

Illuminants and Illuminant Research

David R. Dillehay
107 Ashwood Terrace, Marshall, Texas 75672 USA

ABSTRACT

The use of pyrotechnic compositions for the production of light has a long history. Most improvements were made mainly by trial and error with many misunderstandings about the cause and effect relationships from observations. Significant advancements in the mechanisms and theory of combustion have increased the understanding of many effects and led to improved illuminants both theoretically and practically. Radiative transfer theory explained most of the observed variations in illuminant functioning. Effects of spin, liner thickness and binders have been analyzed, and application of the results has been used to improve illuminant performance and solve production problems.

Keywords: illuminant, photoflash, efficiency, magnesium, sodium, nitrate, binder, radiative transfer

Introduction

Illuminants have been a major factor in pyrotechnic applications for many years. The earliest application was the use of torches prepared with pitch or tar, ignited and used to ward off darkness. This simple application was extended with the utilization of oxidizers, such as saltpeter or niter to enhance burning. When more light was needed, it was found that sodium added to a flame produced an astonishing increase in illumination efficiency.

An early application of illumination was photoflash devices for the military. Photoflash devices released pyrotechnic compositions that burned to produce millions of candela in visible light for a fraction of a second. This allowed aircraft to fly over a region with a camera lens open and release a huge "flashbulb" to illuminate a number of square miles. This was the only

way to do night surveillance. The development of airborne radar and forward-looking infrared (FLIR) has made photoflash obsolete. Photoflash compositions were based on aluminum powder mixed with potassium perchlorate with confinement until ignition which was followed by an explosive dispersion of excess aluminum reacting with the air. It should be noted that aluminum will react with both oxygen and nitrogen in the air.

The efficiency of an illuminant is given in candela per unit weight. Candela is the unit of luminous intensity equal to 1/60 of the luminous intensity per square centimeter of a blackbody radiating at the temperature of solidification of platinum (2,046 K). In jargon, it is frequently referred to as the "candlepower" of a composition. The preferred term, however, is candela. There is an approximation in efficiency that relates burning rate and intensity over a range. This relationship is shown in equation 1.

$$\begin{aligned} \text{Light Integral} & \left(\frac{\text{cd} \times \text{s}}{\text{g}} \right) \\ & = \left(\frac{\text{candela} \times \text{burn time}}{\text{mass of composition}} \right) \end{aligned} \quad (1)$$

This equation shows that it is possible to trade burn time for candela by adjusting the burning rate of the composition without changing the formulations total energy. However, this is only true over a limited range of formulation and candle size. It can be shown that there is an ideal burning rate for a given composition to produce the most efficient output. If the burning rate is slower than the optimum rate, then radiant heat losses will reduce the efficiency. If the burning rate is faster than the optimum rate, then material will be expelled from the flare plume without complete combustion and energy will be lost.

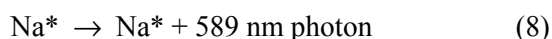
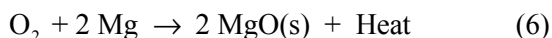
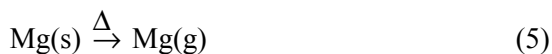
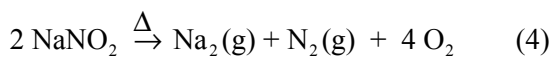
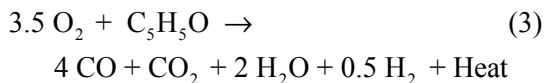
Pressure Effect on Flame

Douda^[1] published a definitive work on the effect of radiative transfer on alkali metal D-line radiation. This treatise identified several *a priori* factors that influence the resonance line broadening in pyrotechnic flames.

