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RESEARCH AND DEVELOPMENT OF CASTABLE ALUMINUM FUELED FLARES

THE DOW CHEMICAL COMPANY

TECHNICAL REPORT AFATL-TR-69-78

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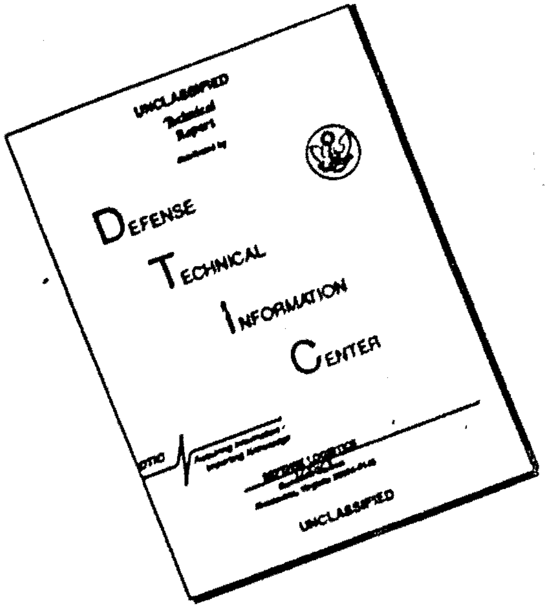

Research and Development of Castable Aluminum Fueled Flares

George A. Lane
Alan C. Kott

[redacted]

FOREWORD

This report covers work performed during the period 29 January 1968 to 29 January 1969 by The Dow Chemical Company, Midland, Michigan, under Contract F08635-68-C-0056, "Research and Development on Castable Aluminum Fueled Flares." The work was sponsored and administered by the Air Force Armament Laboratory, Eglin Air Force Base, Florida, with Mr. Larry Moran and Lt. Farr (ATMP) as program monitors.

Management direction at The Dow Chemical Company was under Dr. E. T. Niles, and technical supervision was under Dr. G. A.Lane. The principal investigator was Mr. Alan C. Kott.

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Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

JOHN E. HICKS, Colonel, USAF
Chief, Non-Explosive Munitions Division

ABSTRACT

Exploratory studies have been conducted on tamp-castable aluminum-fueled illumination flares. Work has been carried out on flare fuels, oxidizers, additives, binders, and flare evaluation. It has been found that small particle size, atomized aluminum yields the highest efficiency. Flares containing aluminum-magnesium alloys and mixtures of aluminum and magnesium were tested but are not superior to the best aluminum fueled flares. Sodium nitrate is the most effective oxidizer. Flame interaction effects were studied using a cavity flare configuration. No performance improvement was obtained. A wide variety of combustion-modifying additives was investigated, but none improves flare performance significantly. A number of flare binders was investigated, and several novel binder materials were prepared. High oxygen content in the binder generally improves the flare performance. The best binder is based on CX-7027 epoxy resin, monoethanolamine nitrate curing agent, and formamide. Maximum castability and density were obtained by tailoring the fuel and oxidizer particle size distribution. The principal barriers to efficient light output appear to be incomplete metal combustion and chimney formation. The optimum metal content for aluminum flares is much lower than that for magnesium flares, resulting in lower energy release. In general, the best aluminum-fueled flares burn very slowly with burn rates in the range of 0.030 to 0.045 in/sec. When evaluated in masking tape-wrapped 1.24-inch diameter candle, the best aluminum flare compositions developed have a luminous efficiency of 35,000 to 40,000 cd.sec./g, less than two-thirds that of an efficient magnesium-fueled flare. The aluminum-fueled flares exhibit intensities of 39,000 to 40,000 cd./in.^{2}, about one-third to one-half that of an efficient magnesium-fueled flare.

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SECTION I

INTRODUCTION

The goal of this study was to develop an aluminum fueled illuminating flare composition which exhibits an efficiency of 50,000 cd. sec./g. and contains sufficient polymeric binder to be poured, tamped, or lightly compacted into flare casings.

The difficulties inherent in the successful development of an aluminum-fueled flare are well known. When compared with magnesium, aluminum exhibits a high heat of vaporization and a high boiling point. Since theoretical aluminum-fueled flame temperatures are only a few hundred degrees above the metal boiling point, the driving force promoting vaporization is relatively low while the resistance, i.e., heat of vaporization, is high. Aluminum melts at a relatively low temperature and tends to agglomerate, thus reducing the surface area available for mass transfer. The problem is compounded by the presence of a relatively large amount of plastic binder which tends to cool and expand the flame.

The difficulties encountered in vaporizing and burning aluminum in pyrotechnics are exemplified by the results of work with solid propellants. Solid propellants function at high pressure, which promotes the aluminum-oxygen reaction. However, the potential of aluminum as a solid propellant ingredient has never been fully realized. Good efficiencies are realized only at metal contents below the theoretical optimum. Significant improvement has been possible only by incorporating exotic and hazardous halogen oxidizers to increase vaporization rates.

Aluminum is theoretically attractive as a flare fuel, however. Theoretical flame temperatures are higher, the heat of combustion is greater, and stoichiometric considerations indicate that efficiently burning aluminum-fueled flares will contain a greater supply of emitters than magnesium-fueled flares. In addition, aluminum is less sensitive and more stable than magnesium; therefore, aluminum particle sizes can be used which would produce unacceptable hazards or instability problems in magnesium flares.

The work on this project was directed toward developing a conventional flare with properties and behavior similar to those of successful magnesium-fueled flares. Approximately 800 experimental flares were fired during the course of the project. All of the test items contained a mixture of solid fuel and oxidizer in a cylindrical geometry. Most contained an excess of fuel over the stoichiometric fuel/oxidizer ratio, so that, as in magnesium flares, the heat from the metal-oxidizer reaction could be used to vaporize additional metal for reaction with atmospheric oxygen. Sodium was used as the emitting species, added as $NaNO_3$.

The efforts under this contract can be divided into two major tasks: (1) to increase the total amount of energy generated in the fuel-oxidizer reaction by improving combustion efficiency or by increasing theoretical heats of combustion, (2) to minimize deleterious effects of the plastic binder by devising polymers with minimal effects on flare efficiency, and by manipulating solid particle size distributions so as to minimize necessary binder levels. The figure of merit used in studying compositions was the efficiency, in cd.sec./g., obtainable from the flares. All formulation efforts were directly or indirectly aimed towards increasing the efficiency of the compositions. Burning rates and candlepowers (intensities) were considered to be dependent variables and were not studied in this exploratory program.

Fuel particle size, oxidizer particle size, additives, transition metal compounds, perchlorate oxidizers, halide oxidizers, magnesium-aluminum alloys, and the cavity geometry were studied in attempts to improve combustion efficiency and light output. In general, these efforts, which are discussed in later sections of this report, were fruitless. None of the unconventional compositions was superior to simple aluminum - sodium nitrate - binder formulations functioned in cylindrical end-burning flares. The only significant improvement in efficiency was achieved by using the smallest particle size aluminum powders available as commercial products.

The best formulations developed are described in Table I. These formulations contain Valimet 818 and Alcoa 123, two of the smallest aluminum powders available in volume. When functioned in an upright position, either as 31-mm or 51-mm diameter end-burning candles wrapped in paper masking tape cases, they exhibit efficiencies of 32,000 - 35,000 cd.sec./g. The formulation in Table IX utilizing binder M shows higher efficiency than the efficiency of the best formulation. The higher efficiency formulation did not have acceptable physical properties; it was extremely spongy.

The compositions shown in Table I exhibit very low burning rates when compared to magnesium flares. In general, this behavior was noted throughout the program. Most of the better compositions burn relatively slow. This behavior is understandable since the primary cause of low efficiencies in aluminum flares is the ejection of unburned metal from the flame. At low burning rates less metal is available on the burning surface to agglomerate and be ejected from the flare. Longer residence times promote vaporization.

TABLE I. PROPERTIES OF MOST EFFICIENT ALUMINUM FLARE COMPOSITIONS

Parameter	I	II	III
Composition, Wt. %			
Aluminum			
Valimet 818	38	38	19
Alcoa 123	--	--	19
Sodium Nitrate			
120-840 micron	--	53	53
-400 mesh	53	--	--
Binder			
CX-7160 epoxy resin	5.94	5.94	5.94
Monoethanolamine nitrate	2.63	2.63	2.63
Formamide	0.43	0.43	0.43
Density*, g./cm^3.	1.65	1.91	1.89
Burning Rate*, in./sec.	0.045	0.040	0.030
Efficiency*, cd.sec./g.	32,000	32,000	35,000
Intensity*, cd./in^2.	39,000	40,000	32,800

*Average of 10 flares, 31-mm diameter.

Although the lower burning rates are associated with the highest efficiencies, and may also be a cause of the higher efficiencies in the best formulations, the low burning rates also result in extremely low intensities. The most efficient aluminum-fueled flares exhibit burning rates of 0.030 to 0.045 inches per second, about half that of efficient magnesium-fueled flares. When coupled with the lower efficiencies of aluminum-fueled flares, the low burning rates result in intensities or candlepowers which are one-third to one-half those of efficient magnesium-fueled flares. The low candlepower values virtually preclude the use of aluminum-fueled flares as substitutes for magnesium-fueled flares in battlefield illumination missions.

Chimney formation is a second cause of low combustion efficiency. When fired under the conditions of this study, flares containing 38% metal and 9% binder form partial oxide chimneys. At higher metal levels, the chimney thickens and tends to form in the original shape of the flare. The chimney increases burning rate and visibly increases the size of ejected metal particles. Free aluminum globules can often be found attached to the inside of the chimney. The optimum metal level in these flares appears to represent the level at which a trend toward higher combustion efficiency, produced by increased fuel levels, is checked by a drop in efficiency caused by the formation of the oxide chimney.

The most efficient flares contain a thermosetting binder composed of CX-7160 epoxy resin, the nitrate salt of monoethanol amine (MEA) curing agent, and formamide to enhance the mutual solubility of the epoxy and curing agent. This binder is the result of a study which confirmed the hypothesis that thermosetting polymers containing large amounts of oxygen in their structure can be useful as flare binders. High oxygen content binders were found to be superior to all other types of binders, including those containing significant amounts of energetic fluorine compounds.

The excellent results obtained with the MEA nitrate binder also serve to underscore another result of the binder program. Although binders with high oxygen content are useful, there is no simple explanation for the effects of any given binder. Compositions containing binders with higher oxygen content than the MEA nitrate binder were at times grossly inferior to those containing the nitrate binder.

The presence of the nitrate salt of monoethanol amine appears to be especially conducive to high light output. When present in binders as a plasticizer and wetting agent, or employed in excess as a curing agent, the salt raises light output. Values as high as 40,000 cd.sec./g. have been realized from this type of composition. This figure is noteworthy since a direct substitution of sodium nitrate for binder in these formulations does not produce as high a value. Unfortunately, the nitrate salt of monoethanol amine is a reactive epoxy curing agent with a relatively low equivalent weight. It was not possible to devise systems containing large amounts of the salt which could resist the reduction in mechanical properties caused by the stoichiometric imbalance between curing agent and epoxy resin.

When mixed, the compositions in Table I form sticky powders which can be poured into flare cases as a loose collection of agglomerates. After compaction at 90 psi, the compositions containing coarse oxidizer exhibit densities which correspond to a packing density* of 0.71. It is thought that further work with surfactants could raise the packing density to 0.83, so that, at the 9% binder level, the composition could be handled as a dough or fluid.

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*Ratio of actual volume of flare solids to bulk volume of candle.

The MEA nitrate salt binder cures extremely rapidly in mass, but relatively slowly when present in a flare composition. Flares must be cured for a period of 20 to 40 hours at 65°C to develop final mechanical properties. The binder cures to a tough, nearly elastomeric gum-stock, which contributes toughness to the flares.

The most efficient aluminum flares, as well as most of the flares studied in this program, are relatively insensitive to impact. As illustrated in Table II, the most efficient Al compositions, compositions containing magnesium-aluminum alloys, and formulations containing a sensitive fluororganic are sufficiently insensitive to impact to be considered safe.

TABLE II. IMPACT SENSITIVITY OF UNCURED
ALUMINUM FLARE COMPOSITIONS

Parameter	I	II	III	IV
Composition, Wt. %				
Valimet 818 Aluminum	38		38	38
Reade 30/70 Mg-Al (200 mesh)		44		
Sodium Nitrate				
120-840 micron			53	53
-400 Mesh	53	47		
Binder	9[1]	9[1]	9[2]	7[2]
TVOPA				2
Kg	2	2	2	2
cm	>128[4]	>128[4]	122	118
E_{50}[3] Kg-cm	--	--	244	236
E_{25}[3] Kg-cm	>256	>256	--	--

[1] D.E.R.®* 732 epoxy resin 1.39%, glycidol 2.98%, maleic anhydride 4.63%.

[2] CX-7160 epoxy resin 5.94%, monoethanolamine nitrate 2.63%, formamide 0.43%.

[3] Bureau of Mines impact tester.

[4] Machine limit.

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*A trademark of The Dow Chemical Company for epoxy resins.

SECTION II

EXPERIMENTAL RESULTS

Work has been carried out in the areas of fuels, oxidizers, binders, and flare evaluation.

A principal task has been to achieve rapid ignition and efficient combustion of the aluminum fuel. The effect of fuel particle size and shape on flare efficiency has been studied. Flame interaction effects have been investigated by the use of cavity flares. A wide variety of combustion-modifying additives has been tested. Mixed Al and Mg fuels and Al-Mg alloys have been studied as fuels.

Sodium nitrate oxidizer was used primarily in this research. However, certain other oxidizers were also tested.

Experiments were conducted on binder level and composition. Novel binders were prepared and investigated.

A PARTICLE SIZING OF SOLIDS

1 Fuel Particle Size

In pyrotechnics, small fuel particles are associated with higher burning rates and greater combustion efficiency. Large particles are less hazardous and more easily handled. The fuel particle size specified for a flare or propellant is usually as small as can be tolerated without unduly increasing hazard, processing difficulties, and cost. At the binder levels used in this study, aluminum-fueled flares are relatively insensitive. Therefore, the aluminum powders used in this project were the smallest sized powders commercially available in volume.

Most of the flares contained either Alcoa 123, the smallest sized powder available as a standardized commercial product, or Valimet 818, a specialty product with a more favorable particle size range and shape.

Alcoa 123 has a particle size range of 5 to 60 microns. Because the material is atomized in air, it contains a larger amount of oxide than powders atomized in inert gas, and it possesses an irregular particle shape.

Valimet 818 has a particle size range of 3 to 30 microns. Since it is atomized in an inert gas, it is nearly spherical, and has a minimum of oxide. It is one of the smallest sized aluminum powders available in volume.

