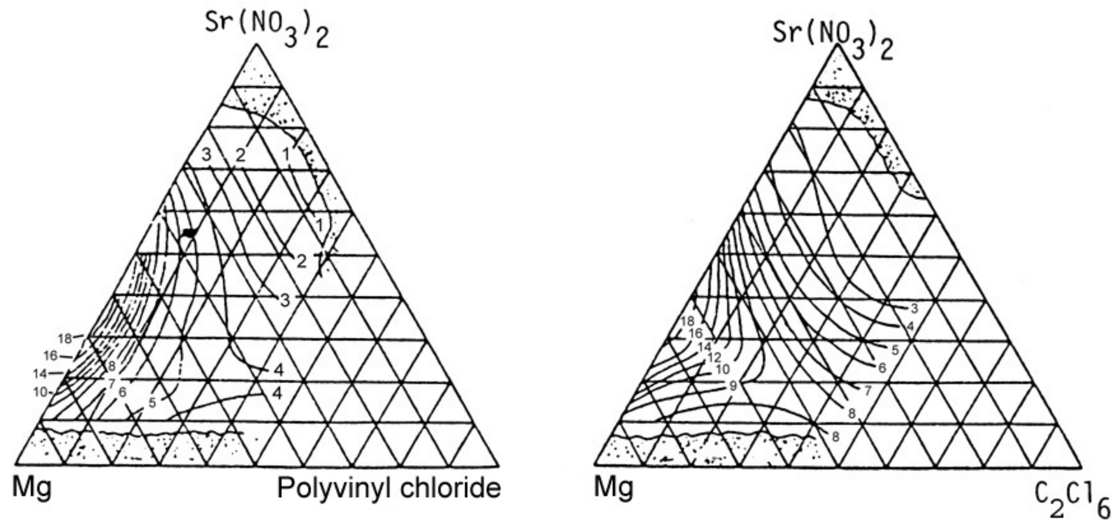

Figure 3. Burn rate (mm/sec) of a part of the above series.

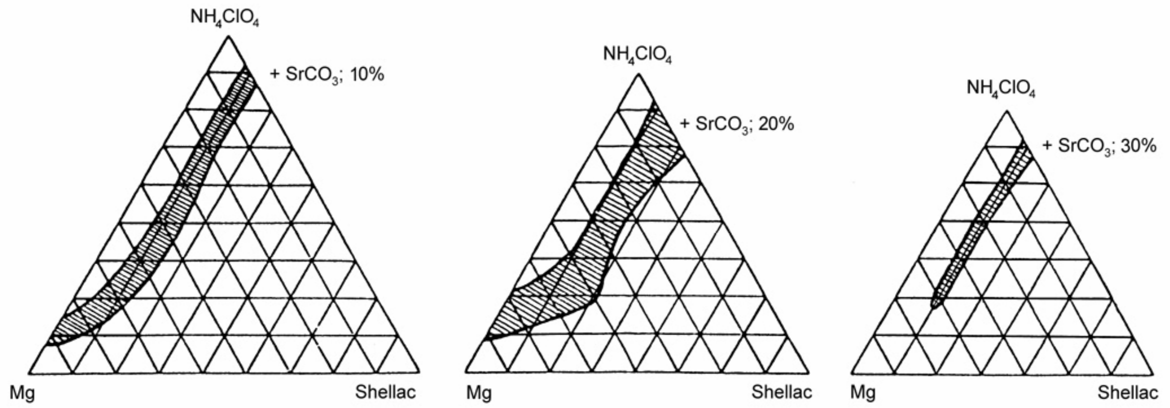

Figure 4. Effective zone of NH_4ClO_4 + Mg + shellac + $SrCO_3$ series

When using materials with no chlorine additive, the shapes of the effective zone are quite different from that described above. Also the effective zone of shellac is different from that of pine root pitch. Namely, shellac produces the best flame color at 10–15%. When using pine root pitch, the effective zone is divided into two areas. The color of the no chlorine flame is slightly different from that of the chlorine containing flame, and it looks slightly yellowish red. This is caused by the strong SrO band with very weak bands of β, γ, and δ.

Examples of burn rate are shown in Figure 3. The numbers on the curves show the values of burn rate in mm/sec. The curves in both figures resemble each other and represent general conditions of such compositions. Namely, in the zone of effective color production the burn rate increases with the increase of the ratio of magnesium to oxidizer.