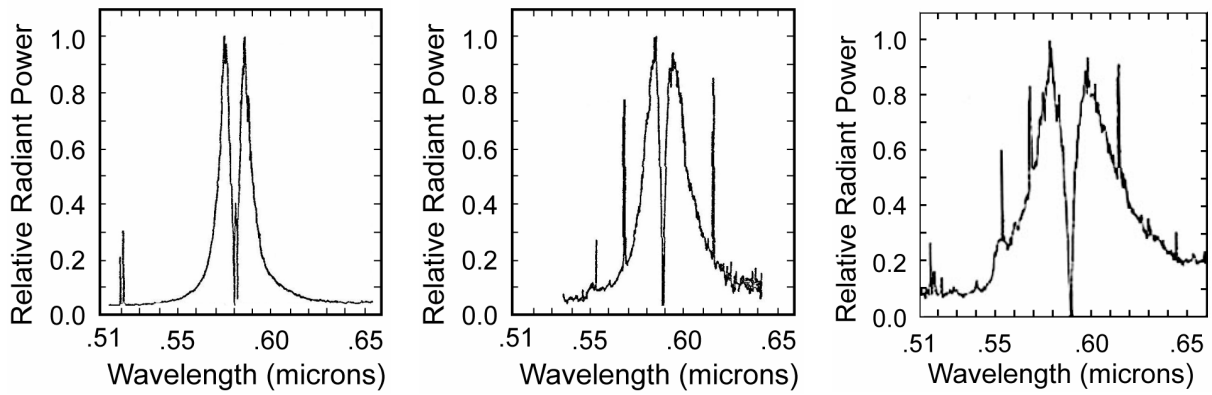
This author^[2] extended Douda's work through flame modeling to determine the effects of these factors without *a priori* assumptions and verified the theory over a wide range of pressures, candle diameters, alkali metals, atmospheric interactions and fuels. This effort finally gave a clear understanding of the effects of combustion on illumination, including interactions with the surrounding atmosphere. This work also provided answers for many of the anomalies that had been observed, such as the increase in light output even though the theoretical flame temperature decreased with increasing magnesium content. It further showed that almost 90% of the visible light from conventional sodium nitrate-magnesium flares comes from the broadened D-line radiation.

Mixtures of magnesium and sodium nitrate, with a binder, have been well characterized. When magnesium and sodium nitrate are burned, the sodium nitrate first melts and then decomposes to release oxygen and form sodium nitrite. The oxygen released immediately reacts with the pyrolyzing binder that coats the sodium nitrate and magnesium and releases enough energy to raise the magnesium to a reactive state. This increase in energy promotes a more rapid decomposition of the sodium nitrite and the magnesium oxidizes on the surface to form a porous capsule of magnesium oxide. The magnesium oxide density is such that it cannot completely encapsulate the magnesium particle, so the internal magnesium starts to vaporize through the pores. This provides gaseous magnesium to mix and burn with the oxygen from the decomposing sodium nitrite and increases the efficiency of combustion. Thermochemical calculations readily show that the maximum temperature of the reaction of magnesium and sodium nitrate will occur at the stoichiometric composition around 46% magnesium. It is well established that the maximum candela occurs well above the stoichiometric composition with a considerable excess of mag-

nesium present. The thermochemistry is represented by the following equations:



The sodium nitrate first melts and then decomposes to sodium nitrite with the release of some oxygen (eq. 2). The oxygen reacts with some of the binder to form carbon monoxide, carbon dioxide and water with the release of more heat (eq. 3). The heat causes the sodium nitrite to decompose into sodium vapor, nitrogen and oxygen (eq. 4). The magnesium is heated and vaporized to provide magnesium gas for easy oxidation (eq. 5). The additional oxygen from equation 4 reacts with the remaining binder and the magnesium fuel (eq. 6). The oxidation of the magnesium provides a very high temperature (3073 K) that is adequate to dissociate the sodium vapor into individual atoms and raise them to a higher state of excitation (eq. 7). The excited sodium atoms then radiate their excess energy as sodium D-lines (a doublet at 589 nm) (eq. 8). This D-line radiation is broadened by a number of mechanisms with pressure as the strongest contributor. This can be seen from sodium vapor street lamps that use high pressure sodium vapor, excited electrically, to produce a high level of visible light. The broadening of the radiation increases the amount of light over a wider range of the spectrum, which reduces the monochromatic nature of the atomic spectra. Examples of this broadening due to increasing pressure are shown in Figures 1 a to c.



(a) Pressure is 76 torr. (b) Pressure is 300 torr. (c) Pressure is 760 torr.