Other materials were examined briefly during the program. Valimet 817 and Valimet 816 contain larger particle sizes than Valimet 818. The particle shape, oxide content, and availability of the three products are very similar. Alcoa 140 is a by-product of the manufacturing process used to produce Alcoa 123. It has a smaller particle size range and more limited availability. Reynolds 3X-D is an aluminum flake, available in volume. It is produced by ball milling an atomized powder and is characterized by a high specific surface area, irregular shape, and an extremely small thickness.

The particle shape and oxide content of aluminum powders, except for the milled flask, have little effect on efficiency. The air atomized products burn almost as well as the inert gas atomized powder. Milled flake appears to burn as well as the atomized powders, but exhibits unfavorable bulk density, making it impractical to incorporate into useable flares.

The efficiency of aluminum-fueled flares, as expected, is affected by the particle size of the fuel. The smaller particle sizes improve efficiency. However, as shown in Figure 1, the effect is not pronounced, and the efficiency of flares containing the smallest sized fuel is considerably less than the target value of 50,000 cd.sec./g.

Mixtures of aluminum fuels tend to produce efficiencies which are intermediate between those exhibited by flares containing the individual components. Mixtures of Valimet 818 and Alcoa 123 are an exception. Flares containing mixtures of the two powders produce higher efficiencies than flares containing either powder as sole fuel. The effect is small and not understood.

One of the most prominent manifestations of poor combustion efficiency in aluminum-fueled flares is the ejection of glowing metal particles from the burning flare. The presence of smaller particles in the fuel tends to reduce the number and size of ejected particles, but, for all flares, the ejected agglomerates are considerably larger than the particles in the original fuel.

Molten aluminum particles have been observed to coalesce on and above the surface of a burning propellant. This same phenomenon is thought to occur in a burning flare. The smaller particle size fuels were expected to minimize losses due to agglomeration by reducing the size of the coalescing droplets and by maximizing the rate and extent of vaporization before coalescence. However, as Figure 1 demonstrates, the improvement is not sufficient.

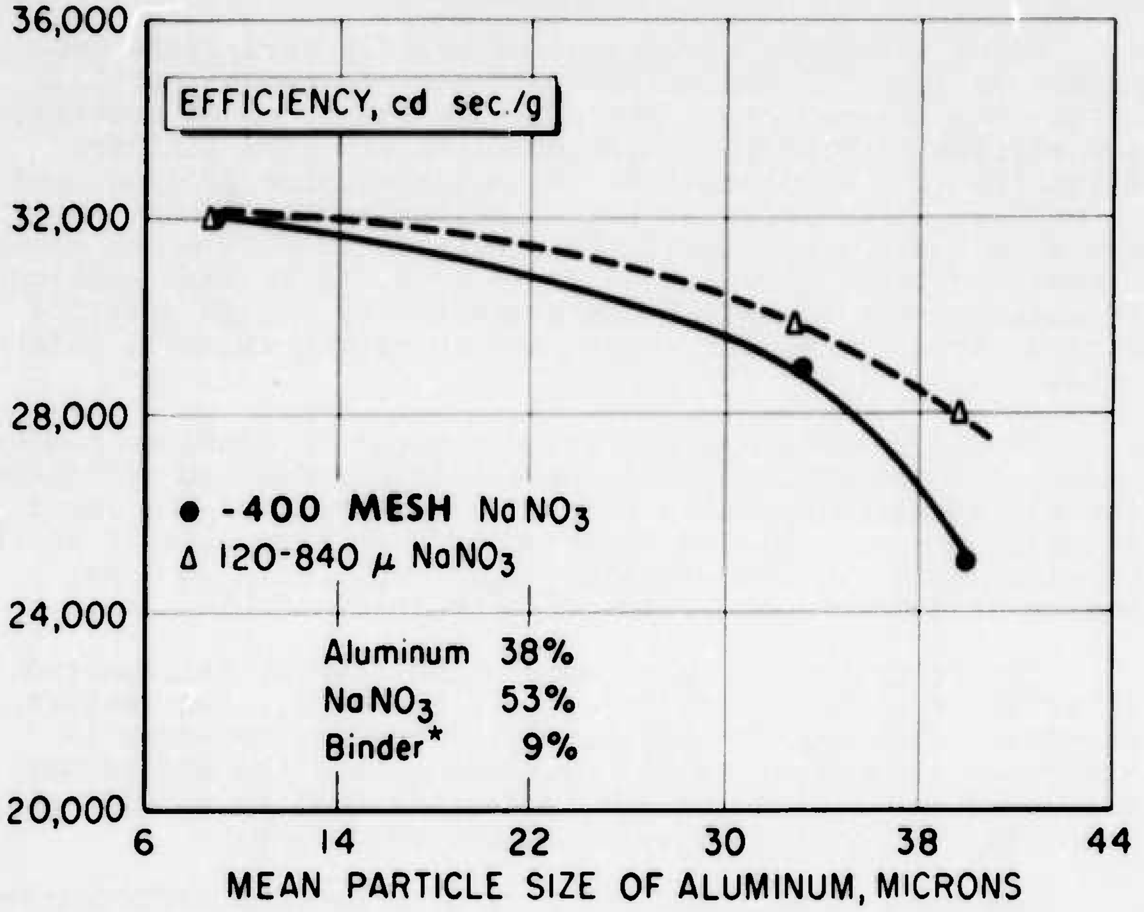

Figure 1. Effect of Aluminum Particle Size on Flare Performance

Microscopic examination of cured flares indicates that the fuel is present in the form of agglomerates. In some cases, the bulk volume of the agglomerates is so great that they merge and form a continuous phase in portions of the flare. When specimens are heated on a microscope stage, the sodium nitrate has been observed to melt and decompose without igniting or disrupting the aluminum agglomerates. Although these observations cannot be rigorously applied to a burning flare, they help to demonstrate that the agglomeration process, operating during fabrication and in the burning flare, cannot be circumvented by a simple reduction in particle size

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*Binder L, Table VIII, 66.0% CX-7160, 29.2% monoethanolamine nitrate, and 4.8% formamide.

More complete dispersion during the mixing process, and the presence of an agent which lowers ignition temperatures might be expected to improve combustion efficiency. Surfactants, surface coatings, novel particle size distributions, and intensive mixing in solvents, therefore, were employed in attempts to improve dispersion. Sodium fluoride and chromium sesquioxide were employed in attempts to initiate combustion reactions before particle agglomeration. None of these efforts was successful in preventing agglomeration or in improving light output.

2 Oxidizer Particle Size

A variety of oxidizer particle sizes was incorporated into flares. The sodium nitrate used in these studies covered a total particle size range of 15 to 840 microns. Each of the oxidizer particle sizes was used alone or in combination with the others. Special size distributions, made by combining sieve fractions of commercial materials, were also employed.

Both the nominal particle size and the particle size range of the sodium nitrate oxidizer can effect the efficiency of an aluminum-fueled flare. If the oxidizer possesses a relatively average particle size, or contains a wide range of particle sizes, the flares exhibit relatively high efficiency. If the average particle size is relatively high and the particle size range low, efficiency is drastically reduced.

The effects of particle size on flare efficiency are presented in Table III. Flares containing sodium nitrate oxidizer with a narrow range of oxidizer particle size, (lines 1, 2, 3, and 5 in Table III) display sharply decreasing efficiencies as the average particle size of the oxidizer increases. However, flares containing a large sized oxidizer with a wide range of particle size, (line 4 in Table III) are equivalent to flares containing the smallest of the narrow size range sodium nitrate oxidizers. The comparison is particularly striking, since the narrow size range sodium nitrates with particle sizes greater than 120 microns were produced by passing an aliquot of the wide range oxidizer through sieves. With the exception of particle size, the chemical and physical characteristics of the oxidizers, therefore, are as similar as possible.

Although the data presented in Table III indicates that oxidizer particle size characteristics can have an effect on flare behavior, these characteristics are not considered to be among the most important parameters. These and other experiments using different oxidizer size distributions were conducted. Essentially no change in efficiency or light intensity could be detected for the following distributions: (1) -400 mesh $NaNO_3$, (2) -400 mesh $NaNO_3$ specially reground, (3) $NaNO_3$ with a log normal distribution from 44 microns to 250 microns, (4) $NaNO_3$ with a log normal distribution from 120 microns to 840 microns, and a variety of mixtures of these grinds. The size distributions which cause degradation in efficiency and light intensity are not commonly employed in pyrotechnics and are artificial in that they are difficult to produce by normal solids handling techniques.

TABLE III. - EFFECTS OF PARTICLE SIZE ON EFFICIENCY

Line	$NaNO_3$ Particle Size		Burning Rate (in./sec.)	Efficiency* (cd.sec./g.)	Intensity* (cd./in^2)
	Average (microns)	Range (microns)			
1		<37	0.045	32,000	39,000
2	135	120-150	0.036	27,600	29,400
3	323	297-350	0.033	22,000	21,200
4	480	120-840	0.040	32,000	40,000
5	545	500-590	0.035	19,300	19,800

*Formulation is 38% Valimet 818 Aluminum, 53% $NaNO_3$, 9% Binder L (66.0% CX-7160, 29.2% monoethanolamine nitrate, 4.8% formamide).

Since the sodium nitrate can melt and decompose before the aluminum fuel melts or ignites, the lack of pronounced correlation between oxidizer particle size and flare light output is understandable. The agglomeration mechanisms which control efficiency probably operate primarily in or above a region of the flare in which the sodium nitrate is liquid. Under these circumstances, oxidizer particle size would only be expected to influence light output through its effect on burning rate. The smallest oxidizer particle size produces the highest linear burning rate. The wider distributions give higher burning rates than any of the narrow range oxidizer particle size distributions.

B OXIDIZERS AND ADDITIVES

Sodium nitrate is a superior oxidizer in illuminating flares. When compared with other suitable sodium salts, sodium nitrate possesses one of the highest heats of reaction per unit weight and contains a high percentage of sodium. The nitrate also delivers sodium to the illuminating flame as the easily sublimed and easily dissociated oxide. In magnesium-fueled compositions these properties contribute to the high efficiency of present operational flares.

The high efficiency of magnesium-sodium nitrate compositions can also be attributed to the relatively low boiling point and low heat of vaporization of magnesium, which allow most of the metal to vaporize and burn in useful portions of the flare flame. Aluminum possesses a higher boiling point and higher heat of vaporization, which restrict vaporization and limit combustion efficiency. In an effort to raise the combustion efficiency of aluminum flares, a variety of oxidizers were used in conjunction with sodium nitrate. The oxidizers were chosen to increase combustion efficiency and compensate for the partial removal of sodium nitrate.

Oxygen-containing compounds, sulfur, and halides were employed as sources of oxidizing species in this study. The oxygen-containing oxidizers were used in an attempt to raise light output by increasing the theoretical heat of reaction of the fuel-oxidizer combination, or to raise combustion efficiency by promoting the vaporization of aluminum metal. Sulfur and the halides were employed in attempts to produce volatile aluminum compounds capable of further reaction after vaporizing.

1 Oxygen Oxidizers

Two types of oxygen oxidizer were considered as partial replacements for sodium nitrate in aluminum flares. Perchlorates were investigated to raise the theoretical heat of combustion of the flare mixture, and transition metal compounds were examined in an attempt to by-pass vapor phase combustion inefficiency by oxidizing aluminum in the liquid phase. Both these types of oxidizer should minimize the ejection of unburned aluminum by reducing the amount of gas generated by decomposing oxidizer.

a Perchlorates

When compared with sodium nitrate, sodium perchlorate and potassium perchlorate exhibit higher heats of reaction with aluminum. Neither of the perchlorates generate nitrogen when decomposed. Therefore, both were used in place of sodium nitrate in attempts to raise light output. It was hoped that a reduction in the amount of non-oxidizing gas generated by the perchlorates would lower the rate at which molten aluminum was ejected from the burning flare and thus raise combustion efficiency. The increase in theoretical heat of combustion should raise light output.

Sodium perchlorate was used as the sole oxidizer, and in combination with sodium nitrate. Potassium perchlorate was used only in combination with sodium nitrate, since no other source of sodium emitter was thought practical.

The results of tests with perchlorate oxidizers are illustrated in Table IV. Although sodium perchlorate is reported[1] to be effective as an oxidizer in magnesium flares, it is not effective in aluminum flares. Flares containing the perchlorate produce massive oxide chimneys, show a pronounced increase in burning rate, eject considerable quantities of unburned aluminum, and display low efficiencies.

Potassium perchlorate does not produce the same drastic changes in flare combustion behavior. When used in mixtures with sodium nitrate, the primary effect of the additive appears to be a reduction in light output, caused by the dilution of useful sodium emitters. Optimized aluminum - sodium nitrate - potassium perchlorate compositions are actually superior to aluminum - sodium nitrate compositions containing the same weight ratio of fuel to oxidizer. However, aluminum- sodium nitrate compositions contain enough sodium to allow higher fuel levels, and these aluminum - sodium nitrate compositions produce higher efficiencies than the best formulations containing potassium perchlorate.

Ammonium nitrate dilutes the supply of useful sodium emitters, as do both sodium perchlorate and potassium perchlorate. However, the ammonium salt has less deleterious effect on efficiencies than the alkali perchlorates. One possible explanation for this behavior may lie in the effects of the three oxidizers on burning rates. Ammonium nitrate lowers the burning rates of flares when substituted for sodium nitrate. It was generally observed throughout the program that the slower burning flares tend to produce the highest efficiencies. The reduction in burning rate associated with the presence of ammonium nitrate may have compensated for the dilution of emitters.

The perchlorates previously discussed and transition metal compounds discussed below were studied in attempts to test the effect of gas generation on the quantity of ejected metal. Since ammonium nitrate increases the amount of gas generated but does not lower efficiency, this approach was dropped.

With the exception of the experiments with ammonium nitrate, the ammonium oxyanion oxidizers were not used in this program.

---

[1] Waite, H.R., and Arikawa, Y., Study of Visual Cast Flare Binder Material, Ordnance Research, Inc., Fort Walton Beach, Fla., RDTR 113, Naval Ammunition Depot, Crane, Indiana, January 1968, (AD 669434).