As in the examples in Figure 2, the effective color producing zone is a long bandlike area parallel to the oxidizer-Mg line. In the area where the weight ratio of Mg to oxidizer is small, the composition does not burn easily and produces many sparks. When the ratio becomes larger, it is easier to burn and has fewer sparks. However, when the ratio becomes too large, the sparks are too numerous, and they interfere with the flame.

(2) Ammonium perchlorate series

The results using shellac as an additive are shown in Figure 4. The numbers indicate that the quantity of 10–15% shellac in weight ratio is the most effective regardless of the quantity of strontium carbonate. The quantity of strontium carbonate has the largest width of the effective zone at a weight ratio of 20% as indicated in Figure 4.

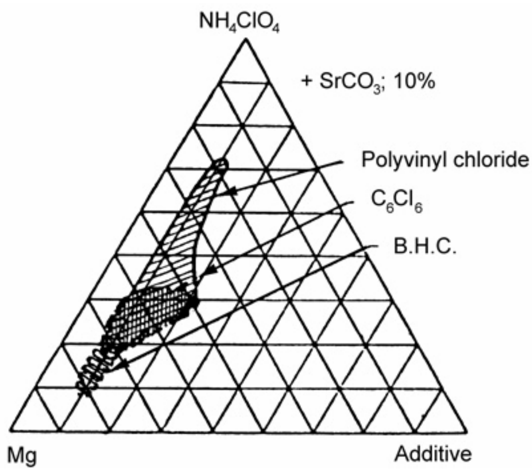

Figure 5. Effective zone of NH_4ClO_4 + Mg + additive + $SrCO_3$ series.

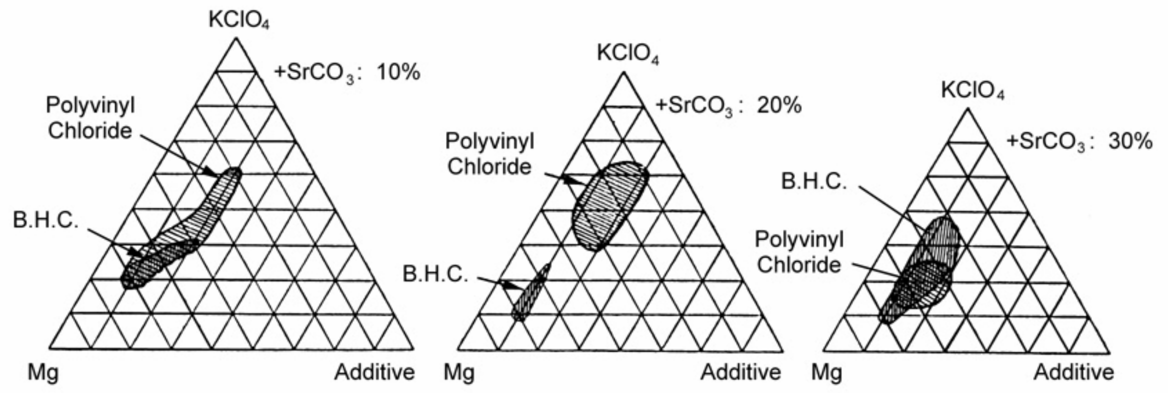

Figure 6. Effective zone of $KClO_4$ + Mg + additive +$SrCO_3$ series.

In the ammonium perchlorate series, HCl gas is produced in the flame, which is favorable for color creation. Therefore, it seems unnecessary to add some additives for color production. When polyvinyl chloride, BHC or hexachloroethane was added to the composition, the effective color producing zone was narrower than that when shellac was added to the composition; compare Figure 5 with Figure 4.

(3) Potassium perchlorate series

i. When additives contain chlorine:

The quantity of color agent needs to be fairly large (i.e., 20–30% of the composition) to obtain a good effective zone. The results of the experiment are shown in Figure 6.

Strontium carbonate is useful until the quantity increases to 30%. This is the case with ammonium perchlorate. The additives are most effective in the 10–20% range. The flame color is somewhat pinkish. The effective zone for polyvinyl chloride is somewhat wider than that for shellac, and for hexachloroethane (10% addition) the flame color is not good even when the strontium carbonate is increased to a higher percentage.

ii. When additives contain no chlorine:

When using shellac as the additive, the flame color is more clear and beautiful than with the chlorine-containing additive. The effective color producing zone is shown in Figure 7.

