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Investigation of Eutectic Oxidizers For Use in Illumination Devices

by

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CHINA LAKE, CALIFORNIA ■ NOVEMBER 1973

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ABSTRACT

Flares and photoflash charges were prepared by fusing a low-melting-point eutectic oxidizer with metal powder. The eutectic replaced an organic binder which did not contribute to illumination capability. The flares and photoflash charges prepared with eutectic oxidizers (nitrate and perchlorates of alkalis and alkali metals) performed better than devices prepared with organic binders.

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FOREWORD

The nitrates and perchlorates of the alkalis and alkali metals together with aluminum and/or magnesium are the basic material for illumination devices. These oxidizers form eutectic mixtures which melt below the decomposition temperatures of the individual substances. This property suggested their possible use in photoflash cartridges to improve light output and improve safety. Their use in illumination flares would eliminate the need for organic binder materials which do not contribute to the illumination capability of the flare.

This work was done over the period 1965–1970 under AirTask A35-532-024/216-1/F008-17-02 and A35-532/216/F17-546-502/70.

This report was reviewed for technical accuracy by E. A. Allen.

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SUMMARY

An investigation was conducted to determine the characteristics of illumination flares prepared without the use of an organic binder. Flares were prepared by fusion of a low-melting-point eutectic oxidizer mixed with metal powder. The work included studies on oxidizer mixtures, metal:oxidizer ratios, particle size of metal powder, and surface treatment of metal. Most of the work was done on magnesium-based compositions. The most efficient mixtures contained magnesium and either the Na/Mg nitrates eutectic or the Na/Mg/Ca nitrates eutectic as the oxidizer. Mixtures having a high enough metal:oxidizer ratio to produce light with maximum efficiency were not fluid enough to be poured; therefore, a process involving in situ fusion of the oxidizer in a dry mix was used to produce the flares. Difficulties in wetting the magnesium powder with molten oxidizer were overcome by a dichromate treatment of the metal. Flares made with dichromated magnesium powder consistently showed a slightly increased burning rate, greater brightness, and higher efficiency, both under ambient conditions and at simulated altitudes to 60,000 feet. Flares up to Mk 21 size were prepared and tested. The binderless flares equaled Mk 21 performance specifications (150,000 cd), but tended to burn slightly faster.

Following the flares investigation, photoflash charges were prepared with a composition similar to that used in the flares. The objective was to find a replacement for the conventional loose-powder mixture of metal and oxidizer, which was highly sensitive and, therefore, hazardous to mix and handle in the loaded form. The new charges were prepared by either of two methods: (1) mixing metal powder with a fused oxidizer and then casting, or (2) heating the composition directly in the charge case until the oxidizer fused and then compacting the mix by vibration. The charges were actuated by an explosive core. Mixtures of aluminum powder with seven different eutectic oxidizers were tested. Best results were obtained with compositions containing the Li/Na perchlorates eutectic. The melt-cast charges were less sensitive to impact and friction than loose-powder compositions; however, due to the high cost (anticipated) of developing safe and efficient production facilities and procedures and the uncertainty of future photoflash requirements, further effort in this area is not recommended (at this time).

BINDERLESS CAST ILLUMINATION FLARES

BACKGROUND

The usual method of producing illumination flares consists of mixing metal powder, oxidizer, and binder, then pressing the mixture incrementally under high pressure into a case. Binder materials, such as resins, plastics, and waxes, serve to make the finely divided particles of metal and oxidizer adhere to each other, thus aiding to obtain maximum density. In addition, metal and oxidizer segregation is prevented so that more uniformly blended compositions can be obtained. As binder content is increased, burning rate is decreased and candlepower is reduced.

The objective of the investigation described herein was to determine the characteristics of illumination flares prepared without the use of an organic binder. Elimination of an organic binder was made possible by employing a readily fusible oxidizer mixture that also served as the binder. Preparation of flares in this manner also eliminated the need for high-pressure incremental pressing techniques.