TABLE IV. LIGHT OUTPUT OF FLARES CONTAINING HIGH ENERGY OXIDIZERS

Composition, Wt. %							
Valimet 818 Aluminum	Sodium Nitrate	Binder	High Energy Oxygen Oxidizer^{7}	Density^{8} (g./cm^{3}.)	Burning Rate (in./sec.)	Intensity^{8} (cd./in^{2}.)	Efficiency^{8} (cd.sec./g.)
31.6	59.4^{6}	9^{3}	0.0 --	1.87	0.045	20,300	14,700^{1}
31.6	51.9^{6}	9^{3}	7.5 $KClO_4$	1.93	0.048	28,400	18,700^{1}
31.6	44.4^{6}	9^{3}	15.0 $KClO_4$	1.96	0.048	28,000	18,200^{1}
31.6	37.9^{6}	9^{3}	21.5 $KClO_4$	1.96	0.048	24,200	15,600^{1}
31.6	29.4^{6}	9^{3}	30.0 $KClO_4$	2.03	0.042	18,400	13,100^{1}
40.0	51.0^{6}	9^{4}	0.0 --	1.91	0.045	34,800	24,600^{2}
40.0	44.5^{6}	9^{4}	6.5 $KClO_4$	1.91	0.042	24,200	18,400^{2}
40.0	41.0^{6}	9^{4}	10.0 $KClO_4$	1.90	0.043	21,400	15,600^{2}
38.0	53.0^{6}	9^{4}	0.0 --	1.91	0.037	30,200	26,000^{2}
38.0	43.0^{6}	9^{4}	10.0 $NaClC_4$	1.94	0.055	47,500	12,700^{2}
40.0	0.0	9^{4}	51.0 $NaClO_4$	2.11	0.054	19,400	10,400^{2}
36.2	0.0	9^{4}	54.8 $NaClO_4$	2.17	0.049	14,000	8,000^{2}
38.0	53.0^{9}	9^{5}	0.0 --	1.91	0.040	40,000	32,000^{2}
38.0	45.3^{9}	9^{5}	7.7 NH_4NO_3	1.89	0.034	32,600	31,000^{2}

[1] Kraft cardboard case.

[2] Paper tape case.

[3] Binder J, 60% CX-7160, 40% maleic anhydride.

[4] Binder H, 33.1% glycidol, 49.6% maleic anhydride, 17.3% CX-7160.

[5] Binder L, 66.0% CX-7160, 29.2% monoethanolamine nitrate, 4.8% formamide.

[6] -400 Mesh.

[7] -100 Mesh.

[8] Three or more 31-mm diameter candles.

[9] 120-840 micron.

b Transition Metal Compounds

Although the aluminum-oxygen combustion reaction is primarily a gas phase reaction, the oxygen contained in chromium sesquioxide can support vigorous solid and liquid phase aluminum combustion[2]. Also, chromium sesquioxide and other transition metal oxides have been reported[3] to increase the efficiencies of milligram sized aluminum-fueled flare pellets. Because of these reports, chromium sesquioxide and other transition metal compounds were incorporated into flares in an attempt to raise light output. It was thought that the transition metal compounds would reduce the waste of fuel and energy associated with the ejection of unburned metal by reacting with liquid phase aluminum on the burning surface.

Chromium sesquioxide was used in most of this work. Other transition metal compounds such as chromium hydroxide, sodium dichromate, manganese dioxide, manganous sulfate, manganous carbonate, cupric oxide, and cupric sulfate were compared with chromium sesquioxide in a limited number of experiments.

Most of the transition metal compounds were studied early in the program, using flares containing relatively coarse aluminum and relatively large amounts of binders with moderate oxygen content. These flares burn poorly. They form massive oxide chimneys, eject copious amounts of unburned fuel and produce little light. Chromium sesquioxide appears to improve the efficiency of these flares by lowering the amount of ejected fuel and reducing the tendency to form chimneys. However, binders with higher oxygen content and smaller fuel particle size also produce more efficient flares. As illustrated in Figure 2, the performance of flares utilizing binders with higher oxygen content and smaller fuel particle size is degraded by the presence of chromium sesquioxide.

Sodium fluoride was used in flares containing chromium sesquioxide in the hope that a greater degree of fluidity in the molten zone of the burning flare would enhance the liquid phase reaction with chromium sesquioxide. However, sodium fluoride does not improve light output, as discussed later.

Other transition metal compounds were compared with chromium sesquioxide, and most were found to produce the same

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[2] Shidlovskiy, A. A., Foundations of Pyrotechnics, (AD 602687)

[3] Personal Communication: Leader, P., and Westerdahl, R., Pyrotechnics Laboratory, Picatinny Arsenal, Dover, New Jersey

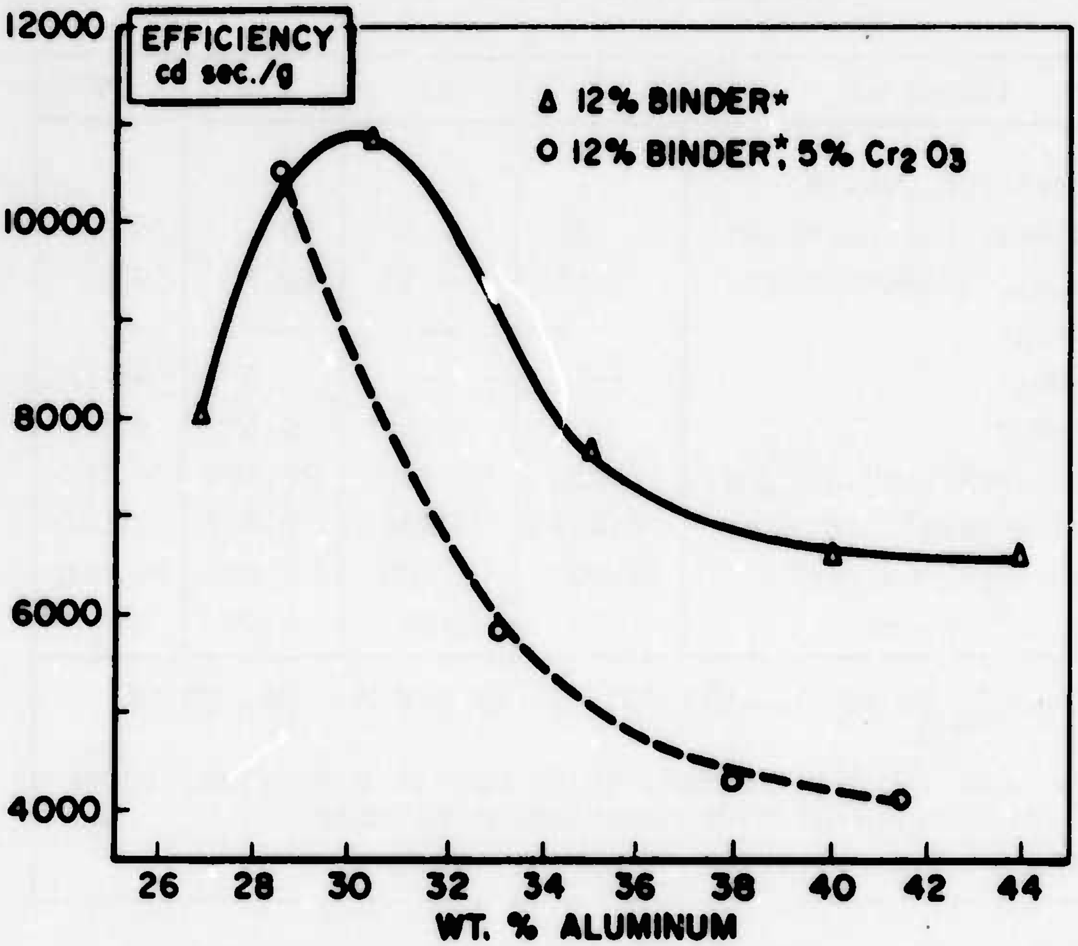

Figure 2. Effects of Chromium Sesquioxide on Light Output

deleterious effects. Two compounds, manganous sulfate and manganous carbonate, produce the most favorable results. As indicated in Table V, the sulfate only slightly decreases efficiency, and the carbonate slightly increases efficiency. However, the carbonate is incompatible with ingredients in the most efficient binders. The reduction in efficiency associated with the change to lower oxygen content binders, compatible with manganous carbonate, overwhelms the favorable effect of the additive.

The transition metal compounds appear to act as low energy oxidizers. The favorable effects of assumed liquid phase oxidation reactions apparently are offset by the reduction in combustion energy delivered to the emitter. The use of more energetic

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*Binder A. Table VIII, -400 mesh $NaNO_3$.

TABLE V. EFFECTS OF MANGANOUS SALTS ON ALUMINUM FLARES

Parameter	I	II	III	IV
Composition, Wt. %				
Valimet 818 Aluminum	38	38	38	38
$NaNO_3$, 120-840 micron	51	53	49.7	52.7
$MnCO_3$	2	--	--	--
$MnSO_4$	--	--	3	--
Binder	9[1]	9[1]	9.3[2]	9.3[2]
Efficiency[3], cd.sec./g.	17,000	15,500	27,400	32,000
Burning rate[3], in./sec.	0.033	0.032	0.037	0.040
Intensity[3], cd./in^2.	17,800	15,700	32,200	40,600
Density[3], g./cm^3.	1.94	1.94	1.94	1.94

[1] Binder B, 50.0% D.E.R.®* 331, 21.4% D.E.R. 732, 28.6% D.E.H.®**31.

[2] Binder K, 29.8% glycidol, 44.6% maleic anhydride, 15.6% D.E.R. 732, 10.0% monoethanolamine nitrate.

[3] Average of three 31-mm diameter candles.

transition metal compounds such as manganic heptoxide or chromic oxide was considered. However, these oxidizers are hypergolic with the binders used in the more efficient flares.

2 Sulfur and Halogen Oxidizers

The aluminum-oxygen combustion reaction is primarily a vapor phase reaction. Most attempts to increase the light output of aluminum fueled flares have been directed toward increasing the amount of vaporized aluminum, available for combustion, in the flame zone. These efforts have been handicapped by the low volatility and high boiling point of the metal.

The sulfide and halides of aluminum vaporize at considerably lower temperatures than the free metal. If present in a burning flare, they could be expected to vaporize completely and react, as a vapor, with sodium and oxygen in the flame.

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*A trademark of The Dow Chemical Company for epoxy resins.

**A trademark of The Dow Chemical Company for amine curing agents.

Aluminum sulfide or halides cannot be incorporated into a flare candle because of sensitivity to moisture and decreased available heat of reaction. However, if these compounds could be formed in the burning flare by using sulfur or halides as oxidizing agents, the components would be stable during storage, and the loss in heat of reaction would be small.

a Sulfur

Sulfur was added to flare compositions in the hope that a reaction sequence, as illustrated in Equations (1), (2), and (3), would increase the net amount of aluminum available for combustion in the flame.

$$2\ Al_{(s)} + 3\ S_{(l)} \longrightarrow Al_2S_{3(s)} \qquad (1)$$

$$Al_2S_{3(s)} \longrightarrow Al_2S_3(g) \qquad (2)$$

$$Al_2S_{3(g)} \longrightarrow 2\ Al_{(g)} + 3\ S_{(g)} \qquad (3)$$

Liquid sulfur is reported[4] to react with solid aluminum to produce aluminum sulfide. The sulfide is easily sublimed and boils at 1,500°C, far below the boiling point of elemental aluminum. Therefore, it should be more readily vaporized than the metal.

Aluminum sulfide is unstable at the high temperature of a flare flame. When passed into the flame, the sulfide should dissociate into sulfur and aluminum vapor. The presence of sulfur in an aluminum-fueled flare could result, therefore, in an increase in the amount of aluminum available for combustion and raise efficiencies.

The presence of sulfur is reported[5] to increase efficiency and reduce the amount of ejected, unburnt aluminum from flares containing coarse aluminum flake and relatively low (3%) amounts of binder. In the present program, it was found that a small amount of sulfur (<10%) in flare compositions containing small sized atomized aluminum and relatively high amounts of binder reduces the amount of unburned metal ejected from the burning flare. However, as indicated in Table VI, the additive tends to lower efficiencies.

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[4] Ellern, H., Modern Pyrotechnics, Chemical Publishing Co., Inc., 1961.

[5] Ibid., Shidlovskiy, A. A.

TABLE VI. EFFECTS OF NON-OXYGEN OXIDIZERS IN ALUMINUM FLARES

Composition, Wt. %				Burning Rate (in./sec.)	Intensity[1] (cd./in^2.)	Efficiency[1] (cd.sec./g.)	Density (g./cm^3)
Aluminum	$NaNO_3$	Binder	Oxidizer				
Alcoa 140							
28.8	54.2[8]	12[2]	5.0 Sulfur	0.054[6]	6,300	3.700	1.93
31.6	56.4[8]	12[2]	0.0 --	0.049[6]	17,500	11.000	1.98
31.8	54.2[8]	9[2]	5.0 Sulfur	0.083[6]	30,600	13,600	1.65
32.9	58.1[8]	9[2]	0.0 --	0.050[6]	20.600	14,500	1.73
Valimet 818							
30.7	55.3[8]	9[3]	5.0 MgF_2	0.035[7]	16.400	15.800	1.81
28.0	53.0[8]	9[3]	10.0 MgF_2	0.061[7]	34,200	18.800	1.82
32.0	49.0[8]	9[3]	10.0 MgF_2	0.075[7]	39,400	17,200	1.84
32.0	59.0[8]	9[3]	0.0 --	0.031[7]	17.900	19,400	1.81
38.0	53.0[8]	9[3]	0.0 --	0.046[7]	36.400	26,000	1.86
38.0	53.0[8]	8.7[5]	0.3 FX-161	0.029[7]	33,600	35.000	2.02
38.0	53.0[8]	8.0[5]	1.0 FX-161	0.042[7]	38.400	27.000	2.05
38.0	53.0[8]	9.0[5]	0.0 --	0.034[7]	34.600	32.000	1.95
38.0	53.0[8]	3.0[5]	6.0 Teflon	0.048[7]	37.800	26.000	1.85
38.2	38.0[8]	9.3[5]	14.1 Teflon	0.065[7]	27.400	14.300	1.72
38.0	48.0[8]	9	5.0 Rare Earth Fluoride	0.041[7]	27.400	21.400	1.90
29.9	56.1[8]	9[2]	5.0 HC208-4	0.029[7]	27.200	9.800	1.99
29.9	56.1[8]	9[2]	5.0 NH_4F	0.047[7]	13.200	10.300	1.74
33.0	58.0[8]	9[2]	0.0 --	0.027[7]	15.000	19.500	1.73
38.0	53.0[9]	9[4]	0.0 --	--	39.400[6]	23.000	--
38.0	53.0[9]	7[4]	2.0 TVOPA	--	35.600[6]	20.700	--

[1] Two or more 31-mm diameter candles.

[2] Binder A, 80% CX-2679, 20% maleic anhydride.

[3] Binder H, 33.1% glycidol, 49.6% maleic anhydride, 17.3% Epon 812.

[4] Binder L, 66.0% CX-7160, 29.2% monoethanolamine nitrate, 4.8% formamide.