(4) Potassium nitrate series

It can be predicted that some additives that contain chlorine may be effective because potassium nitrate does not contain chlorine. An

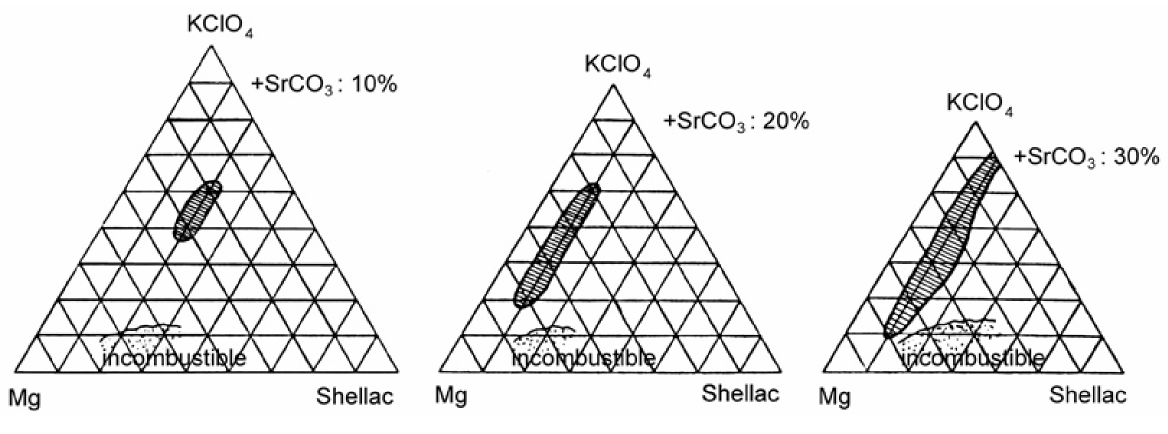

Figure 7. Effective zone of $KClO_4$+ Mg + shellac + $SrCO_3$ Series.

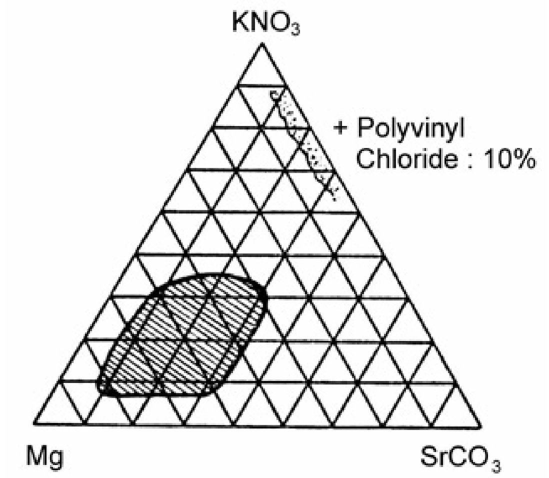

Figure 8. Effective zone of KNO_3 + Mg + $SrCO_3$ + polyvinyl chloride series.

experimental result when using polyvinyl chloride is shown in Figure 8.

The experiment with 20% potassium nitrate and 20% strontium carbonate produced the most effective flame color. Using potassium nitrate for color production is limited only in high flame temperature compositions.

With the above experiments it was shown that polyvinyl chloride or shellac gave the widest effective zone of color production. However, shellac gave slightly orange red flames due to the strong α band and Na spectra from impurities.

4.3.2 Yellow flame series

Na-D lines appear very easily and the effective zone is very wide; so there are no problems except when a pure yellow flame is required. Generally in high temperature flames, a large width of continuous spectrum CS(Na) accompanies the Na-D lines. Therefore, the flame color is slightly reddish yellow, so-called golden yellow.

The effective zones for ammonium perchlorate and potassium perchlorate are shown in Figure 9.

However, when ammonium perchlorate is used as the oxidizer, the zone in the graph is surrounded by an incombustible area. Fortunately, the combustible part produces a good flame color when it burns.