Figure 1. Spectra showing that increased pressure results in a broadening of the D-line radiation.

Plume Effect

The plume of a burning flare entrains air as it exits the canister and the oxygen in the air reacts with the magnesium to increase the outer temperature of the plume and keep the sodium atoms at a highly excited state. A diagram of the plume of a burning flare is shown in Figure 2. When the temperature drops below about 1800 K, radiation of the sodium D-lines ceases. The more magnesium present in the flame, the longer the flare plume becomes as the magnesium continues to react with the air and bolster the surface area. The insulated central portion of the plume continues to cool by radiation and lose radiative efficiency but the overall increase in flare plume surface area compensates and provides the observed increase in candela.

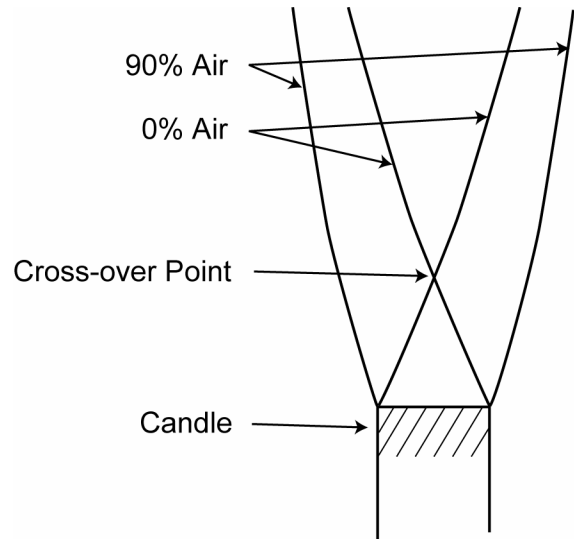
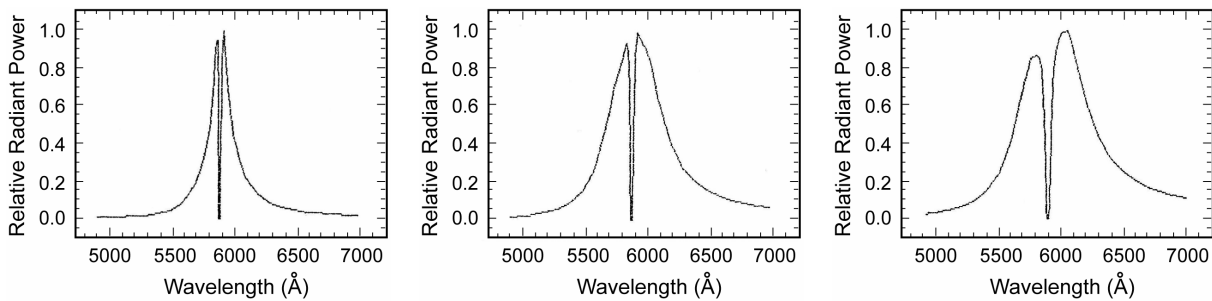


Figure 2. Plume diagram.

Figures 3 a to c show the decrease in broadening for sodium D-lines at a fixed distance above the surface as the percent magnesium increases.



(a) 40% magnesium. (b) 50% magnesium. (c) 60% magnesium.

Figure 3. Graphs showing that the sodium D-lines broaden as the percent of magnesium increases.