[5] Binder K, 29.8% glycidol, 44.6% maleic anhydride, 15.6% D.E.R. 732, 10.0% monoethanolamine nitrate.

[6] Kraft cardboard case.

[7] Paper tape case.

[8] -400 Mesh $NaNO_3$

[9] 120m - 840m $NANO_3$

The slag produced by the sulfur-containing flares reacts vigorously with water to produce H_2S. It is not known whether this gas is produced from Al_2S_3 or sodium sulfides. The presence of sulfur in the slag, however, indicates that the sulfur or sulfides do not wholly vaporize, and therefore do not sufficiently aid in the production of gaseous aluminum.

Cavity flares do not generate as much slag as end-burning flares. Sulfur was employed as an additive in one of the cavity experiments (discussed in Section D). It was hoped that the sulfides trapped by slag in end-burning flares would volatilize in cavity flares. However, the cavity flares showed no improvement in light output.

b Halogens

Magnesium or aluminum halides will react with sodium oxide. The resultant sodium halides are a less efficient source of emitter than the original sodium oxide. In magnesium flares, the presence of halides decreases light output[6].

Aluminum flares contain a larger proportion of oxidizer and hence more sodium than magnesium flares. Loss of sodium should not be as serious in aluminum flares. Therefore, halide oxidizers were incorporated into aluminum flares in the hope that an increase in the amount of vaporized aluminum would more than compensate for the reduction in sodium content.

Fluorinated organic compounds improve the combustion efficiency of aluminum propellants. When compared with reactions with the other halogens, the aluminum - fluorine reaction produces the most energy and, theoretically, could result in vaporization of the most aluminum per unit weight of additive. Therefore, most of the work with halogens utilized fluorine compounds.

Teflon, TVOPA, FX 161 fluorocarbon surfactant, and HC-208-4 fluorocarbon oil were used as organic sources of fluorine.

Ammonium fluoride, magnesium fluoride, and a mixed rare earth fluoride were also employed as sources of fluorine. The inorganic fluorides were used in an attempt to minimize the total amount of carbon introduced into the flare formulations.

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[6] Blunt, R. M., <u>Evaluation of Processes Occurring in Pyrotechnic Flames</u>, Denver Research Institute, Denver, Colorado, RDTR 91, Naval Ammunition Depot, Crane Indiana, March 1967, (AD 655820).

Although magnesium fluoride will not react with aluminum at ambient temperatures, the reaction[7]:

$$MgF_2(l) + 2\ Al(l) \xrightarrow{t \geq 1700°C.} Mg(g) + 2\ AlF(g)$$

has been reported. Rare earth compounds are reported to enhance the light output of carbon arcs. The rare earth fluorides were tested in the hope that enhanced emission caused by the rare earth would compensate for the eventual formation of poorly emitting sodium fluoride.

The effects of halogen oxidizers were tested, at various times during the program, by substituting fluorocarbon or fluoride for fuel, oxidizer, or binder in the most efficient formulations available at the time of testing. The results of some of the tests are presented in Table VI. None of the flares containing fluorocarbons or fluorides exhibited a pronounced increase in light output. Most of the flares were less efficient than controls.

A small amount of the fluorocarbon surfactant FX 161 produces a small increase in light output when substituted for binder ingredients. The presence of HC-208-4, Teflon, TVOPA, or larger amounts of FX 161 reduces light output when they are substituted for binder ingredients.

The surfactant FX 161 is reported[8] by the manufacturer to form a thin adherent coating on aluminum. Flares containing the additive also exhibit an increase in packing density, which is attributed to improved dispersion of fuel agglomerates. The surfactant thus exhibits unique properties which may have influenced the observed increase in light output.

TVOPA dissolves in, and acts to plasticize the flare binder. The flares used as a control in the TVOPA experiment did not contain a plasticizer. The addition of a plasticizer, such as the nitrate salt of monoethanolamine, with a high oxygen content will increase light output. The comparison, therefore, of the TVOPA plasticized flares and the control in Table VI probably minimizes the deleterious effects of TVOPA.

Nearly all of the flares containing fluorocarbons exhibit higher burning rates than the controls. This behavior is consistent with the presence of sodium fluoride in the molten zone of the burning flare, indicating that molten sodium oxide may have reacted with aluminum fluoride in a molten zone, or may have reacted directly with the fluorocarbon.

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[7] U. S. Patent 3,397,056.

[8] Promotional brochure, "Fluorad Fluorochemical Surfactants," Minnesota Mining and Manufacturing Co., St. Paul, Minnesota.

Sodium fluoride is not an effective source of emitter in magnesium flares. When work with aluminum flares first indicated that fluorocarbons were not helpful, flares containing NaF and potassium perchlorate were made to determine the effectiveness of sodium fluoride as a source of emitting species in aluminum flares. Although these aluminum flares possess theoretically higher flame temperatures than magnesium flares, the sodium fluoride was found to be completely ineffective.

If, as suspected, the presence of fluorocarbon causes sodium fluoride to form in the molten zone of the burning flare, the lack of improvement in light output is understandable. The fluorocarbons remove emitting species through the formation of sodium fluoride, reduce the potential heat of reaction by displacing fuel and oxidizer, and introduce carbon into the flare. They do not compensate for these effects by increasing the amount of vaporized aluminum in the flame.

The possibility of conducting the halogen-aluminum reaction so that liquid sodium oxide could not contact the halocarbon or liquid aluminum halides was briefly investigated. Heterogeneous flares containing (1) a cylindrical core of aluminum-halogen oxidizer and (2) an outer skin of conventional aluminum-sodium nitrate-binder composition were fabricated. It was thought that the core would generate volatile aluminum halides which would further react in the vapor phase with sodium and oxygen produced by the composition in the skin. The heterogeneous flares were compared with homogeneous control flares of the same dimensions and containing the same average amounts of ingredients. As illustrated in Table VII, the heterogeneous flares are inferior to the homogeneous flares.

Binders containing bromine or chlorine were examined in a study of the effects of various binder heteroatoms on efficiency. The presence of either of these halogens lowers light output.

3 Miscellaneous Additives

Sodium fluoride, cryolite, boron, and sodium metaborate were incorporated into flares in attempts to improve combustion efficiency or to increase the amount of emitter in the flame.

Aluminum-fueled flares containing the relatively high (9-18%) amounts of binder used in this program exhibit a

TABLE VII. EFFICIENCY OF HETEROGENEOUS FLARES

Compositions, Wt. %										
Valimet 818 Aluminum	$NaNO_3$[6]	$NaClO_4$	Teflon	Hexachloro-benzene	Binder	Efficiency (cd.sec./g.)	Intensity (cd./in^2.)	Burning Rate (in./sec.)	Density (g./cm^3.)	Remarks
45.3	--	--	45.4	--	9.3[1]	--	--	--	--	Core[3]
36.1	54.6	--	--	--	9.3[1]	--	--	--	--	Skin[4]
40.2	30.9	--	19.6	--	9.3[1]	8,800	9,750	0.040	1.69	Net[5]
38.2	38.0	--	14.5	--	9.3[1]	14,300	26,200	0.065	1.72	Homogeneous[5] halocarbon control
38.0	52.7	--	--	--	9.3[1]	32,000	34,000	0.034	1.91	Non-halocarbon control[5]
26.7	--	17.3	--	37.0	9.0[2]	--	--	--	--	Core[3]
31.0	60.0	--	--	--	9.0[2]	--	--	--	--	Skin[4]
29.2	35.0	7.2	--	19.6	9.0[2]	6,100	5,650	0.029	1.94	Net[5]
29.2	35.0	7.2	--	19.6	9.0[2]	7,100	8,250	0.035	2.02	Homogeneous[5] control

[1] Binder K, 29.8% glycidol, 44.6% maleic anhydride, 15.6% D.E.R. 732, 10.0% monoethanolamine nitrate.

[2] Binder A, 50.0% D.E.R. 331, 21.4% D.E.R. 732, 28.6% D.E.N. 31.

[3] Cylinder, 31-mm O.D.

[4] Toroid, 31-mm I.D., 51 mm O.D.

[5] Cylinder, 51-mm O.D.

[6] -400 Mesh.

pronounced tendency to form massive, restrictive oxide chimneys when functioned. If not a prime cause of poor efficiency, the chimneys are at least a contributary cause and are invariably associated with low efficiencies.

Sodium fluoride, and the mineral cryolite are used as fluxes to lower the melting point of aluminum oxides. They were incorporated into aluminum flares in an attempt to reduce the thickness and strength of oxide chimneys, and possibly prevent their formation. Sodium fluoride was also used in conjunction with novel oxidizers to determine if a presumed fluxing action would accelerate desirable solid and liquid phase combustion reactions. Aluminum fluoride is reported[9] to lower the ignition temperature of metal-oxidizer combinations. Cryolite, $3\ NaF \cdot AlF_3$, was used as a source of aluminum fluoride to test this effect.

Sodium fluoride or cryolite, as sole additives, do not reduce chimney formation. Cryolite increases burning rate and drastically reduces light output. Sodium fluoride increases burning rate, reduces the variation in light output between nominally identical flares, and increases sensitivity to ignition by direct flame. For these reasons, sodium fluoride was used in the initial series of cavity experiments to minimize procedural difficulties. However, as illustrated in Figure 3, sodium fluoride acts to decrease light output, and also shifts optimum fuel/oxidizer ratios toward the metal-rich stoichiometry.

When used together, sodium fluoride and chromium sesquioxide reduce the tendency to form chimneys. The slag produced by the burning flares falls off as a loose powder at low metal levels, and as cylindrical chunks at high metal levels. However, the absence of a chimney does not result in an increase in light output.

The additives displace the more energetic reactants, aluminum and sodium nitrate, and abstract heats of vaporization from the energy available for the production of light. This apparently nullifies the improvement in combustion efficiency which is visibly manifested by the reduction in chimney formation and in the reduced ejection of unburned metal.

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[9] Freeman, E., and Anderson, D., "The Effects of Aluminum Fluoride on the Combustion of Aluminum in the Presence of Potassium Perchlorate and Oxygen," Combustion and Flame, Vol. 10, No. 4, December 1966, Butterworths Publications., Ltd., London.

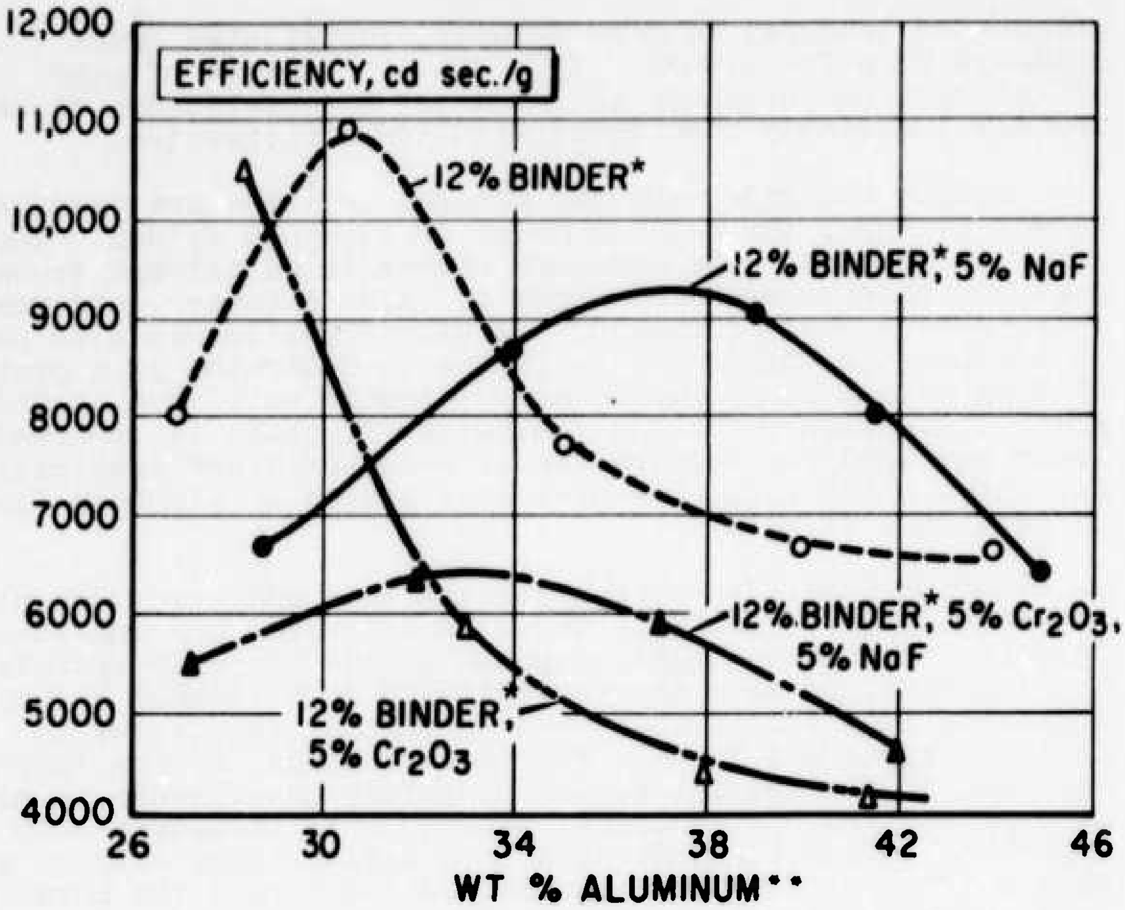

Figure 3. Effect of Aluminum and Additive Levels of Flare*** Performance

The compound BO_2 is reported[10] to act as an efficient emitter in gaseous flares. Elemental boron or sodium metaborate were incorporated into flares in attempts to produce an incremental increase in efficiency as secondary emitters, or to perform well enough to act as primary emitters in systems containing perchlorate oxidizers. However, boron and borates have a pronounced detrimental effect on light output. As little as 1% boron in an aluminum flare can reduce light output by 35%.

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*Binder A, Table VIII

** Alcoa 140 aluminum

*** -400 mesh $NaNO_3$ used in all flares

[10] Tischer, R. L., and Scheller, K., "Measurement of Illumination-Source-Related Characteristics of the Cyanogen-Oxygen-Boron Trichloride Flame System," Proceedings of First Pyrotechnics Seminar, Blunt, R. M., Denver Research Institute, Denver, Colorado, RDTR 131, Naval Ammunition Depot, Crane, Indiana, October 1968.

C MAGNESIUM-ALUMINUM ALLOYS

When injected into a powder torch, aluminum powder melts and burns slowly without fragmenting[11]. In flares, this behavior appears to cause the loss of a portion of the aluminum fuel, which forms agglomerates capable of passing through the flame zone without vaporizing and burning. Magnesium powder fragments and burns quickly in a powder torch[11]. In flares, this behavior is reflected in higher efficiencies, fragmentation of ejected particles, and, in some cases, a total absence of ejected particles.