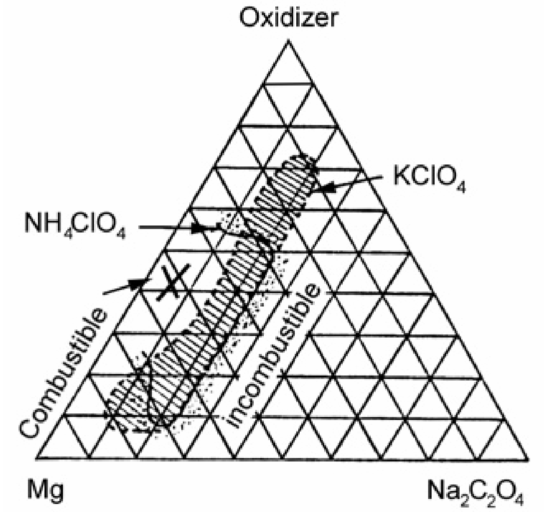

Figure 9. Effective zone of oxidizer + Mg + $Na_2C_2O_4$ series.

When potassium perchlorate is used as the oxidizer, 10% sodium oxalate gives the best flame color zone.

When potassium nitrate is used as oxidizer, the effect of adding 10% polyvinyl chloride is shown in Figure 10. Polyvinyl chloride has a role to suppress the continuous spectra. The effective zone is very wide and with no problems.

4.3.3 Green flame series

(1) Barium nitrate series

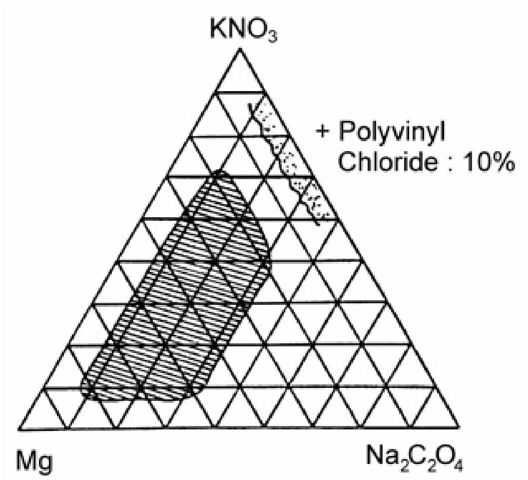

Figure 10. Effective zone of KNO_3 + Mg + $Na_2C_2O_4$ + polyvinyl chloride series.

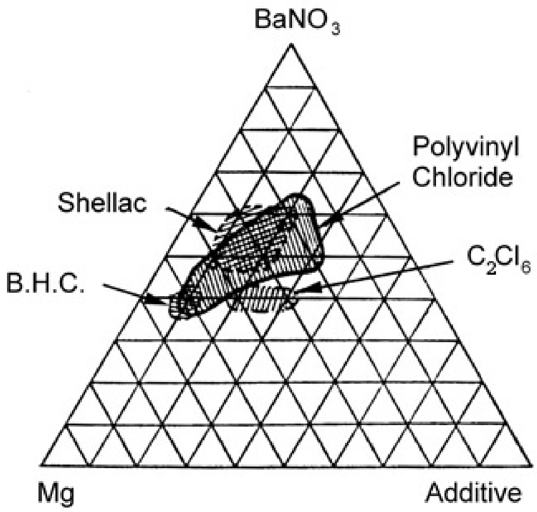

Figure 11. Effective zone of $BaNO_3$ + Mg + additive series.

This oxidizer has no chlorine; therefore, it is necessary to add chlorine donors to intensify the BaCl band and suppress the continuous spectra. The experimental results are shown in Figure 11.

Figure 11 shows that polyvinyl chloride gives the widest effective zone of color production zone, and 20% polyvinyl chloride produces the best green flame. BHC and hexachloroethane give very narrow effective zones and the color is not as good as with polyvinyl chloride.

When shellac is used as the additive, the color of the flame appears faint and not very clear. This is due to the fact that shellac does not increase the intensity of the BaCl band.

(2) Ammonium perchlorate series

This oxidizer produces HCl in the flame. In this study additives that contain chlorine were added to further suppress the continuous spectrum. The effects are shown in Figure 12.

Polyvinyl chloride as an additive gave the widest effective zone. The flame color for the hexachloroethane is not good.