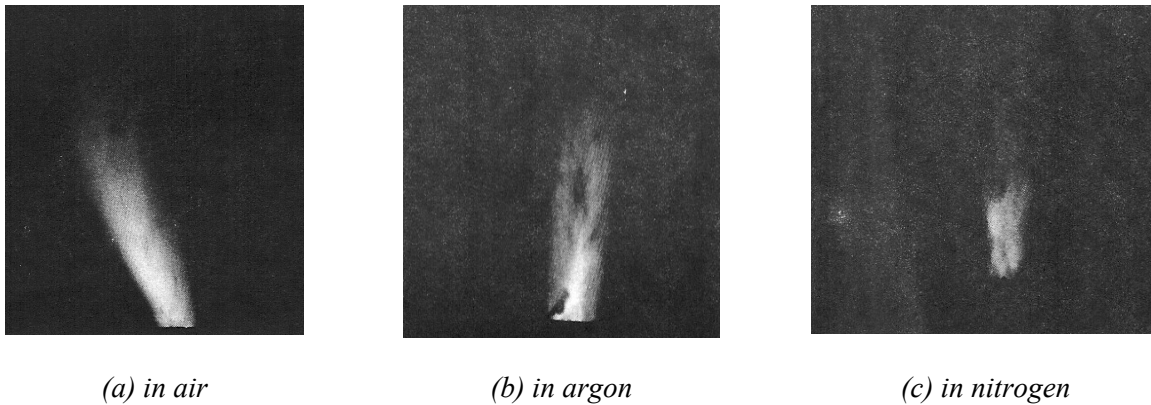


Figure 4. Plume length effect on a stoichiometric formulation burned in (a) air, (b) argon, or (c) nitrogen.

The plume length was experimentally found to increase as a function of diameter and fuel richness so that flare surface area increases as the fuel increases. This analysis also explains the effect of candle diameter on efficiency.

As the diameter increases, the entrainment of air into the central portion of the plume is less efficient and the radiative transfer mechanisms lose efficiency.

An interesting set of tests were performed in a large chamber (6 m³) with different atmospheres. The purpose of the tests was to determine how much the oxygen in the air was contributing to the efficiency of magnesium-sodium nitrate flares. Stoichiometric and fuel rich compositions were burned in atmospheres of air, nitrogen or argon. The results from the stoichiometric formulations clearly showed little difference in plume length and candela. See Figures 4 a to c.

With the fuel rich composition, however, the tests in air showed a much longer plume and higher candela. See Figures 5 a to c. In argon, the plume length was shorter and the candela much lower. In nitrogen, the plume was very short and the candela was very low. The argon does not react with the excess magnesium, so the lower flame temperature of the fuel rich composition results in greatly reduced D-line radiation.

The flare plumes in a nitrogen atmosphere are much shorter than the plumes in an argon atmosphere in keeping with the prediction that nitrogen is more effective in collisional de-excitation of excited sodium atoms. This is another of the radiative transfer mechanisms that is treated in the theory.

Hooymayers and Alkemade^[3,4] reported measured values for quenching cross sections of various species with sodium and potassium. Their results indicated that the apparent quench-

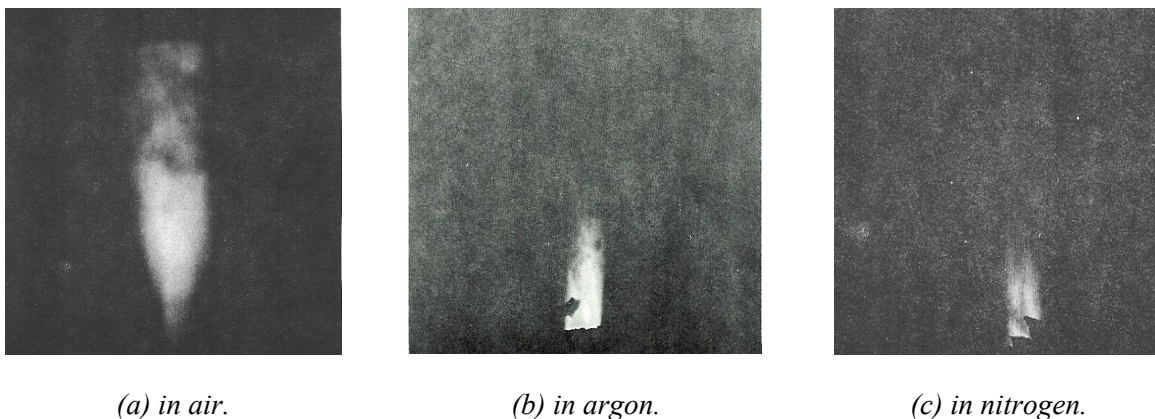


Figure 5. Plume length effect of a fuel rich formulation burned in (a) air, (b) argon, or (c) nitrogen.

ing cross section of a species with an alkali metal would be inversely proportional to the atomic weight of the alkali metal. A higher value indicates a more efficient quenching cross section for the species. See Table 1 for a compilation of quenching cross sections for various species with sodium.