Magnesium-aluminum alloy powders containing as little as 28% magnesium reportedly[11] fragment when burned in a powder torch. Therefore, several magnesium-aluminum alloy powders were used as flare fuels in the hope that alloy agglomerates would fragment and produce finely divided droplets capable of burning rapidly and completely in the flare frame.

The three alloys tested in this program contained 50% magnesium or less. A 30/70 magnesium-aluminum alloy was studied as a ground 200 mesh powder, a ground 325 mesh powder and as coarse atomized granules with a particle size range of 37 to 840 microns. When these materials were found to produce mediocre light output, a coarse atomized 40/60 magnesium-aluminum alloy with a particle size range of 37 to 840 microns, and a 50/50 alloy, ground to pass 325 mesh, were studied. Mixtures of magnesium and aluminum and mixtures of these metals with the alloys were also investigated.

The alloy powders and mixtures of aluminum and magnesium powders were incorporated into formulations containing 9% of the glycidol - maleic anhydride - D.E.R. 732 binder, an effective high oxygen binder. Table IX reports an efficiency of 28,000 cd. sec./g. for an aluminum fueled flare using this binder. The binder used in the best aluminum fueled flares could not be used in flares containing magnesium because the formulations got hot enough during mixing to catch fire. The light output form the alloy-fueled flares is thought to be relatively unaffected by the binder level or type of binder and therefore represent as high a value as can be obtained.

The fuel/oxidizer ratio of compositions containing 200 mesh 30/70 alloy was optimized. Since the light output of the most efficient 30/70 alloy-fueled composition was unimpressive, 325 mesh 50/50 alloy was studied. As illustrated in Figure 4, themost efficient 30/70 alloy-fueled composition contains 52% metal and exhibits an efficiency of 25,000 cd. sec./g. The most efficient 50/50 alloy-fueled composition contains 55% metal and has an efficiency of 27,000 cd.sec./g.

The effect of particle size on performance was determined by replacing the powders in the optimized formulations with finer or coarser materials. However, the particle size of the alloy fuels had no effect on efficiency.

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[11] Summerfield, Martin, Solid Propellant Rocket Research, Academic Press, New York, 1960.

Flares containing identical amounts of 325 mesh, 200 mesh, or coarse atomized 30/70 alloy produced the same efficiency. Coarse atomized 40/60 alloy produced the same light output as 325 mesh ground 50/50 alloy.

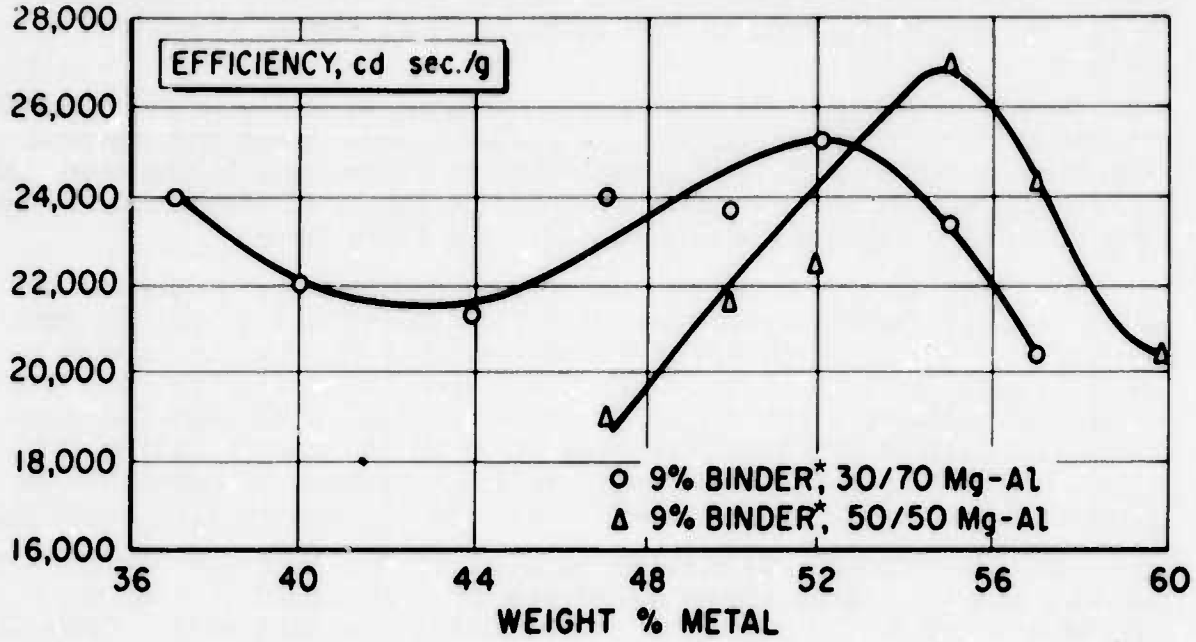

Figure 4. Effect of Magnesium-Aluminum Alloy Concentration on Flare** Performance

The apparent lack of correlation between metal particle size and the light output of alloy-fueled flares is not consistent with the effects observed in aluminum or magnesium-fueled flares. The smaller sized fuels used in this study were ground particles with highly irregular shapes. Sieve analysis, the only available means of measuring the size, is probably inadequate for this type of study.

Flares containing the coarse, atomized alloys exhibit higher densities, lower mass burning rates, and lower linear burning rates than flares containing the ground powders. Since the combustion efficiency of flares containing aluminum is restricted by the ejection of unburned fuel, the slower burning atomized alloy fuels may increase the residence time of unburned aluminum on the burning surface and in the flame zone. The longer residence time for larger alloy particles

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*Binder J, Table VIII

** -400 mesh $NaNO_3$ used in all flares may offset the expected improved combustion of small particles, so that the efficiencies are equal.

The fuels in the optimized compositions were replaced by various mixtures of magnesium, aluminum, and alloys in an attempt to separate the effects of magnesium as an alloy ingredient from the effects of magnesium as a flare ingredient.

The efficiency of flares containing a 30:70 ratio of magnesium to aluminum is not dependent on the mode in which magnesium is added to the flare composition. Flares fueled with 30/70 alloy, or a 30:70 mixture of elemental magnesium (30/50 mesh) and elemental 6-micron aluminum powder, or a mixture of elemental aluminum and 40/60 alloy with a net magnesium-to-aluminum ratio of 30:70, produce virtually the same light output.

At higher magnesium levels efficiencies are dependent on the amount of unalloyed magnesium in the original charge. Flares containing a 50:50 mixture of magnesium and aluminum powders are superior to those containing a mixture of 30/70 alloy and magnesium powder with a net magnesium-to-aluminum ratio of 50:50. Flares containing either the 50:50 mixture of aluminum and magnesium powders or the mixture of magnesium powder and magnesium-aluminum-alloy are superior to those containing the 50/50 alloy. The most efficient flares fueled by both magnesium and aluminum contained a 50:50 mixture of the elemental powders and produced an efficiency of 32,000 cd.sec./g.

Flares containing aluminum and magnesium eject smaller agglomerates than comparable aluminum-fueled flares. They exhibit maximum efficiencies at high metal loadings and are considerably more efficient than aluminum-fueled flares at these metal levels. This behavior indicates that the presence of magnesium in the fuel does contribute to the vaporization of aluminum.

Unfortunately, the useful effects of magnesium are not pronounced. Although molten alloy droplets fragment in powder torches, there is no evidence that the alloys fragment in burning flares. The use of alloys or mixtures containing as much as 50% magnesium does not prevent the waste of fuel and energy through the ejection of molten metal from the burning flares. This waste is reflected in low light output, at best no better than the most efficient aluminum-fueled flares.

As indicated above, chromium sesquioxide and sodium fluoride can have beneficial effects on certain aluminum-fueled flare compositions. In alloy-fueled formulations, chromium sesquioxide reduces efficiency and burning rate. Sodium fluoride increases burning rate and decreases efficiency.

D CAVITY FLARES

The efficiency of magnesium flares has been reported[12] to increase when pairs or groups of flares are positioned so that their flames intersect. Certain magnesium-fueled flares have been reported to exhibit enhanced efficiency when fabricated with a cylindrical internal cavity extending partially through the flare. The walls of the cavity were considered to behave as separate flares, and the flame passing through the center of the cavity was considered to be similar to the flame produced by intersecting flares. Because of these reports, aluminum-fueled flares were functioned in a cavity geometry in attempts to raise combustion efficiency and light output.

Cavity flares were fabricated and tested to determine if: (1) an enhancement effect exists, (2) geometry affects light output, and (3) composition affects light output. The experimental approach involved firing a given formulation in flares with different cavity length to diameter (L/D) ratios, and comparing the light output with that of end-burning flares to detect possible enhancement and to determine possible optimum configuration.

Six formulations were tested in the cavity geometry. They include the most efficient composition available at the time of the cavity experiments, as well as less efficient formulations containing combustion modifiers. The combustion modifiers were included in the hope that an analysis of their effects would help to define the factors controlling the expected cavity enhancement.

The flares in the initial cavity experiments possessed L/D ratios covering the range 0.5 to 10.0. The few flares tested at the high L/D ratios performed so poorly that later flares were restricted to the lower L/D ratios. The results of these tests are illustrated in Figure 5.

The light output of the cavity flares is unimpressive. As indicated in Figure 5, the best cavity flares possess low L/D ratios. None is superior to the end-burning configuration. There is no apparent correlation between composition and cavity effect.

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[12] Cronk, W., and Schmeling, W., "Radiance Characteristics of Interacting Flames," RTD Technology Briefs. September 1964.

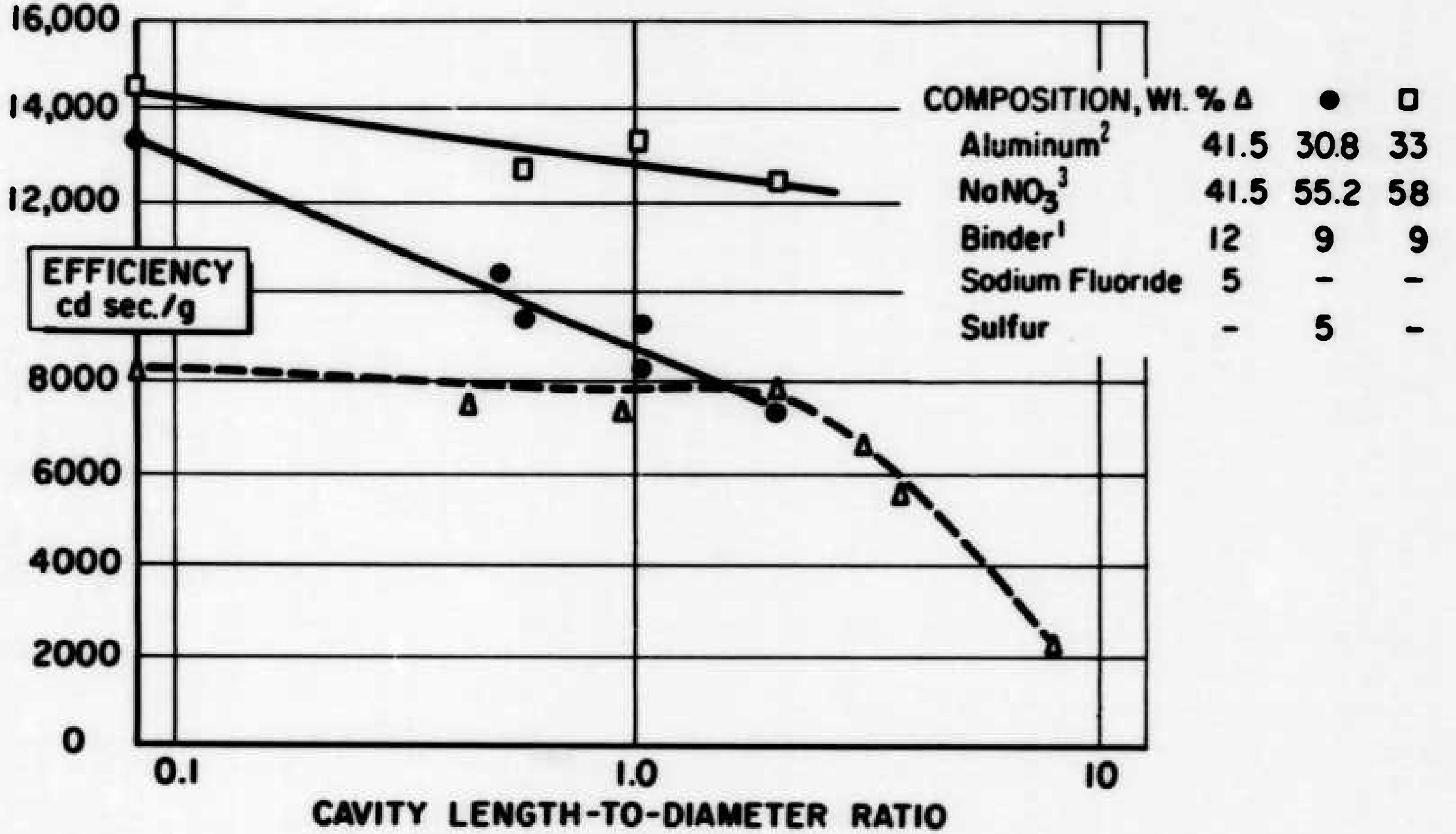

Figure 5. Performance of Aluminum-Fueled Cavity Flares

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[1] Binder B, Table VIII.

[2] Valimet 818.

[3] -400 Mesh.

Cavity flares are more difficult to fabricate and contain less material than end-burning flares with comparable linear outside dimensions. Cavity experiments were terminated when it became apparent that, at best, cavity flares are equivalent to end-burning flares of the same weight, and inferior to end-burning flares with the same exterior dimensions.

All of the flares fabricated in this investigation were smaller than typical production sized items. The combustion behavior of small flares is significantly affected by many of the factors which differentiate cavity flares from end-burners. A major portion of the work with cavity flares was devoted to devising properly controlled experiments, i.e., experiments which minimized size effects so that the intrinsic merit of the two geometries could be evaluated.

The case material on the small end-burning flares used as controls affects burning rate and light output. Cavity flares are not sensitive to case effects. The end-burning flares used initially were fired in epoxy-impregnated cardboard cases which reduced the light output.

The ratio of case weight to flare weight falls as flare diameter increases. In an attempt to simulate the behavior of larger flares, paper masking tape cases were used for the end-burning standards. The lighter paper tape case appears to have a minimal effect on flare behavior. The tape-wrapped flares burned at the same linear rate as cavity flares. Both 31-mm and 51-mm diameter end-burning flares exhibit the same burning rate and efficiency.

