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INTERIM REPORT
PART II
LIGHT SOURCE EVALUATION

February 1970

1. FACTORS AFFECTING THE PERFORMANCE OF PYROTECHNIC MIXTURES

The object of this study is to investigate the feasibility of utilizing high intense light emitted from rapidly burning pyrotechnic mixtures for optical incapacitation. Several mixtures have been selected for initial study. The compositions of these mixtures were itemized in a previous progress report.[1]

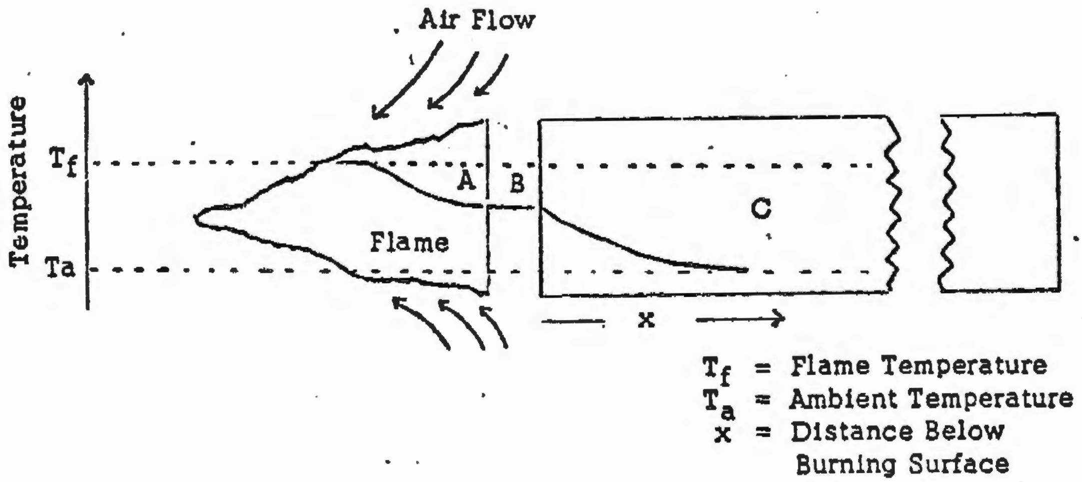
It is useful to review the mechanisms of pyrotechnic burning and the important factors, relevant to light emission, so as to fully understand the utility of this approach.

1.1 DESCRIPTION OF BURNING PROCESS

The basic ingredients of most pyrotechnic compositions consist of a fuel and an oxidizer. These ingredients should be stable under normal shelf conditions, yet they should be easy to ignite. Further, once ignition occurs, the heat released during burning should be sufficient to sustain the burning process.

It is useful to consider the following model to explain the burning behavior of a pyrotechnic mixture.

Three thermal zones are established when an illuminating composition is ignited and burns propagatively (see Figure 1).



T_f = Flame Temperature
T_a = Ambient Temperature
x = Distance Below Burning Surface

Figure 1. Profile of Combustion Zone

The temperature profile within the body of the pyrotechnic (i.e., Zone C) can be approximated by the Rosenthal equation[2]

$$T_x = T_a + (T_s - T_o) \exp(-vx/\alpha) \qquad (2)$$

where T_x is the temperature at distance x below the reacting surface (Zone B), T_a is the ambient temperature, T_s is the temperature within Zone B, v is the burning rate, and α is the thermal diffusivity of the mixture: It should be noted that thermal diffusivity is related to more conventional thermal properties, i.e.,

$$\alpha = k/\rho c, \quad \text{cm}^2/\text{sec} \qquad (3)$$

where k is the thermal conductivity, ρ is density and c is the specific heat.

1.2 FACTORS AFFECTING LIGHT OUTPUT

The distribution of radiation in any spectral region is determined by the chemical nature and physical state of the products which emit in that region, and the temperature reached by these emitting species. The rate at which a pyrotechnic mixture burns depends on the amount and rate at which heat is evolved. Sufficient heat must be produced to raise the temperature of the ingredients to a point at which an exothermic reaction will be initiated and the reaction rate must be sufficient to more than compensate for heat losses in order for the burning to be sustained. Mathematically, the burning rate, v, can be related to the energy fedback from the exothermic processes and the rate determining endothermic process which must occur to produce the reactive intermediates

$$v = \Sigma(I)/\rho\,(\Delta H + C\,\Delta T) \qquad (4)$$

where $\Sigma(I)$ is the radiative, convective and conductive heat flux fedback to the pre-ignition zone, ΔH is the heat absorbed in the pre-ignition zone by the endothermic processes and $C\,\Delta T$ is the heat required to elevate the temperature of the pyrotechnic (i.e., at the boundary between Zones B and C) to the reaction temperature. The latter ($\rho C\,\Delta T$), can be best described as a heat loss term.