Table 1. Quenching Cross Section Values for Species with Sodium.

| Species | Temperature (K) | Na Value |
|------------------|-----------------|----------|
| CO | 2000 | 72 |
| CO ₂ | 1670 | 113 |
| Ar | 2070 | 2.3 |
| H ₂ O | 2070 | 1 |
| N ₂ | 1940 | 40 |
| O ₂ | 1885 | 66 |

Formulation Effect

Effective illumination is based on magnesium, sodium nitrate and a binder. The binders are important in the production processes of the illuminant composition, where they serve to maintain homogeneity of the composition while in process and then hold the composition together and bonded to the container during functioning. The binder also provides an initial reaction with the oxygen released from the sodium nitrate to provide a transition to burning of the magnesium. There can be some difference in performance as the binders change due to their stability under pyrolyzing environments (i.e., some binders are more stable and pyrolyze more slowly and reduce burn rates). Magnesium particle size and shape also play a role in the burning rate of the composition. Use of other metals has been shown to be less effective than magnesium in illuminants. This is mainly due to the low melting and boiling points of magnesium coupled with the very high heat of combustion. Other low melting and boiling metals do not have the high heat of combustion and are, therefore, not as effective in sodium excitation. Sodium nitrate particle size distribution affects the consolidation characteristics of formulations.

A typical illuminating composition consists of 50% (200 μ) magnesium powder, 43% (30–50 μ) sodium nitrate and 7% binder. Early binders included linseed oil and polyester resin. Army formulations currently use vinyl-alcohol acetate resin (VAAR) or polysulfide-epoxy resin binder systems. The VAAR binder is dissolved in a solvent and then mixed with the magnesium and sodium nitrate until the solvent is evaporated. This composition can then be stored and used whenever needed. No curing is required after consolidation. The polysulfide-epoxy combination is mixed with an amine cure agent and mixed with the magnesium and sodium nitrate. This mixture has a pot life and must be consolidated before the cure has progressed to the point that it will no longer flow under pressure. After consolidation, the candles are cured at an elevated temperature to complete the process. This binder gives a small amount of flexibility to the composition to prevent shrinkage and separation from the case.

Diameter Effect

It can also be shown that increasing the diameter of a candle does not produce a corresponding increase in output. This can be shown to be the effect of the entrainment of air into the plume along the plume axis. Diffusion of air into the plume can only occur at a certain rate. As the diameter increases, the central portion of the flare plume will begin to cool from radiative heat loss and there will be a corresponding loss of efficiency from the composition. The graph in Figure 6 shows a typical response of candela for a fixed composition as the diameter of the flare increases.

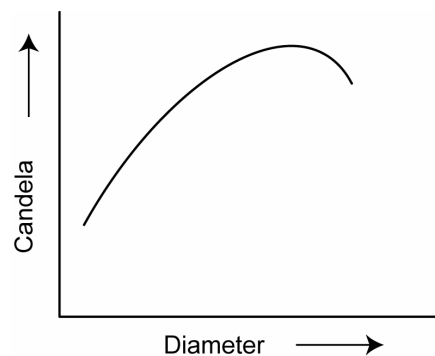


Figure 6. Typical response of candela for a fixed composition as flare diameter increases.

Spin Effect

A number of physical effects on flares were observed and their causes identified. For example, in military illuminants, many of the larger caliber illuminants are gun launched with high spin rates. Air brakes were frequently used to stop the spin on ejection of the payload. Field tests sometimes showed that the illuminants put out very low intensity light, followed by a large illuminant drop-out about half-way into the burn. Recovery of the rounds usually showed that the air brakes had failed and the illuminant in the canister had an unusual appearance. There were marked protrusions up from the center of the illuminant composition remaining in the canister. It appeared that the composition was burning faster around the periphery of the canister. It was assumed that the failure of the air brakes led to the flare spinning at a high rate, but the mechanism for reduced output was not obvious. The prevalent theory assumed that the sodium nitrate was melting and centrifugal force was carrying the reacting materials to the sidewall of the canister and choking the canister to cause a rise in pressure and shorten the burn time. The reduced opening for the plume explained the loss in light intensity. To test the theory, a spin test fixture was built to spin the illuminant canisters at controlled speeds while suspended upside down. A water jet was positioned to extinguish the burning composition at any point during the burn. The 105-mm candle was tested first. The graph in Figure 8 shows the results of the first set of spin tests.