Other size-related variables were controlled in the investigation, but were not studied extensively. The light output of cavity flares is sensitive to a critical diameter effect. The aluminum-fueled formulations used in the investigation performed poorly and erratically if the cavity is less than 25-mm diameter. Since cavity diameters between 25 and 50 mm have no apparent effect on output, 31-mm cavities were used for most of the work.

Two sizes of end-burning flares were used as controls in each cavity experiment. The 31-mm diameter controls had the same outside diameter as the cavity diameter; the 51-mm diameter controls had the same outside diameter as that of the cavity flares. The larger end-burning flares also exhibited a mass burning rate equal to that of at least one of the cavity flares. All of the flares used in any given cavity experiment exhibited the same or similar density.

E BINDERS

An object of this program was to develop a flare composition which could be tamped or lightly pressed into cases. This type of composition requires a larger amount of plastic binder than that generally used in conventional flares. At these binder levels, the composition and amount of binder are important determinants of efficiency.

1 Binder Level

The amount of binder in an aluminum-fueled flare composition can have pronounced effects on efficiency. In the higher ranges the binder level is the most important parameter affecting efficiency. At lower levels, binder content has a smaller effect.

The efficiency of magnesium flares is reported to be an exponential function of binder level. As demonstrated in Figure 6, aluminum-fueled flares exhibit similar behavior. However, the curve representing aluminum-fueled flares exhibits an inflection point. The presence of the inflection is related to a drop in light output caused by chimney formation. At binder levels greater than that at the inflection, nearly all flares form chimneys. At lower binder levels, the more efficient flares do not. The compositions represented by the data points for 12, 9, 7, and 5 percent binder in Figure 6 contain a fuel level which produces maximum efficiency in flares containing the binder levels shown. Compositions containing more than 12% binder were formulated by modifying the composition containing 12 percent binder. Magnesium content was held constant, oxidizer level was reduced, and binder level was increased. The latter compositions are not optimized, but the flares at these binder levels produce so little light that the absolute deviations from optimum are relatively small when compared to the efficiencies at lower binder levels.

The curve in Figure 6 illustrates the effect of a "good" binder*, i.e., an effective, high oxygen content binder. There is evidence that the location of the curve inflection is related to the chemical composition of the binder. The use of a "poor" binder may cause the inflection to shift in the direction of the lower binder levels. This effect was not studied extensively.

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*Sixty-six percent CX-7160, 29.2% monoethanolamine nitrate, 4.8% formamide.

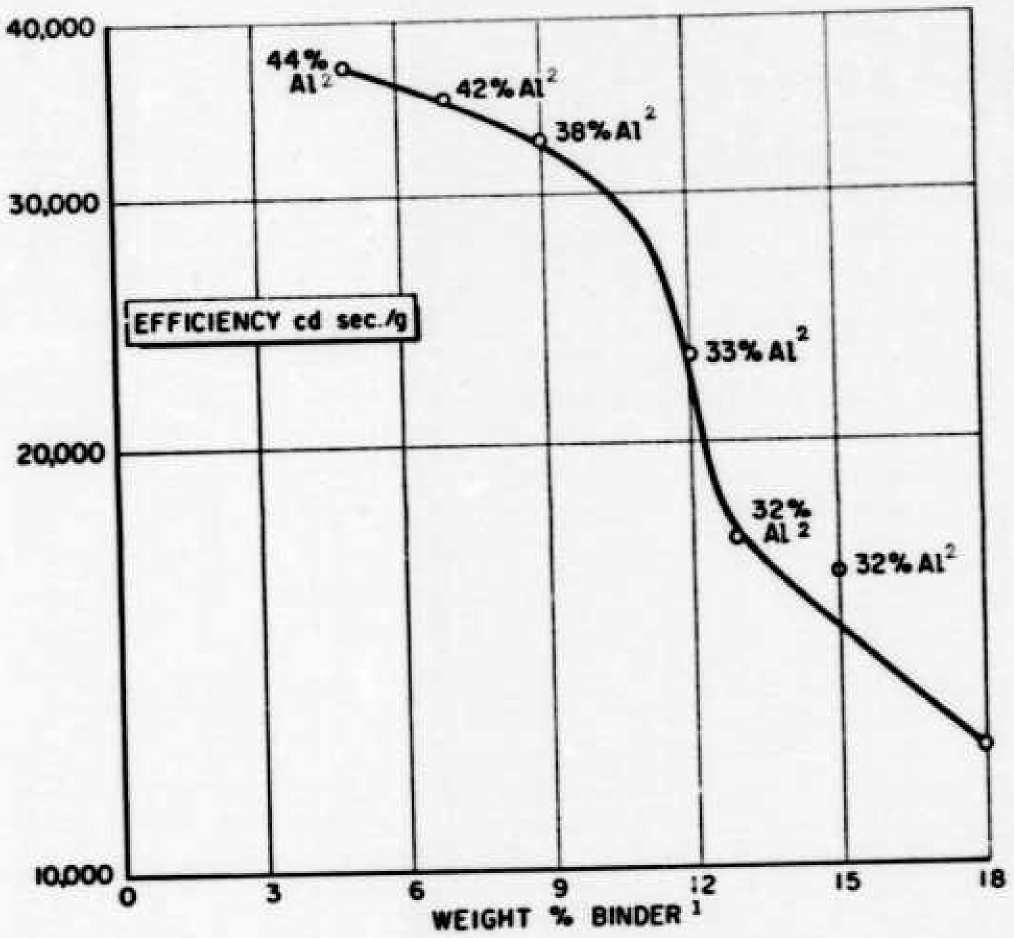

Figure 6. Effect of Binder Level on Aluminum-Fueled Flare[3] Performance

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[1] Binder L, Table VIII
[2] Valimet 818 Aluminum
[3] 120m - 840m $NaNO_3$

Most of the flares fabricated in this program contained 9 to 12% binder. This range was chosen because studies indicate that it is possible to produce acceptable processing properties in such a mix. Most of the work with binders was devoted to developing a binder which produces acceptable light output in this range. This work was successful. As Figure 6 illustrates, flares with 9% of the best binder contain less binder than the level associated with the inflection point. As such, the binder exhibits a minimal deleterious effect on efficiency.

2 Binder Composition

Binders reduce the output of illuminating flares. They displace fuel and oxidizer, and generate decomposition products which cool the flame while emitting in undesirable portions of the spectrum. The object of binder studies was to develop a binder which minimizes these effects.

Studies of binder composition were based on the theory that the presence of carbon in the polymer binder was one of the principal causes of the reduction in efficiency. Accordingly, binders with a high heteroatom content were investigated.

Oxygen, bromine, chlorine, fluorine, and nitrogen were the heteroatoms of interest. They were incorporated into flares as an integral part of a crosslinked binder, or were contained in non-curing plasticizers dissolved in the binder. Whenever possible, heteroatoms were studied as part of the crosslinked binder. The mere presence of relatively mobile plasticizers in flares tends to affect the light output, thus complicating an analysis of the effects of heteroatoms. The composition of the binders studied is given in Table VIII.

The effect of various binder heteroatoms on light output is illustrated in Table IX. The data indicate that a high oxygen content is a desirable feature of illuminating flare binders and that the presence of the other heteroatoms is undesirable.

The presence of halogen is particularly detrimental to light output. Similar effects have been noted in the study of magnesium flares and were not unexpected in this application.

A variety of binders with differing oxygen contents was studied. As Table IX illustrates, increasing oxygen content was generally accompanied by increasing light output. However, a comparison of the efficiencies of flares containing the binders K, L, M, and N (Table IX) demonstrates that there is no simple correlation between binder oxygen content and flare light output. The cause of the differences in light output

TABLE VIII. BINDER COMPOSITIONS STUDIED

Binder Number	Components	Composition wt. %
A	CX-2679[1] - maleic anhydride	80-20
B	D.E.R. 331[1] - D.E.R. 732[1] - D.E.H.[2] 31	50.0-21.4-28.6
C	Epon 812[3] - maleic anhydride	60.0-40.0
D	Formrez F-17-80[5] - ERLA 0510[4]	77.8-22.2
E	Glycidol - maleic anhydride	43.0-57.0
F	PEI[2] 18 - D.E.R. 331[1] - D.E.R.[1] 732	79.5-6.1-14.4
G	Epon 812[3] - D.E.H. 31[2] · 0.8 HNO_3	60.0-40.0
H	Glycidol - maleic anhydride - Epon 812	33.1-49.6-17.3
I	Binder C - Teflon	33.3-66.7
J	Glycidol - maleic anhydride - D.E.R. 732[1]	33.1-49.6-17.3
K	Glycidol - maleic anhydride - D.E.R. 732[1] - monoethanolamine nitrate	29.8-44.6-15.6-10.0
L	CX-7160[1] - monoethanolamine nitrate - formamide	66-29.2-4.8
M	CX-7160[1] - monoethanolamine nitrate formamide	28-66-6
N	CX-7160 - D.E.H. 31[2] · 0.8 HNO_3 - triethylene glycol dinitrate	29.2-20.8-50

[1] Epoxy resin - The Dow Chemical Company.

[2] Amine curing agent - The Dow Chemical Company.

[3] Epoxy resin - Shell Chemical Company.

[4] Epoxy resin - Union Carbide Chemical Company.

[5] Acid curing agent - Witco Chemical Company.

TABLE IX. EFFECTS OF BINDER ELEMENTAL CONTENT ON EFFICIENCY

Binder Number	Elemental Composition					Efficiency (cd.sec./g.)
	Carbon[5]	Nitrogen[5]	Halogen[5]	Oxygen[6]	Total Heteroatom	
A	67	2	--	24	36[7]	13,500[1]
B	56	--	--	21	23	13,500[1]
C	48	--	7[3]	39	46	17,000[1]
D	53	1	--	40	41	22,000[1]
E	47	--	--	47	47	23,000[1]
F	59	26	--	5	31	13,000[2]
G	49	4	7[3]	31	42	19,000[2]
H	49	--	2[3]	43	45	26,000[2]
I	34	--	51[4]	13	64	26,500[2]
J	51	--	--	43	43	28,000[2]
K	48	2	--	44	46	32,000[2]
L	43	9	--	38	47	32,000[2]
M	31	16	--	44	60	39,000[8]
N	39	7	--	45	52	15,100[8]

[1] 31.6% Valimet 818 - 59.4% $NaNO_3$ (-400 mesh) - 9% binder.

[2] 38% Valimet 818 - 53% $NaNO_3$ (-400 mesh) - 9% binder.

[3] Chlorine.

[4] Fluorine.

[5] Calculated, ±10%.

[6] Measured, nuclear activation, ±3%.

[7] Contains 12% sulfur.

[8] 38% Valimet 818 - 53% $NaNO_3$ (120-840 micron) - 9% binder.

observed in these flares is not known. Binders K, L, and M are thought to produce relatively more gaseous product and less solid carbonaceous residue when pyrolyzed. This type of correlation was not studied further, however. The number of available binders which met the criteria of pot life, exotherm, cure time, and mechanical properties is not sufficient to study adequately parameters other than heteroatom content.

F PACKING DENSITY

The development of a tamp-castable flare composition was one of the primary goals of this study. A composition containing enough plastic binder so that it could be poured into flare casings was a desirable ultimate goal of the program; however, the immediate object was to develop a composition which could be consolidated at low pressures, or tamped into casings.

By definition, this type of composition requires relatively large amounts of plastic binder. Since the presence of significant amounts of binder degrades the performance of illuminating flares, the development of an efficient castable flare required the successful completion of two tasks. A binder which has a minimal effect on light output was developed, and an effort was made to minimize the amount of binder necessary for acceptable processing properties.

A castable flare containing the minimum amount of binder contains just enough binder to fill the voids between solid particles. Necessary binder levels may be lowered by reducing the void space in a composition, or by reducing the density of the binder so that a given weight of binder fills a larger volume of void. Since the chemical nature of the binder in this study has a pronounced effect on light output, it was not possible to manipulate binder densities. Instead, the particle size distributions of the solids were varied to reduce void space.

The packing density* of a mixture of solids is a convenient measure of void space. The higher the packing density of a composition, the lower the void space. Most of the work on the processing properties of aluminum-fueled flare compositions involved the study of packing density.

The binders which have the least deleterious effect on light output were most useful in compositions containing 9% binder or less. Therefore, the object of packing density

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*Ratio of actual volume of flare solids to bulk volume of flare candle.

studies was to develop a composition in which the void space in a lightly compacted mixture of 91 grams of fuel and oxidizer was equal to the volume of 9 grams of liquid binder. Unfortunately, binders which contain a large amount of oxygen also tend to exhibit a high density. Therefore, to be castable at the 9% binder level, flares containing the most efficient ratio of fuel to oxidizer and the most efficient binder have to exhibit a density of 2.26 g./cm^3. and a packing density of 0.83. These are relatively high values. However, experimental propellants have been fabricated at higher packing densities.

The initial studies of packing density were based on fuel-oxidizer mixtures possessing a logarithmic-normal distribution of particle sizes. Mixtures of solids with a random or logarthmic normal distribution of particle sizes are reported[13] to exhibit minimum void space, minimum viscosity as slurries, and optimum mechanical properties as cured grains.

Aluminum-fueled flares did not respond to logarithmic normal particle size distributions as expected. Mixtures containing an excess of large particles pack more efficiently than mixtures containing a logarithmic normal distribution, and blends containing an excess of small particles pack less efficiently.

The results of these experiments are illustrated in Figure 7. All of the formulations contained 38% aluminum, 53% oxidizer, and 9% binder. This was the most efficient composition developed and was used in all of the packing density studies. The broken lines in Figure 7 represent particle size data obtained from the manufacturer. The densities in Figure 7, as well as all of the others in this section, exhibit an error of less than 1%.

The literature is not in complete agreement on the merits of logarithmic-normal particle size distributions in this type of application, since size distributions based on sieve analysis do not accurately reflect shape factors or the effects of incomplete particle dispersion. Both the fuel and the oxidizer used in this work are thought to be sensitive to these effects. The oxidizer, a general purpose commercial material, was not treated to generate uniform spheroidal particles. The fine aluminum powders, although spheroidal, are known to disperse poorly. Therefore, in an effort to test the possible influence of shape factors and dispersion effects, the oxidizer particle size distribution was optimized by trial and error. In addition, a non-logarithmic normal size distribution used for solid propellants was tested.

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[13] Leeming, H., Gillis, T., "The Mechanics of Highly Filled Propellants," Bulletin of the 4th Meeting of the ICRPG Working Group on Mechanical Behavior, U.S. Naval Training Center, San Diego, California, CPIA No. 944, October 1965.