Theoretically, the performance of a binderless flare should be superior to one containing a binder, because a binder contributes very little energy to the system. The presence of a binder lowers both the heat of reaction and the maximum adiabatic temperature reached by a pyrotechnic mixture. For example, magnesium and sodium nitrate reacting in stoichiometric proportions yield 2,024 cal/g and reach a calculated adiabatic temperature of approximately 3200°K. With 6.4% Laminac 4116 as binder, the heat of reaction is reduced to 1,811 cal/g and the calculated adiabatic temperature is reduced to approximately 2500°K. Because flares contain metal fuel in excess of stoichiometric proportions, this excess metal must be vaporized, then burned by atmospheric oxygen. Compositions containing a binder, as shown above, have less heat available for metal vaporization. Thus, the preparation of flares without binder appeared to be an attractive area for investigation.

LABORATORY STUDIES

A literature search made at the beginning of the investigation showed that melting point and composition data were available for a number of inorganic oxidizer systems having potential application in flares. From these systems, six eutectic mixtures composed of alkali and alkaline earth metal nitrates and perchlorates were chosen for further consideration. These mixtures had melting points in the 120-230°C range; however, because of safety considerations only those mixtures below 150°C were tested in binderless flares. Compositions and melting points are given in Table 1.

Initial work included preparation of small quantities of the various eutectic oxidizers and of metal powder/oxidizer mixtures.[1] This work showed immediately that mixtures having a metal:oxidizer ratio in the range customarily used in illumination flares (50:50 to 65:35) were not fluid enough to be pourable. Therefore, it became necessary to prepare such compositions by fusion <u>in situ</u> of the oxidizer in the metal/oxidizer mixture.

Laboratory work was also conducted on dehydration of calcium and magnesium nitrates. These compounds are commonly available as the hydrates: $Ca(NO_3)_2 \cdot 4H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$. Calcium nitrate can be dehydrated by heating at elevated temperatures (approximately 170°C) without causing decomposition. However, magnesium nitrate decomposes on heating, with the loss of nitric acid to yield basic salts. During this effort it was revealed that both of these compounds could be dehydrated conveniently by a method used by Jänecke (Ref. 4). This method involved heating the hydrated compounds together

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[1] All laboratory work and flare preparation was conducted with Reagent grade chemicals.

TABLE 1. Composition and Melting Points of Eutectic Oxidizers.

Components	Wt., %	Melting point, °C	Data source
$LiNO_3$ $NaNO_3$ KNO_3	23.5 16.3 60.2	120	Ref. 1
$LiNO_3$ $LiClO_4$	36.0 64.0	172	Ref. 2
$LiNO_3$ $NaNO_3$ $Ca(NO_3)_2$	30.5 40.0 29.5	170	Ref. 3
$NaNO_3$ $Ca(NO_3)_2$	55.0 45.0	230	Ref. 4
$NaNO_3$ $Mg(NO_3)_2$	49.0 51.0	135	Ref. 4
$NaNO_3$ $Mg(NO_3)_2$ $Ca(NO_3)_2$	49.6 45.4 5.0	130	Ref. 4

in such proportions that water removal during fusion would give the eutectic mixture of anhydrous components. Great care was necessary during preparation of the Na/Mg nitrates and Na/Mg/Ca nitrates eutectics to avoid overheating the mixture during dehydration, which would result in some decomposition of the magnesium nitrate.

During the initial preparation of small quantities of metal/oxidizer mixtures, it was noted that magnesium powder was difficult to incorporate into the mix. This was due in part to the greater density of the oxidizer, which was 2.2-2.3 compared to 1.74 for the magnesium. An additional difficulty was caused by the lack of wetting of the magnesium by the molten oxidizer. Both factors caused difficulty during the preparation of binderless flares. To improve the wetting of the magnesium, various methods of altering the metal surface were explored. The most effective and convenient method was found to be the dichromating procedure of Hart and Eppig (Ref. 5).