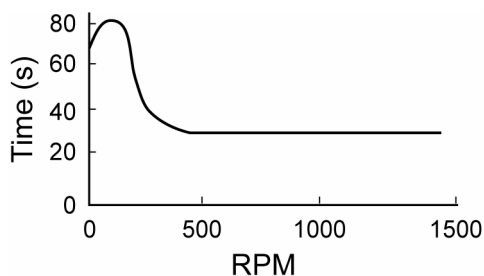


Figure 8. Results of the first set of spin tests.

The tests were repeated several times and the slight rise in burn time followed by a precipitous drop around 250 rpm was noted each time. This

provided the proof that the effect was spin related. A series of tests were then run with extinguishment of the burning candle at various times into the burn. Examination of the surface provided an unexpected result. The illuminant was noted to regress faster at the edge producing a spiked appearance towards the end of the burn. This is shown in the Figure 9.

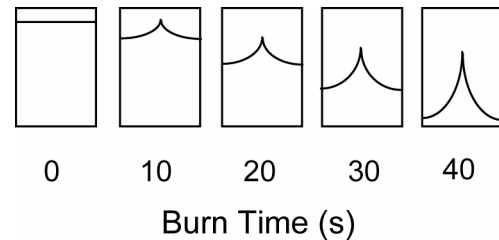


Figure 9. Diagrams showing the change in burn surface inside spinning candle over time.

The patterns observed did not agree with the original expectation of more rapid combustion down the center of the candle. A new theory was developed that involved the effect of decoupling of the gases from the illuminant surface. As the illuminant starts to spin, the gases evolved from the surface start to rotate with the surface. At a critical rpm, in this case 250 rpm, the gases start to lag behind the surface. The difference in rotation produces an increase in heat transfer. (This effect is well known and demonstrated by many physical phenomena, such as blowing on your hands to warm or cool them. The increased velocity of your breath either warms or cools the skin depending on which has the highest heat content.) As the spin velocity increases, the effect increases up to a maximum value determined by the thermal conductivity of the illuminant composition. Since the rotational velocity is greatest at the periphery, the heat transfer is greatest at that point. The slowest rotational velocity—in the middle—results in the slowest burn rate and leads to the formation of the spike. When the edge burning reaches the bottom of the canister, the center spike falls out, explaining the observed illuminant drop-out. To test the theory, a set of candles was loaded with a “paddle-wheel” of metal plates inserted in the canister. A split ram was used to press illuminant into each quadrant to load the candles. See Figure 9.

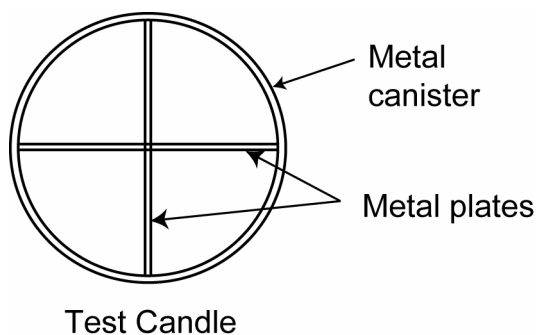


Figure 9. A cross-section of the “paddle wheel” of metal plates in a canister.

When these candles were burned in the spin fixture, there was no change in the burn time even at 1500 rpm. This is consistent with the paddles acting to keep the gases in sync with the burning surface thus preventing the differential spin rates and eliminating the increase in heat transfer. Once the principle was understood, other problems could be addressed.