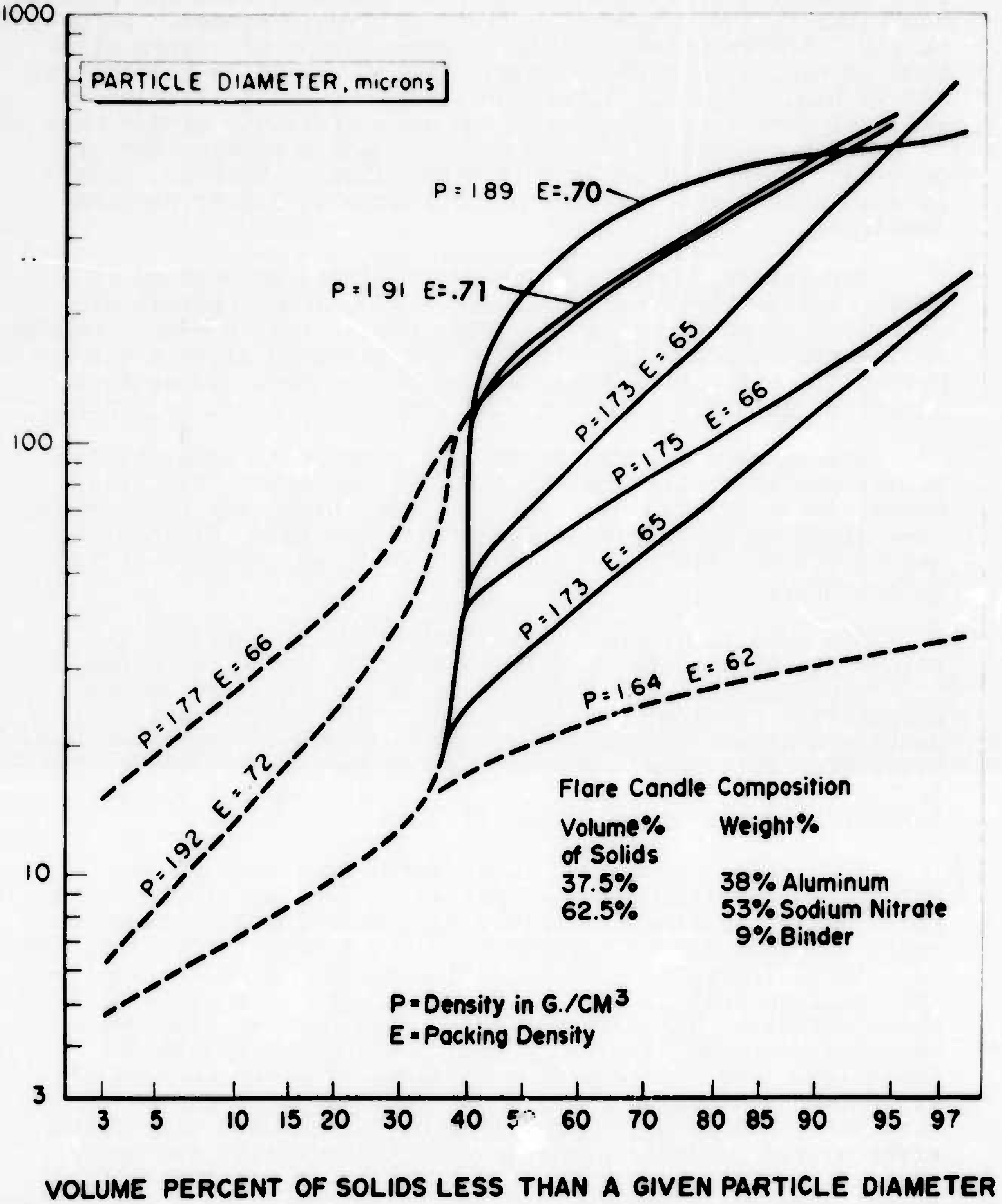

Figure 7. Packing Density as a Function of Particle Size Distribution

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*Binder J, Table VIII.

Blends of three commercial cuts of sodium nitrate were incorporated into flares in attempts to raise packing density by trial and error. The oxidizers exhibited particle size ranges of 14-44 microns, 44-250 microns, and 120-840 microns. The blends were formulated in an attempt to generate density data suitable for a steepest ascent optimization algorithm. However, as illustrated in Figure 8, none of the flares containing blends was superior to flares containing only the largest of the three particle sizes. The density increases monotonically as the proportions of large sized oxidizer increase. The best formulation contains 3-30 micron spheroidal Valimet 818 and 120 to 840 micron sodium nitrate. This composition has a density of 1.91 g./cm^3 and a packing density of 0.71.

Several optimized particle size distributions give highly favorable packing densities when used in solid propellants. One of these[14] contains an aluminum powder with properties similar to Valimet 818, and a volumetric fuel/oxidizer ratio almost identical with that of the most efficient flares.

The ammonium perchlorate size distribution used by these workers was duplicated by combining several sieve fractions of commercial sodium nitrate. The mixture was incorporated into flares in an effort to improve packing efficiency. However, it produced lower packing densities than the best size distribution developed under the current program.

Microscopic examination of cured flares indicates that the primary cause of difficulty in packing density experiments is a pronounced tendency of the small aluminum powders to form agglomerates. These agglomerates tend to fill pockets between oxidizer particles in flares containing large sized oxidizer particles. In flares containing smaller sized oxidizer, the agglomerates are strong enough to displace oxidizer crystals. Therefore, in flares containing coarse oxidizer, the aluminum agglomerates fill voids and produce the highest packing density. In flares containing small sized oxidizer, the agglomerates help to generate voids, and packing density is low.

The presence of the fuel agglomerates defeated attempts to produce significant increases in packing density and may have contributed to unsatisfactory combustion behavior.

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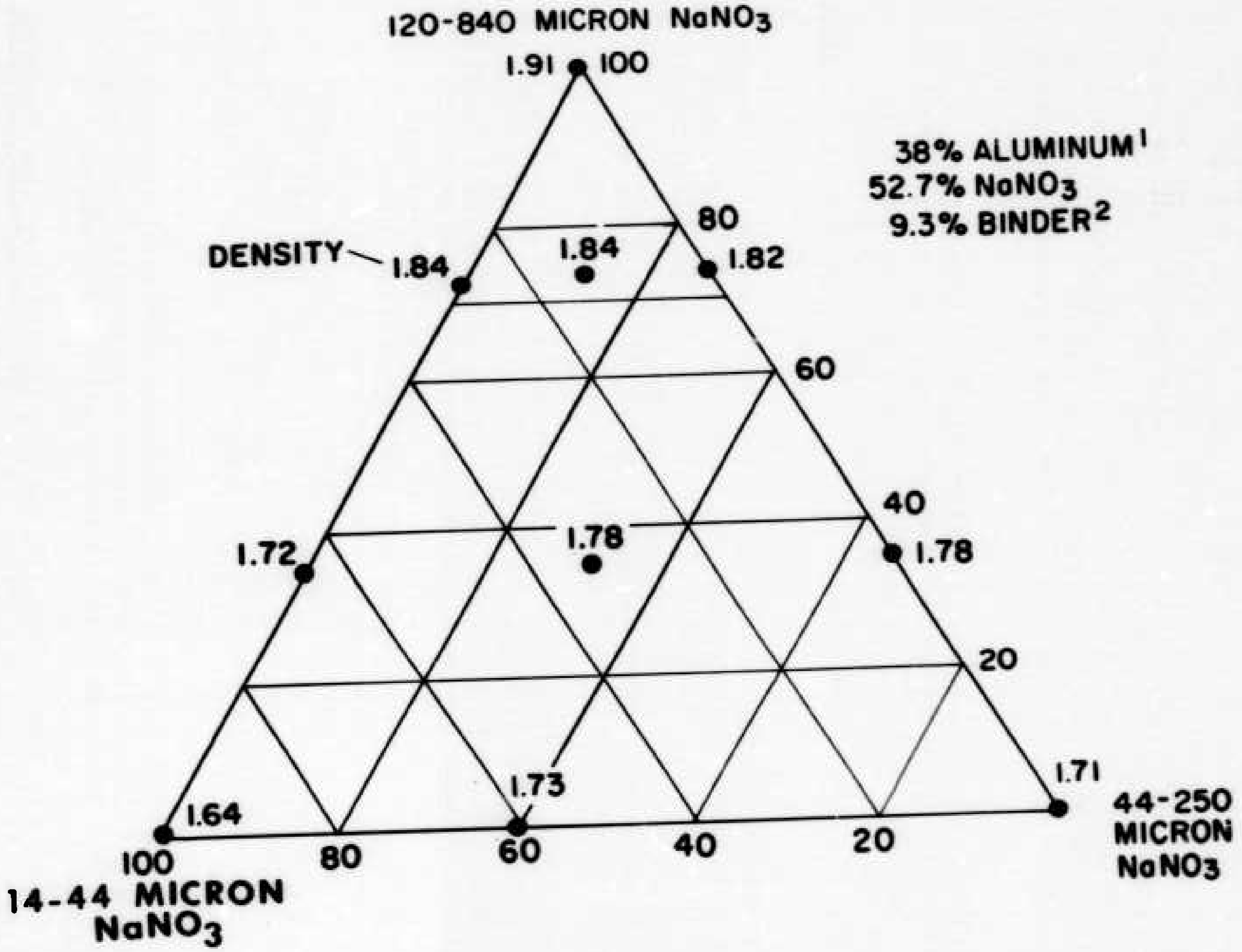
[14] Alley, Bernard J., and Dykes, Hiram W., Optimizing the Packing of Ammonium Perchlorate and Aluminum Particle Size Mixtures for Solid Propellants, Project DA 1S222901A211, Army Missile Command, Redstone Arsenal, p.24. Mixture B was employed.



[1]Valimet 818 aluminum
[2]Binder J, Table VIII

Figure 8. Trial and Error Optimization of Packing Efficiency

Therefore, a variety of physical methods was employed in attempts to disrupt the agglomerates.

The order of addition of ingredients was varied, mixing times were extended, intensive shear mixers were employed, and surfactants were incorporated into the formulation. Compositions were also mixed, at high shear, in an excess of inert solvent. However, none of these methods was successful in totally disrupting fuel agglomerates.

When surfactants were utilized in an attempt to improve the dispersion of the powders, partial success was realized. Nonionic surfactants with a high hydrophile-lipophile balance, such as Tween 80 or the long chain ethylene oxide-nonylphenyl adducts, improve the dispersion characteristics of the aluminum powders.

Tween 80 produces the most favorable effects in flare processing properties. A mixture of Valimet 818 and the monoethanolamine binder (Binder L),in the proportions used in flares, is a moist powder. When Tween 80 is added to the mixture, the moist powder liquefies and becomes a slurry. Since microscopic examination of cured flare grains reveals that compacted grains consist of discrete oxidizer particles dispersed in a matrix of aluminum agglomerates, surfactant-induced liquifaction of the aluminum phase suggested that it should be possible to disperse the oxidizer into the fluid aluminum-binder mixture to form a dough or paste. However, when oxidizer was added to the slurry, the fluid properties of the mixture were destroyed and the density of the complete flare formulation was not greatly increased.

Although Tween 80 improved processing properties, and surfactants such as Aerolube 78 and Dowfax®*9N9 increased packing density, none was judged to be a satisfactory additive. Compositions containing as much as 1% surfactant showed, at best, a 10% increase in packing density in the most efficiently packed formulation. At this level, the surfactants began to reduce light output. The reason for the decrease is not entirely clear; however, the surfactants contain less oxygen than the most efficient binders, and therefore reduce the overall oxygen content of the organic constituents of the flare. Binder experiments indicated that such a change should lower light output, but the specific effect of surfactant structure was not studied.

One of the surfactants, FX 161, an anionic fluorocarbon, improves light output when present in small concentrations. However, the fluorocarbon is a waxy solid, insoluble in the

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*Dow wetting agent, a trademark of The Dow Chemical Company.

best binder (Binder L, Table VIII). FX 161 is reported to be preferentially absorbed by aluminum, forming a tenacious layer capable of protecting the metal from reaction with aqueous hydrochloric acid. The surfactant also lowers burning rate when used in small concentrations. These factors may be responsible for the increase in light output.

SECTION III

EXPERIMENTAL PROCEDURE

A MATERIALS

The aluminum powders used in this program react rapidly and irreversibly with atmospheric moisture and oxygen. Therefore, they were incorporated into flares as received, with no attempt to dry, de-agglomerate, or otherwise process the powders before use. Exposure to the atmosphere during weighing operations tends to degrade unused material. It was necessary to monitor the quality of the inventory by fabricating standardized flares periodically. Material was discarded when a drop in the light output and burning rate of the standardized flares indicated that exposure to the atmosphere had degraded the reactive powders.

Sodium nitrate was purchased in 100-pound containers and repackaged. The material was dried at 70°C for one week and then sealed for storage. Agglomerates in coarse oxidizer were broken by screening through a 25-mesh sieve. Nominal $30\ \mu$ material was reground in a Waring blender or a Metals Disintegrating Co. Bantam Mikro-Pulverizer and passed through a 400-mesh sieve immediately before use. This is designated "-400 mesh" oxidizer.

Solid combustion modifiers were dried at 70°C for one week. Coarse materials were ground to pass a 100-mesh sieve. Liquid binder ingredients were used as received.

Monoethanolamine nitrate, the curing agent in the most attractive binder discussed in Section II-E, was synthesized on a small scale as needed. The synthesis procedure is described below.

The synthesis reaction and assumed structure of the monoethanolamine nitrate are illustrated by Equation (1).

$$HO-CH_2-CH_2-NH_2 + NH_4NO_3 \rightarrow HO-CH_2-CH_2-NH_3NO_3 + NH_3\uparrow \quad (1)$$

(i) Add one mole (80.04 g.) anhydrous ammoniun nitrate to one mole (61.08 g.) anhydrous monoethanolamine (2-aminoethanol).

(ii) Place in shallow pan, hold at ambient temperature and 38 cm.Hg. pressure for sixteen hours.

(iii) Raise temperature to 70°C, lower pressure to approximately 5 cm.Hg. Maintain for four hours or until all dissolved ammonia is removed.

Monoethanolamine nitrate exists as a hygroscopic solid or supercooled liquid at room temperature. The material is fluid at 70°C. When mixed with water, monoethanolamine, or formamide, the compound does not crystallize at room temperature.

A list of materials used and the source of each are presented in Table X.

B FABRICATION

Most of the flare formulations were mixed in an Atlantic Research Model 35 Z Blade Laboratory mixer. The mixer produces acceptable results, but is slow and difficult to clean. A 5-quart Hobart KitchenAid Mixer was also used to blend certain formulations. The KitchenAid is a superior mixer for formulations which contain a small range of particle sizes but tends to segregate the components of formulations containing a wide range.