The rate of burning, the products formed, and the flame temperature are affected markedly by the composition of the mixture, as well as by the physical condition of the materials and the ambient conditions under which it is burned. Some of the more important factors which affect the performance of light producing pyrotechnics which were considered in our initial selection compositions are as follows,

1. heat of reaction
2. composition of emitters
3. particle size
4. consolidation
5. pyrotechnic diameter
6. container design

1.2.1 Heat of Reaction

The heat of a reaction is defined thermochemically as the difference between the thermodynamic heats of formation of the reactants and products of the reaction. For example, referring to the energy diagram shown in Figure 2, one selects a pyrotechnic mixture having substituents which have a higher heat of formation than the reaction products and one which requires a minimal amount of input energy, ΔH_a, to initiate burning.

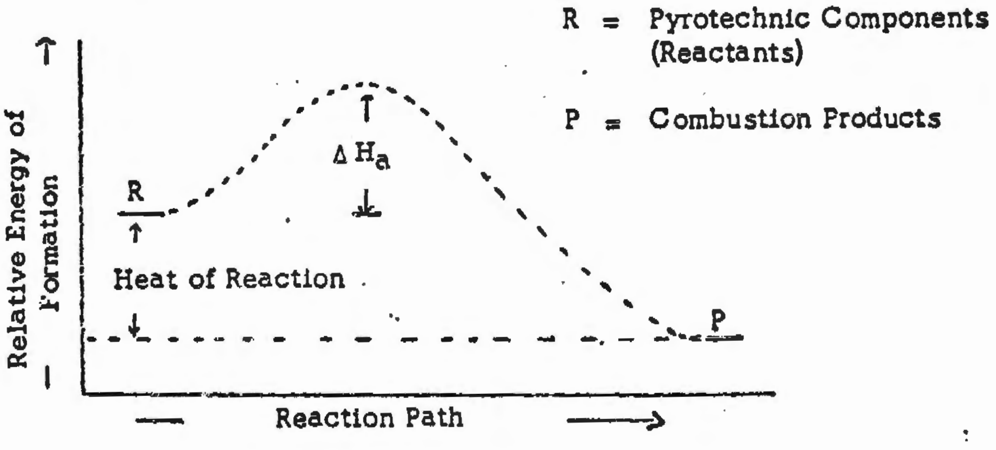


Figure 2. Reaction Energy Diagram

One of the important factors in determining the luminous intensity of a light-producing pyrotechnic device is the temperature reached by the emitting species in the flame and produced by the burning of the pyrotechnic mixture. The temperature reached depends, in turn, on the amount and rate at which energy is released by the reaction. Therefore, the energy released during combustion should be high and the products formed should be stable at the high temperatures necessary to produce the desired luminous intensity.

1.2.2 Desired Output Spectra

The ultimate pyrotechnic composition must emit intense light in regions most sensitive to the eye. It can be seen from the "standard observer curve", shown in Figure 3 that the eye is only sensitive to a very narrow region of electromagnetic radiation.