The 60 mm illuminant was changed from a fin-stabilized round to a spin-stabilized round. The small size of the candle precluded the use of air brakes to stop the spin. The burn times were observed to change from 60 seconds in the static testing to 40 seconds in flight tests. The problem obviously resulted from the spinning of the illuminant, but there was no way to stop the spin, or even reduce it. The only control available seemed to be the thermal conductivity of the illuminant composition. The oxidizer was being ground from prilled sodium nitrate to a weight mean diameter (WMD) of about $50\ \mu$; the magnesium was 30–50 mesh (about $200\ \mu$ WMD); and the binder content was about 6%. The formulation gave the needed candela and could not be readily changed. By grinding the sodium nitrate to a much finer particle size, it was possible to provide a more uniform distribution of the oxidizer to isolate the particles of magnesium, thereby reducing the thermal conductivity. This provided a reduced sensitivity to the heat transfer induced by the spin and the flight burn times were raised to about 55 seconds, which met the specification requirements. This is a prime example of the benefits of understanding both the chemistry and physics of the pyrotechnic reactions.

Liner Effect

Another example of applying analysis to the solution of problems involved the use of liners in illuminants. The 81-mm illuminants were changed from a cardboard tube to a metal canister. The canisters were lined with the binder solution and cured to provide a bonding surface for the illuminant composition. The liner thickness was not considered a serious problem and was allowed to vary during production. It soon became obvious that too little liner resulted in unbonded areas and high heat transfer down the canister wall resulting in short burn times. To avoid this, the liner amount was doubled. While this stopped the short burn times, it was noted that the candela of stationary flares had dropped to an unacceptable level. To determine the magnitude of the problem, a series of candles were loaded with carefully controlled liner thickness. It was found that a maximum thickness could be applied without loss of candela. Analysis revealed the cause. At low liner thickness, the heat transfer through the liner was absorbed by the metal canister, and this kept the liner from pyrolyzing from the heat of the flame. When a critical thickness was reached, the thick layer of liner could not transfer heat fast enough to keep the surface below the pyrolyzing temperature of the liner and the liner began to decompose and add carbonaceous residue to the flare plume. This acted just like an increase in inert binder, which reduced the thermochemical energy of the flare plume and lowered the candela. Again, the understanding of the chemistry and physics of the pyrotechnic reactions allowed a knowledgeable solution of the problem.

Shifting Spectral Output

The latest move in battlefield illumination is now directed towards “covert” illuminants. These illuminants are loaded with compositions that radiate most of their energy in the infrared part of the spectrum. The use of these illuminants with advanced night vision devices permits the observation of troops, equipment or areas without visibly showing illumination in the observed area. This covert illumination has definite advantages in operations that are close to the observers. They can light up an area with

infrared light without showing themselves to an enemy that does not utilize the same night vision devices. The formulations used in the covert illuminants vary but generally do not use metal powders to avoid a broad continuum from hot particles producing visible light. The alkali metals cesium and rubidium have their D-line radiation in the near infrared with little overlap in the visible. Achieving higher burning rates without the use of metal powders has been one of the main challenges to their use.

Pyrotechnic illuminants continue to be a major battlefield item to permit identification and targeting of enemy positions. The shift in spectral output provides new challenges to the formulation developers to keep up with advancing technology.

Acknowledgment

The author wishes to express thanks to Dr. Bernie E. Douda and David W. Turner for reviewing this paper and providing helpful comments.

References

- 1) B. E. Douda, *Radiative Transfer Model of a Pyrotechnic Flame*, RDTR No. 258, Naval Weapons Support Center, Crane, Indiana, Sept. 1973. AD-769 237.
- 2) D. R. Dillehay, *Resonance Line Broadening of Alkali Metals in Pyrotechnic Flames*, PhD Thesis, Clayton University, St. Louis, Missouri, April 1983.
- 3) H. P. Hooymayers, and C. Th. J. Alkemade, "Quenching of Excited Alkali Atoms and Related Effects in Flames: Part I. Theoretical Analysis", *J. Quant. Spectrosc. Radiat. Transfer*, Vol. 6, pp 847-874 (1966).
- 4) H. P. Hooymayers, and C. Th. J. Alkemade, "Quenching of Excited Alkali Atoms and Related Effects in Flames: Part II. Measurements and Discussion", *J. Quant. Spectrosc. Radiat. Transfer*, Vol. 6, pp 501-526 (1966).