Flare compositions were mixed in two stages. Binder and fuel were blended first, then oxidizer and other solid ingredients were added. The complete mixing process took 20-30 minutes. All of the mixes were processed at ambient temperature, pressure, and humidity. Batch sizes varied from 300 to 400 grams. Three to five flares were pressed from each batch.

Most end-burning candles were pressed into 1.24-inch I.D., 1.3-inch O.D., cardboard tubes, in two increments, at 90 psi. The tube walls were supported by a plastic mold. If the flare was to be functioned in the cardboard tube, the tube was dried and impregnated with epoxy resin before use. This treatment prevents binder ingredients from migrating into the cardboard. If the flare was to be removed from the tube and tape wrapped, a polyester film liner was used to prevent binder migration. Larger diameter flares were fabricated in stainless steel or epoxy-fiberglass molds.

Flares were cured at 70°C under ambient humidity and pressure. Most were cured for 14-24 hours. Binders D, L, M, and N (Table VIII) required a 40- to 48-hour cure.

Nearly all of the flares tested during this program were 31-mm (1.24") diameter, 70-mm (2.75") length, and weighed approximately 100 grams. Initially, flares were fired in epoxy-impregnated kraft cardboard tubes. A typical case for a 100-gram flare contained 16 grams of epoxy resin and 9 grams of cardboard. These cases are unsatisfactory, because they reduce the light output of the flares and amplify the normal variation in light output between nominally identical flares. Except where noted otherwise, data presented in this report are for tape-wrapped candles.

TABLE X. LIST OF MATERIALS AND SOURCES

Material	Source
Aerolube 78 Surfactant	Unknown
Aluminum	
Alcoa 123 atomized powder Alcoa 140 atomized powder	Aluminum Company of American Alcoa Building Pittsburg, Pennsylvania
Reynolds 3X-D flake	Reynolds Metals Company Richmond, Virginia
Valimet 816 atomized powder Valimet 817 atomized powder Valimet 818 atomized powder	Valley Metallurgical Processing Company, Incorporated Centerbrook, Connecticut
Ammonium fluoride Ammonium nitrate	Fisher Scientific Company Fairlawn, New Jersey
Boron	U.S. Borax 50 Rockefeller Plaza New York, New York
Chromium sesquioxide Cryolite Cupric oxide Cupric sulfate	Fisher Scientific Company Fairlawn, New Jersey
CX-2679 epoxy resin CX-7160 epoxy resin CX-7165 amine curing agent D.E.H. 31 amine curing agent D.E.R. 331 epoxy resin D.E.R. 732 epoxy resin Dowfax 9N9 surfactant	The Dow Chemical Company Midland, Michigan
Epon 812 epoxy resin	Shell Chemical Company 20575 Center Ridge Road Cleveland 16, Ohio
ERLA 0510 epoxy resin	Union Carbide Corporation Chemical Division Bound Brook, New Jersey
Formamide	Fisher Scientific Company Fairlawn, New Jersey

TABLE X. LIST OF MATERIALS AND SOURCES (Contd.)

Material	Source
Formrez F-17-80 curing agent	Witco Chemical Company Organics Division 75 E. Wacker Drive Chicago, Illinois
FX 161 fluorocarbon surfactant	3M Company Chemical Division St. Paul, Minnesota
Glycidol	Aldrich Chemical Company, Incorporated Milwaukee, Wisconsin
HC 208-4 fluorocarbon oil	Halocarbon Products Corporation 82 Burlews Court Hackensack, New Jersey
Hexachlorobenzene	Fisher Scientific Company Fairlawn, New Jersey
Magnesium powder 30/50 mesh	Valley Metallurgical Company Centerbrook, Connecticut
Magnesium-aluminum alloy 30/70, 50/50, Ground	Reade Manufacturing Company Lakehurst, New Jersey
Magnesium-aluminum alloy 30/70, 40/60, atomized	The Dow Chemical Company Freeport, Texas
Magnesium fluoride	Allied Chemical Company General Chemical Division Morristown, New Jersey
Maleic anhydride Manganous carbonate Manganese dioxide Manganous sulfate Monoethanolamine	Fisher Scientific Company Fairlawn, New Jersey
Monoethanolamine nitrate	Synthesized (per text)
PEI 18 amine	The Dow Chemical Company Midland, Michigan 48640

TABLE X. LIST OF MATERIALS AND SOURCES (Contd.)

Material	Source
Potassium perchlorate	Fisher Scientific Company Fairlawn, New Jersey
Rare earth fluoride, mixed	American Potash and Chemical Corporation West Chicago, Illinois
Sodium metaborate Sodium chromate Sodium fluoride	Fisher Scientific Company Fairlawn, New Jersey
Sodium nitrate 15-45 micron (nominal 30 micron)	Davies Nitrate Company Meyeuchen, New Jersey
Sodium perchlorate Sulfur	Fisher Scientific Company Fairlawn, New Jersey
Teflon fluorocarbon resin	E. I. du Pont de Nemours and Company Wilmington, Delaware
Triethylene glycol dinitrate (TEGDN)	Propellex Chemicals Division Chromalloy Corporation P.O. Box 187 Edwardsville, Illinois
TVOPA	Classified chemical compound*
Tween 80 surfactant	Atlas Chemical Industries, Incorporated Chemicals Division Wilmington, Delaware

*Justice, B. H. and Carr, I. H., The Heat of Formation of Propellant Ingredients, The Dow Chemical Company, Midland, Michigan, AFRPL-TR-67-311, Air Force Rocket Propulsion Laboratory, Edwards, California, December, 1967.

The efficiencies of tape-wrapped flares are more reproducible than those of flares fired in cardboard tubes. Therefore, flares fabricated in the later months of the project were encased by bifilarly wrapping two layers of kraft paper tape about the flare. A typical 100-gram flare was covered with 2.5 grams of tape.

C MEASUREMENT

Most of the flares were fired in a 30' x 8' flare tunnel. The tunnel has a blackened surface and a baffle to minimize reflections. Flares were fired in an upright position with the burning end of the flare candle up.

Flares are functioned directly beneath the tank vent, but the flare itself is in still air. The smoke rises into the tank air stream by free convection and is blown through the vent. The tank ventilating system is capable of removing all of the smoke from end-burning candles up to two inches in diameter. The smoke from cavity flares is more than can be controlled by the tank ventilation system.

Cavity flares and the end-burning flares used as controls in cavity experiments were fired out of doors at night. A three-foot stand was used at the beginning of the program, and a six-foot stand at the end. All flares were set on the stand and fired in an upright position with the flame protruding upward. There was no difference in measured light output between controls fired in the tunnel and those fired out of doors.

The light from the flares was sensed by a Weston 856 YYV selenium photovoltaic cell. The effective spectral sensitivity of this cell is corrected, by the manufacturer, to match the standard I.C.I. luminosity curve. When employed in the electrical circuit used in this program, the manufacturer suggests a sensitivity of 9.75 ± 1.2 ft.cd./mv. The observed sensitivity was 8.75 ft.cd./mv. The cell was enclosed in a blackened, baffled box.

The signal from the photocell was amplified and recorded as an analogue signal by a Honeywell Model 906B Viscorder. The signal was also integrated and recorded digitally by a Dymec Model 2210 voltage-to-frequency converter and a Hewlett Packard Model 523CR electronic counter.

Flare densities were determined by measuring the weight, height, and diameter of well-formed cylindrical flares and computing the density. The densities presented in the text, therefore, are a direct measure of the weight of flare solids which can be carried in a given volume.

Two types of candles were used in measuring densities. Critical data, such as that presented in Section II under the heading "Packing Density", or that presented in Table I, "Properties of the Most Efficient Aluminum Flare Composition", were obtained by pressing two or more flares, in 25mm increments, at 90 psi, into a 50.5-mm I. D. cylindrical steel mold; measuring the 50-mm height of well-formed candles to the nearest 0.5-mm; weighing the 200 g. candles to the nearest 0.05 g., and computing the densities. The error is thought to be less than 1%. Less critical data were obtained routinely by pressing three to five flares at 90 psi in 25-mm increments into a 31-mm I. D. aluminum-supported, cardboard mold, measuring the 70-mm height of unmarred candles to the nearest 1-mm, weighing the 100 g. candles to the nearest 0.1 g., and computing the density. The latter densities were measured routinely to control flare quality. The measuring error is estimated at less than 4%. Most are believed to exhibit an error of 2% or less.

D CALIBRATION

Two General Electric 1M/T20 BP lamps, calibrated at a color temperature of 2854° Kelvin, were used as standards. The calibration is traceable to the National Bureau of Standards. The two standards were used interchangeably with no effect on the measured sensitivity.

When measured under the controlled temperature and humidity of the laboratory, the sensitivity of the cell did not change over the course of the project. However, when used in the instrument room attached to the flare tunnel, the response of the cell occasionally varied. The variation was apparently related to the low temperature experienced during the winter. Because of this variation, a standard lamp was set up in the instrument room and the photocell was calibrated before each firing session.

SECTION IV

CONCLUSIONS

Work has been carried out on flare fuels, oxidizers, additives, binders, and flare geometry. Small particle size aluminum fuel yields the highest efficiency in aluminum-fueled flares. Aluminum-magnesium alloys and mixtures of elemental aluminum and elemental magnesium are not superior to aluminum.

Sodium nitrate is the most effective oxidizer.

Flame interaction effects were studied using a cavity flare configuration. No performance improvement was obtained.

A wide variety of combustion-modifying additives was investigated, but none improves flare performance significantly.

Several novel flare binder materials were investigated. High oxygen content in the binder generally improves the flare performance. The best binder investigated contains CX-7160 epoxy resin, monoethanolamine nitrate curing agent, and formamide.

The most efficient aluminum-fueled flares burn very slowly. The flares exhibit burning rates of 0.030 to 0.045 inch per second and intensities of 35,000 to 40,000 cd./in^2. The candlepower is about one-third to one-half that of an efficient magnesium-fueled flare.

The optimum metal content for aluminum flares is much lower than that for magnesium-fueled flares. When evaluated in a masking tape wrapped 1.24-inch-diameter candle, the best aluminum-fueled flare compositions developed have a luminous efficiency of 35,000 to 40,000 cd.sec./g., less than two-thirds that of an efficient magnesium-fueled flare.

SECTION V

RECOMMENDATIONS

Based on the results of this research and development effort, the following recommendations are made:

1. Aluminum-fueled compositions should be investigated as slow-burning white signal flares. The tendency of these flares to sparkle might enhance visibility.

2. The infrared output of aluminum-fueled illuminants should be studied.

3. Aluminum and magnesium-aluminum alloy powders should be considered as fuels for liquid flares where better combustion of the metal might be obtained.

REFERENCES

1. Waite, H. R., and Arikawa, Y., Study of Visual Cast Flare Binder Material, Ordnance Research, Inc., Fort Walton Beach, Fla., RDTR 113, Naval Ammunition Depot, Crane, Indiana, January 1968, (AD 669434).

2. Shidlovskiy, A. A., Foundations of Pyrotechnics, (AD 602687).

3. Leader, P., and Westerdahl, R., Personal Communication, Pyrotechnics Laboratory, Picatinny Arsenal, Dover, New Jersey.

4. Ellern, H., Modern Pyrotechnics, Chemical Publishing Co., Inc., 1961.

5. Ibid., Shidlovskiy, A. A.

6. Blunt, R. M., Evaluation of Processes Occurring in Pyrotechnic Flames, Denver Research Institute, Denver, Colorado, RDTR 91, Naval Ammunition Deport, Crane Indiana, March 1967, (AD 655820).

7. U. S. Patent 3,397,056.

8. "Fluorad Fluorochemical Surfactants," Promotional brochure, Minnesota Mining and Manufacturing Co., St. Paul, Minnesota.

9. Freeman, E., and Anderson, D., "The Effects of Aluminum Fluoride on the Combustion of Aluminum in the Presence of Potassium Perchlorate and Oxygen," Combustion and Flame, Vol. 10, No. 4, December 1966, Butterworths Publications., Ltd., London.

10. Tischer, R. L., and Scheller, K., "Measurement of Illumination-Source-Related Characteristics of the Cyanogen-Oxygen-Boron Trichloride Flame System," Proceedings of First Pyrotechnics Seminar, Blunt, R. M., Denver Research Institute, Denver, Colorado, RDTR 131, Naval Ammunition Deport, Crane, Indiana, October 1968.

11. Summerfield, Martin, Solid Propellant Rocket Research, Academic Press, New York, 1960.

12. Cronk, W., and Schmeling, W., "Radiance Characteristics of Interacting Flames," RTD Technology Briefs, September 1964.

13. Leeming, H., Gillis, T., "The Mechanics of Highly Filled Propellants," Bulletin of the 4th Meeting of the ICRPG Working Group on Mechanical Behavior, U.S. Naval Training Center, San Diego, California, CPIA No. 944, October 1965.

14. Alley, Bernard J., and Dykes, Hiram W., Optimizing the Packing of Ammonium Perchlorate and Aluminum Particle Size Mixtures for Solid Propellants, Project DA 1S222901A211, Army Missile Command, Redstone Arsenal, p.24. Mixture B was employed.

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13. ABSTRACT

Exploratory studies have been conducted on tamp-castable aluminum-fueled illumination flares. Work has been carried out on flare fuels, oxidizers, additives, binders, and flare evaluation. It has been found that small particle size, atomized aluminum yields the highest efficiency. Flares containing aluminum-magnesium alloys and mixtures of aluminum and magnesium were tested but are not superior to the best aluminum fueled flares. Sodium nitrate is the most effective oxidizer. Flame interaction effects were studied using a cavity flare configuration. No performance improvement was obtained. A wide variety of combustion-modifying additives was investigated, but none improves flare performance significantly. A number of flare binders was investigated, and several novel binder materials were prepared. High oxygen content in the binder generally improves the flare performance. The best binder is based on CX-7027 epoxy resin, monoethanolamine nitrate curing agent, and formamide. Maximum castability and density were obtained by tailoring the fuel and oxidizer particle size distribution. The principal barriers to efficient light output appear to be incomplete metal combustion and chimney formation. The optimum metal content for aluminum flares is much lower than for magnesium flares, resulting in lower energy release. In general, the best aluminum-fueled flares burn very slowly with burn rates in the range of 0.030 to 0.045 in/sec. When evaluated in masking tape-wrapped 1.24-inch diameter candle, the best aluminum flare compositions developed have a luminous efficiency of 35,000 to 40,000 cd.sec./g, less than two-thirds that of an efficient magnesium-fueled flare. The aluminum-fueled flares exhibit intensities of 39,000 to 40,000 cd./in.^{2}, about one-third to one-half that of an efficient magnesium-fueled flare.

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