(3) Potassium perchlorate series

The three component compositions of potassium perchlorate, magnesium and barium carbonate produce a weak green flame (only producing visible color at 20% potassium perchlorate). This defect comes from the very strong continuous spectrum caused by heated metal oxide particles, which at high temperatures emit white light. Additives result in better flame color. The results are shown in Figure 13.

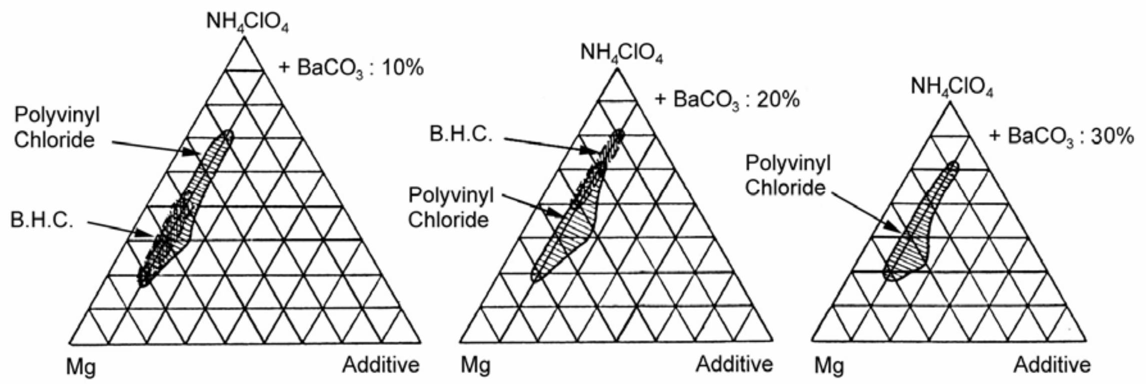

Figure 12. Effective zone of NH_4ClO_4 + Mg + additive + $BaCO_3$ series.

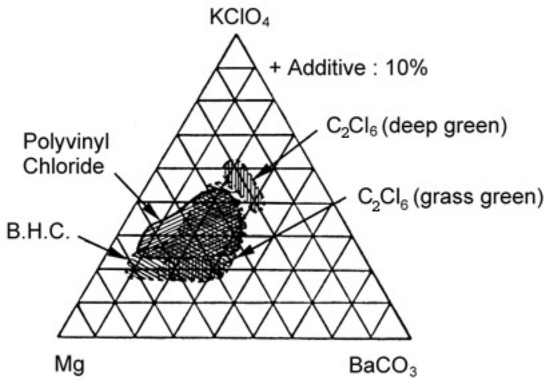

Figure 13. Effective zone of $KClO_4$ + Mg + $BaCO_3$ + additive series.

With polyvinyl chloride as an additive, the flame color is good and the effective zone is wide. BHC is not good for color production. Hexachloroethane makes two effective zones producing special effects (i.e., as the percentage of magnesium increases, first the flame is colored deep green, becomes white, then changes to a pretty grass green).

(4) Potassium nitrate series

Three component compositions of potassium nitrate, magnesium and barium carbonate were tested, the effects are shown in Figure 14.

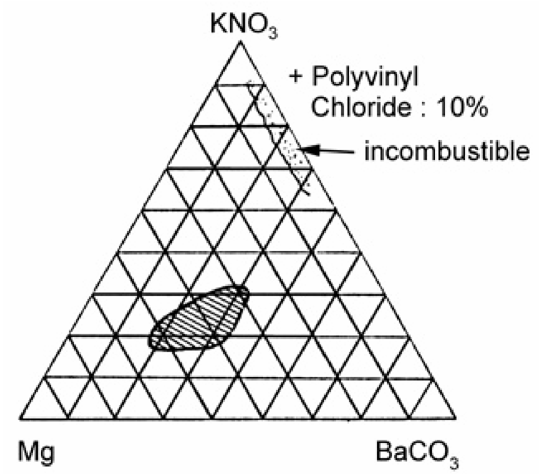

Figure 14. Effective zone of KNO_3 + Mg + $BaCO_3$ series.