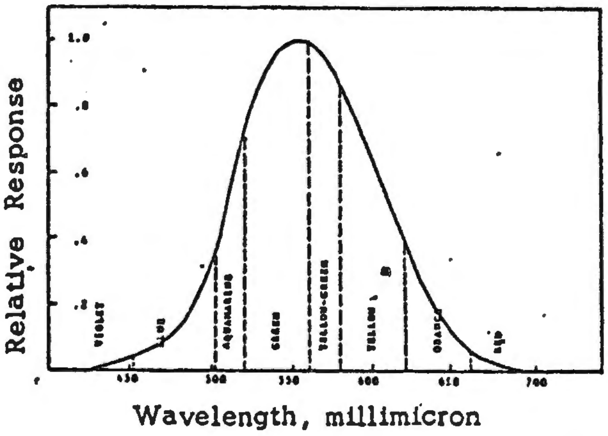


Figure 3. Standard Observer Curve

This region extends between approximately 400 to 700 mμ (or 4000 to 7000 Angstroms). In Figure 4, the visual response curve of the human eye is shown. In this figure the effective radiation, in terms of photometric units (lumens) as a function of wavelength is shown. The absolute photopic luminosity is defined as the ratio of the electromagnetic flux sensed by the eye (in units of lumens) to the total radiant flux (in terms of watts). The most sensitive region in this narrow spectrum lies between 500 and 560 mμ. Therefore, for effects related to visibility of the light source, the pyrotechnic mixtures should be designed to emit strongly in this wavelength region. A separate question arises as to whether optical incapacitation effects are similarly correlated over the visible range. This answer is not known at present but will be assumed to be positive for the present.

Special design features must be included in a pyrotechnic to insure that a significant fraction of the total radiation emitted by the flame is in the visible region. The emission from a pyrotechnic flame is composed of line spectra, band spectra and continuum. The latter is directly dependent on the temperature of the flame. The continuum is essentially blackbody or greybody radiation. The distribution of the radiant energy versus wavelength can be estimated from Planck's equation