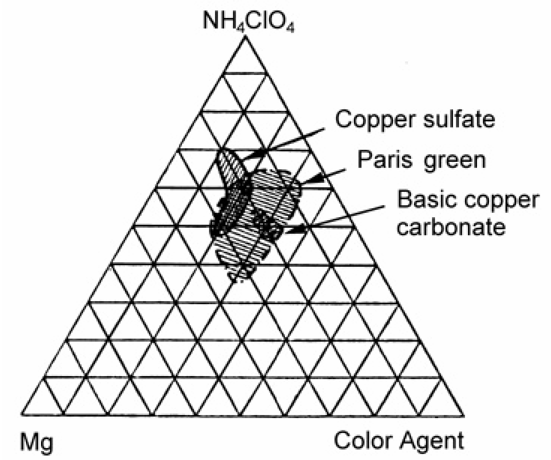

Figure 15. Effective zone of NH_4ClO_4 + Mg + color producing agent series.

The color in the effective zone was grass green.

4.3.4 Blue flame series

Producing blue colored flame is difficult when using the CuCl band at high temperatures (See Part V).

(1) Ammonium perchlorate series

i. No fuel additive:

The effect of the three component composition of ammonium perchlorate, magnesium and color agents is shown in Figure 15.

Paris green gives the prettiest blue flame and the widest effective zone of all.

ii. With 10% polyvinyl chloride additive:

Ten percent polyvinyl chloride was added to the above composition and tested. The effect is shown in Figure 16.

Basic copper carbonate gives the prettiest blue flame and the widest effective zone; next is Paris green. From other spectral studies the author did not notice much difference among the various color agents; however, in this case fairly large differences appear. This might be due to the Na impurity due to using industrial grade chemicals.

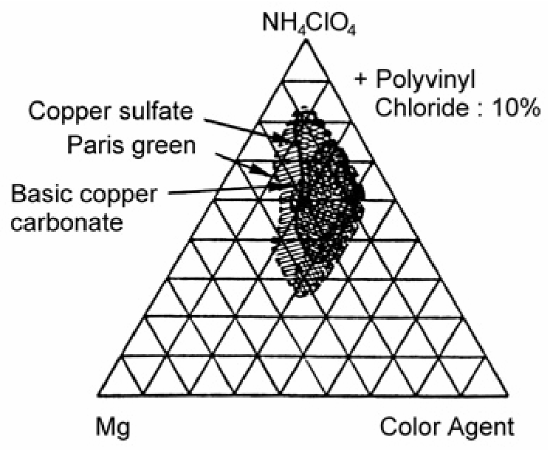

Figure 16. Effective zone of NH_4ClO_4 + Mg + color agent + polyvinyl chloride series.

Compositions using copper powder as the color agent that give good blue flame color are as follows:

Polyvinyl chloride %	NH_4ClO_4 %	Mg %	Cu (additional %)
10	70	20	2
10	80	10	2
10	70	20	4
10	80	10	4
10	60	30	6
10	70	20	6
10	80	10	8

The result of the experiment using BHC in place of polyvinyl chloride is shown in Figure 17.

Using BHC as an additive and copper powder as the color agent did not produce good flame color. The flame was whitish and not a clear blue. Hexachloroethane did not give good color to the flame. Shellac was tested as an additive fuel and the result is shown in Figure 18.

(2) Potassium perchlorate series

The continuous spectrum of potassium interferes with the flame color and the color is not as good as when using ammonium perchlorate.

i. Three component compositions that consisted of potassium perchlorate, magnesium and color agent were tested. As the color agent, Paris green, copper sulfate and basic copper carbonate were used. None produced good flame color; however, a composition of 60% potassium perchlorate, 10% magnesium and 30% Paris green gave a slightly blue flame.

ii. An experiment was carried out that added 10% polyvinyl chloride to the above compositions. Paris green gave the best flame color. Copper powder made the flame whitish and is not practical. The above results are shown in Figure 19.

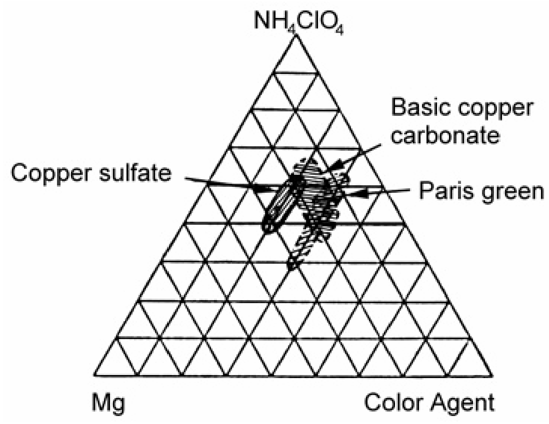

Figure 17. Effective zone of NH_4ClO_4 + Mg + color agent + BHC series.