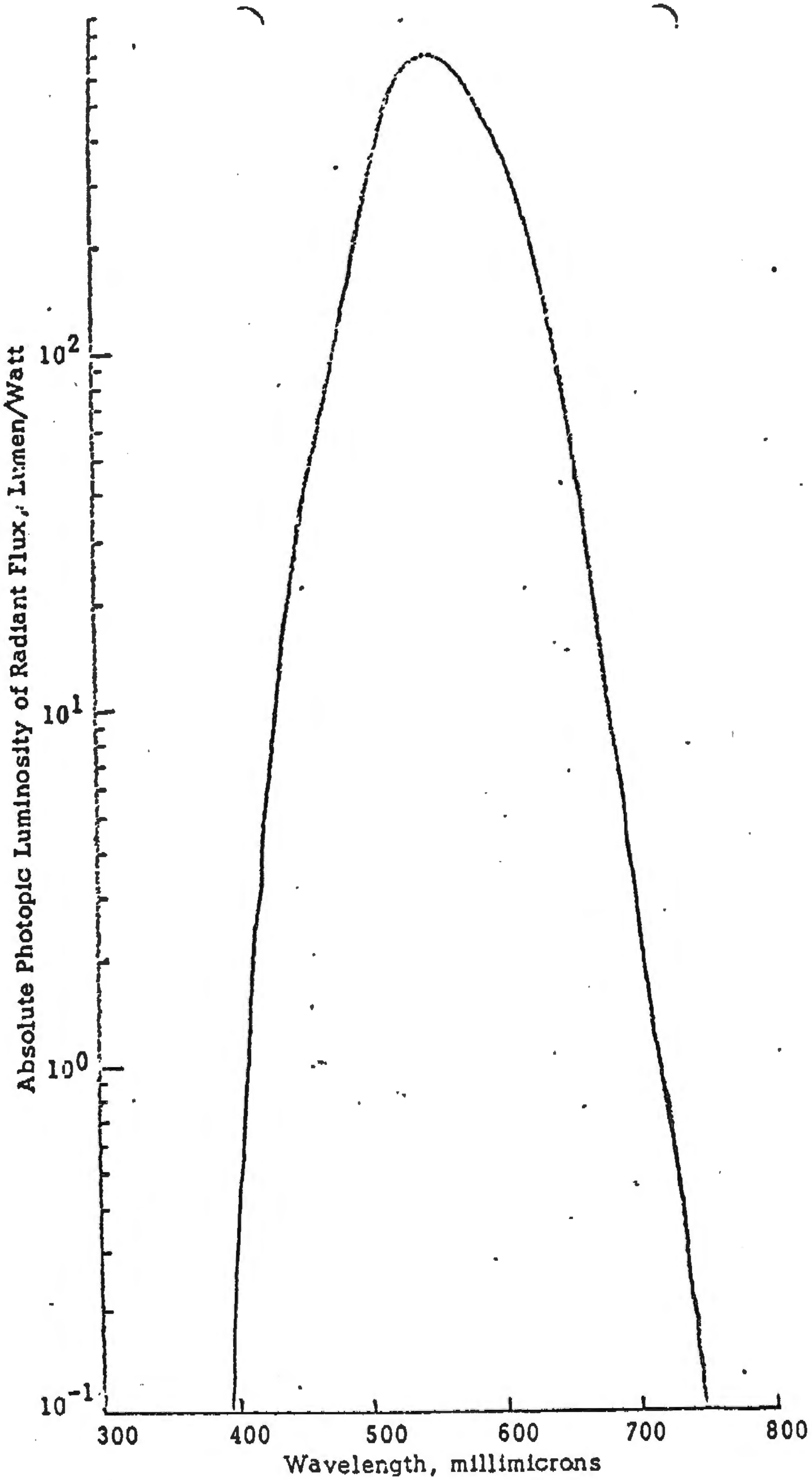


Figure 4. Visual Response Curve of the Human Eye, Spectral Dependence of Luminous Flux (Reference 3)

$$I_\lambda = \frac{2\pi c^2 h \epsilon}{\lambda^5 (\exp(hc/k\lambda T)-1)} \qquad ((5)$$

where I_λ is the radiant flux, in terms of energy per unit area per unit time at wavelength λ, emitted by a hot source at temperature T, h is Planck's constant, c is the speed of light, k is Boltzmann's constant and ϵ is the emissivity of the flame. Typical flux-wavelength distributions calculated from this equation are shown in Figure 5.

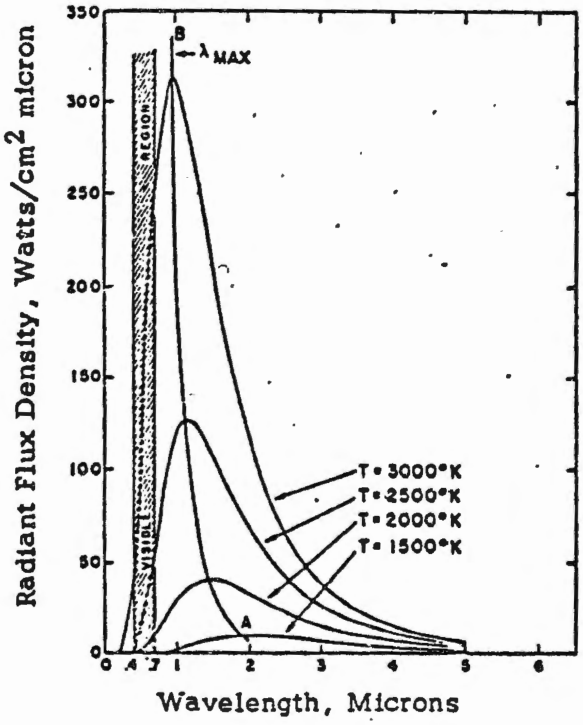


Figure 5. Planck's Law: Radiance as a Function of Wavelength for Various Temperatures

It can be seen from this figure that very little of the energy emitted by blackbody radiation is distributed in the wavelength band most sensitive to the eye. Further, in order to generate an intense source in the visible spectrum, a very high flame temperature will be required and even under these conditions the efficiency of the source in terms of the fraction of visible light energy generated out of the total radiation energy would be very low.

1.2.3 Desirable Pyrotechnic Ingredients

This observation leads one to recognize that pyrotechnics composed of organic fuels which have the highest heat of reaction cannot be considered since these mixtures produce flames having characteristics similar to blackbody emitters. This is particularly true for fuel rich compositions which have a tendency to generate significant amounts of carbon and aromatic soot particles.

The radiant emission in the visible can be improved by including chemicals in the pyrotechnic mixtures that will form thermally excited reaction products capable of emitting radiation at desired wavelengths. This process can be described by the following equation,

$A + B$	$\rightarrow$	$[C + \text{heat}]$	$\rightarrow$	$[C^*]$	$\rightarrow$	$C + h\nu$	(6)
Pyrotechnic Components		Reaction Product in Flame		Thermally Excited Product Species		Light Emission	

Many inorganic salts exhibit this phenomena. Several elements which react in pyrotechnic flames forming oxides, hydroxides and chlorides have been used to "color" flames. These include, strontium which produces a red color, barium (green), sodium (yellow), calcium (yellow-green and orange) and copper (blue to green). Lithium (red), boron (green), thallium (green), rubidium (red) and cesium (blue) are also strong color producers but their use is not as practical because of cost, toxicity or the nature of their compounds.

The actual emitting species of these metals are known to be the di- and tri-atomic species which can exist at high temperatures in the flame. For example,

a. the red light produced by flares containing strontium and a source of chlorine is a result of SrCl emission (strong emission near 640 mμ). In the absence of chlorine, emission has been attributed to SrO.

b. $BaCl_2$ emits in the 505-535 mμ region (green).

c. BaO emits over a broad spectrum, 400 to 800 mμ.

d. The hydroxides of these metals also emit in the respective wavelength bands.

e. MgO emits at approximately 500 mμ.[4]

1.2.4 Color Intensifiers

Where possible, chlorides are added to the pyrotechnix mixtures to enhance the color of the flame. Perchlorate oxidizers contribute the minimal requirements without reducing the efficiency of the energy output. In some cases it has been found that the addition of chloro-organics significantly increase the color intensity. Substances such as hexachlorethane, hexachlorobenzene, polyvinylchloride are sometimes employed for this purpose.

2. CRITERIA USED TO SELECT CANDIDATE PYROTECHNIC MIXTURES

The following considerations were made in selecting candidate pyrotechnic formulations[1] for the initial experimental investigations. Based on the premised desirability of producing flames which emit radiation in the visible wavelength region, primary consideration has been given to inorganic compositions.

2.1 OXIDIZER

Comprehensive literature surveys by Shock Hydrodynamics and other investigators have shown that perchlorates are the most desirable oxidizers. They contain a relatively high ratio of oxygen to total molecular weight, their heats or reaction with metals such as aluminum and magnesium are significantly better than other oxidizers and they generate only oxygen as a gaseous product. Perchlorates are generally stable, yet they are easily ignited, unlike oxidizers such as nitrates and metallic oxides. Nitrates suffer additional disadvantages in that they are not as exothermic and thus tend to have a slower burning rate with fuels such as aluminum and magnesium (see Equation 4), and they generate a non-reactive gaseous product, nitrogen.

Of the alkali perchlorates, lithium and sodium perchlorates have the highest rates of oxygen to total molecular weight, viz., 64/106.4 and 64/127.45, respectively. However, these compounds are extremely hygroscopic. This characteristic decreases the storage life of a pyrotechnic system. The absorption of water by these oxidizers is an exothermic process. Because of this factor one must also be concerned with the design of special safety precautions.

Potassium perchlorate was selected as a primary oxidizer for the initial candidate mixtures. This oxidizer has an oxygen-total weight ratio of 64/138.55, which is somewhat lower than $LiClO_4$ and $NaClO_4$, however, it is a stable compound and its heat of reaction with aluminum, for example, is slightly greater than the reactions between $LiClO_4$ or $NaClO_4$ and aluminum.

2.2 FUEL COMPONENTS

It has been found that aluminum and magnesium are the best fuels for use in photoflash mixtures. The heat of reaction and peak light intensities resulting from $Al/KClO_4$ are much higher than equivalent $Mg/KClO_4$ compositions. The radiation emitted follows generally what would be expected for continuum radiation. Peak light intensities for stoichiometric mixtures of $Al/KClO_4$ and $Mg/KClO_4$ have been measured to be approximately 40 and 18 million candles, respectively.

2.3 CONSOLIDATION OF MIXTURE

It has been shown, that the manner in which the fuel and oxidizer are incorporated in the pyrotechnic device will greatly influence its performance.[5] Consolidated compositions contain binders, usually organic polymers, which form a rigid or semi-rigid body. The consolidated composition however is a burning system which has a relatively large spatial separation between fuel and oxidizer. Thus, the burning rates are relatively slower than a comparative non-consolidated system. Non-consolidated systems under confinement usually have higher deflagration rates than consolidated systems and the intensity of the emitted light is greater. Most photoflash systems are thus non-consolidated, and this type of system was selected for these studies.

2.4 OUTPUT IMPROVEMENT (SELECTION OF STANDARD MIXTURE)

A standard photoflash composition, III-A, was selected as a reference. The composition of this mixture is shown in Table I. The addition of barium nitrate to this mixture increases the radiation output in the visible spectrum over that of the basic $Al/KClO_4$ mixture. As discussed in a previous section, the BaO and $BaCl_2$ formed in the burning processes emits strongly in the wavelength region most sensitive to the eye.