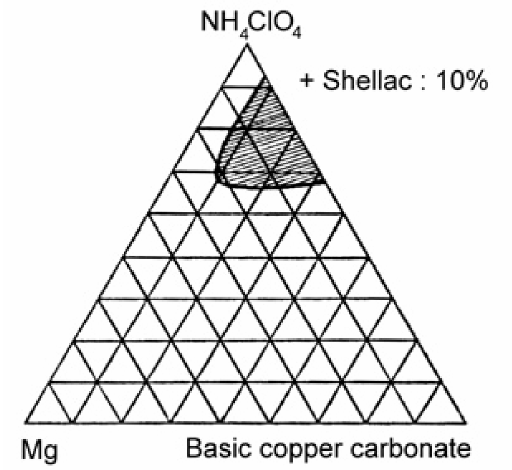

Figure 18. Effective zone of NH_4ClO_4 + Mg + basic copper carbonate + shellac series.

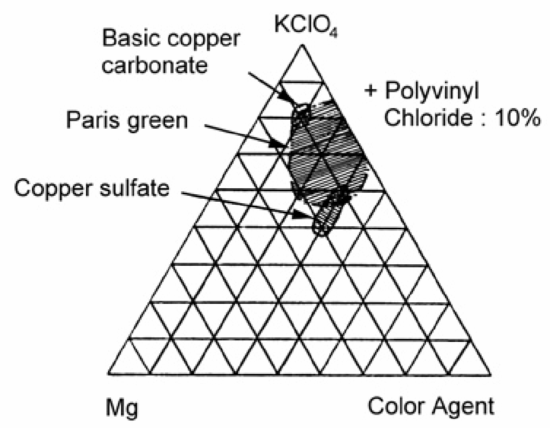

Figure 19. Effective zone of $KClO_4$ + Mg + color agent + polyvinyl chloride series.

5. Conclusion

On the basis of the former spectrometric study the author investigated practical, useful effective zones of various compositions from the standpoint of producing good colored flames. In the practical case, we could easily select the composition for our purpose, considering the color producing conditions. However, it will be more useful, when we prepare the data of burn rate, light intensity, or loading density, etc. for the effective zones. This remains as a future problem.

The common important factors in Part VII are as follows:

(1) Effective color producing zone:

The low temperature series is mostly affected by oxygen balance; the effective color producing zone is very narrow and the selection is difficult. On the other hand, the high temperature series is not as much affected by the oxygen balance, and the selection of flame color, burn rate or light intensity is far easier than for the low temperature series.

(2) Storage problem:

The high temperature flame series generally contains magnesium as a fuel. Therefore, for storage the compositions should be completely waterproof or moistureproof, or the magnesium should be coated to protect it from corrosion.

When using the low temperature series of compositions, generally there is no need for such processes.

(3) At present the most pretty and deep flame color is obtained by using an additive that produces HCl gas in the flame like ammonium perchlorate or polyvinyl chloride. However, ammonium perchlorate is only useful when it is protected from effects due to water or moisture.

(4) In the high temperature series potassium perchlorate is useful for red or yellow flame without ammonium perchlorate.

(5) Potassium nitrate is practical for use only in the high temperature series of red, yellow and green (grass green) for special purpose. The low temperature series are useful only for red, yellow, and green (grass green) but not for blue.

(6) Of the chlorine or hydrogen chloride containing material, polyvinyl chloride, hexachloroethane, etc., polyvinyl chloride is the most effective for producing good colored flame; BHC follows the next, and third is hexachloroethane, which is not as good for color production.

(7) Shellac has no chlorine but is effective for producing red or yellow flames.

As described earlier, the sample specimens were of small diameter. The compositions that did not burn with such a small diameter would often burn when the diameter is larger than the samples used. For example, a superior blue composition is here given. This composition burns producing a beautiful blue when the diameter is more than 20 mm.

Ingredient	Percentage
Barium nitrate	50
Magnesium	20
Hexachloroethane	30
Copper powder	5 (additional)

Acknowledgement

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1) T. Shimizu, *Hanabi* (1957) p 151.
2) Ibid., p 277.
3) Ibid., p 129.