2.4.1 Mixture "D"

During the Korean conflict[5] an experimental photoflash mixture having a very high fuel to oxidant ratio was developed having a peak

TABLE I. CHARACTERISTICS OF TYPE III PHOTOFLASH COMPOSITION[6]

Ingredients	Specification	Microns	Percent
Aluminum, atomized	JAN-A-289	15	40
Potassium Perchlorate	PA-PD-254	24	30
Barium Nitrate	PA-PD-253	147	30

PHYSICO-CHEMICAL DATA:

Heat of Reaction, cal/g—2774 (calc)

Reaction Temperature, °C—approx. 3500

Gas Volume, cc/g—24 (calc)

Tapped—1.67

Vac. Stab, 120°C, cc gas/40 hrs—0.16

SENSITIVITY DATA:

Impact:	PA, inches—40 +
Friction Pend:	Steel—Crackles; Fiber—No Action
Ignition Temp, °C:	5 sec value—610; DTA—No Ignition
Hygroscopicity:	57% RH, room temp; Hrs 24; % Wt Gain < 0.1
Electrostatic Sensitivity:	Joule, Min 2.14; 50% Pt—3.5; 100% Pt—4.5; Temp—65°F; % RH—40: Unconfined—Yes

light output twice that of the Type III mixture. This mixture consisted of 70% Al/30% $KClO_4$. A further improvement in performance is anticipated by replacing a portion of the $KClO_4$ oxidizer with $Ba(NO_3)_2$ which will act as an oxidizer and color enhancer (see Table II for compositions of candidate pyrotechnic mixtures).

TABLE II

Pyro* Composition Designation	Arbitrary Type Designation			
	A	B	C	D
Ingredients	%	%	%	%
Al	40	50	25	70
$KClO_4$	30	40	30	20
$Ba(NO_3)_2$	30		10	10
Ca Si		10		
Mg			35	
TOTAL	100	100	100	100

*All mixtures prepared in accordance with PA-PD-267.

TYPE A Follows the formulation given in PA-PD-267 for Type III Class A (Fine Oxidizers).

TYPES B, C, & D follows the same guidelines including particle size given in PA-PD-267.

2.4.2 Mixture "B"

The addition of calcium silicide should have two effects on the basic $Al/KClO_4$ reaction:

1. Because of the exothermic nature of CaSi in an oxidizing environment, the heat of reaction of this mix should be greater than the selected reference (i.e., mixture A). This increase in the heat of reaction will raise the flame temperature and the radiation intensity of the flame.

2. The flame emission of calcium is at 550 and 620 mμ. This is in the yellow-green and orange areas of the spectrum and as can be seen from Figure 4 should improve the flame luminosity in the most sensitive wavelength regions.

A smaller percentage of calcium silicide than barium nitrate is required because of molecular weight differences. Calcium has an atomic weight of less than a third that of barium. Thus, on a weight basis calcium should be more efficient.

2.4.3 Mixture "C"

It has been observed that the use of magnesium-aluminum fuel mixtures results in flashes of longer duration. This fuel combination is also easier to ignite as compared with aluminum. Mixture "C" was therefore formulated for purposes of determining the differences in potential effectiveness with flash duration.

2.5 PARTICLE AND SHELL SIZE

The same guidelines of particle size suggested for the reference photoflash mixture (designation "A") are being used for the other mixtures. This control is necessary so as to minimize the number of unknown experimental parameters.

A representative array of shell sizes have been included in the experimental plan. These shells were described in Reference 1. All of the casings are composed of aluminum.

2.6 METHOD OF INITIATION

An additional variable which was included in the experimental plan was the method of initiation. Simple central burster initiation as well as an imploding initiation system are included in the test plan for comparison.

REFERENCES

1. [redacted]

2. D. Rosenthal, Trans. Amer. Soc. Engrs. 68, 849 (1946).

3. R. L. Tischer and K. Scheller, "A Gaseous System of High Luminous Efficiency", (Presented at the Western States Combustion Institute Meeting, 1967), Report WSCI-67-12, Aerospace Research Labs.

4. D. M. Johnson, "Proposed Kinetics and Mechanics of Illuminant Flares: Maximizing Efficiency", U. S. Naval Ammunition Depot, RD-TR-32 (June 1966), AD 627 649.

5. "The Compilation of Flame and Shockwave Information Applicable to Photoflashes", Final Summary Report, Contract DAI-28-017-501-ORD(P)-1096, Arthur D. Little Inc. (September 1955).

6. Engineering Design Handbook, "Military Pyrotechnics Series", AMCP 706-185, U. S. Army Materiel Command (April 1967).