SCREENING OF OXIDIZER SYSTEMS

Many difficulties were encountered in the early work on the fabrication of binderless test flares, most of which was done with the eutectic composed of Li/Na/K nitrates. Laboratory work showed that, in addition to differences in density from system to system, there were also differences in viscosity. These factors, together with the different melting points of each system, indicated that it would probably be necessary to make modifications in procedures and equipment to prepare binderless flares from each different oxidizer. Therefore, to select the most useful systems more rapidly, the oxidizers were first tested in pressed flares.

The pressed flares were made from a composition containing 57.6% magnesium (gran 17), 38.4% prefused and ground oxidizer (<50 mesh), and 4% paraffin binder. This was mixed in a twin-shell blender. The magnesium was first coated with the wax by evaporation from hexane. The test flares weighed 30 grams and were pressed in a stainless steel case (inhibited with Laminac 4116) in a single pressing. Six flares were made from each oxidizer except the Na/Mg/Ca nitrates eutectic, which was included in the work later. Six comparison flares were made using sodium nitrate as the oxidizer. The light output data obtained in light tunnel tests are given in Table 2. The method of light output measurement is given in the Appendix.

TABLE 2. Comparison of Eutectic Oxidizers With Sodium Nitrate in Pressed Flares.

Oxidizer	Burn time, sec	Light output, cd	Efficiency, cd-sec/g	% efficiency compared to $NaNO_3$
$NaNO_3$	11.0	116,000	43,000	...
$LiNO_3$ $NaNO_3$ KNO_3	13.8	31,000	14,000	32.6
$LiNO_3$ $LiClO_4$	10.8	34,000	13,000	30.2
$LiNO_3$ $NaNO_3$ $Ca(NO_3)_2$	10.8	104,000	36,000	83.7
$NaNO_3$ $Ca(NO_3)_2$	14.8	111,000	53,000	123.3
$NaNO_3$ $Mg(NO_3)_2$	18.1	64,000	39,000	90.7

APPARATUS AND PROCEDURE FOR PREPARING BINDERLESS FLARES

Initially, a number of difficulties were encounted in producing a well-compacted flare candle. The first flares (40 grams) were made by fusing the Li/Na/K nitrates eutectic in a 50:50 dry mix with 5μm aluminum powder. In this case, vibration alone of the heated mixture produced a candle free of voids. Similar results were obtained when the metal powder was a Mg/Al alloy having a density approximately the same as the oxidizer. Most of the difficulties arose during preparation of flares containing magnesium powder, due chiefly to the difference in density between metal and oxidizer, which tended to cause separation of the two components when the oxidizer was heated to fusion.

At the beginning of the work on flares containing magnesium powder, numerous modifications of method and apparatus were made before well-compacted, uniform flare candles could be made consistently. On the basis of this work, it was found that to prevent separation of metal and oxidizer, confinement of the mixture during oxidizer fusion was necessary. Accordingly, the apparatus shown in Fig. 1 was evolved. In this apparatus, a ram was utilized to maintain pressure (0-100 pounds) on the contents of the flare case during heating of the oxidizer. The ram was actuated by a jack which raised and lowered the heating block. Vacuum and vibration during the heating period also aided in preventing voids. This apparatus worked best when the metal:oxidizer ratio was such that the oxidizer was not appreciably in excess of the quantity required to fill the free space in the metal powder. If much of an excess was present, care had to be taken to prevent forcing oxidizer out of the mixture and up between the ram and flare case wall.

At the start of the investigation, flares were prepared in 3-inch-long Micarta cases with a 1 1/4-inch OD and a 15/16-inch ID. Later, larger flares were prepared in Mk 21 aluminum cases. An adapter was made to hold the Mk 21[2] cases and a larger heating block was installed.

RESULTS AND DISCUSSION

The first binderless flares, prepared in Micarta cases, contained the Li/Na/K nitrates eutectic oxidizer. Much of this early work was done to gain experience and to develop techniques for flare fabrication. As expected, the efficiency of the flares containing aluminum was low (3,500 cd-sec/g) due to inefficient combustion of the metal. Some of the magnesium powder (gran 17 and 18) flares also performed poorly and burned too rapidly, probably because of poor combustion. During this period 20-gram flares were prepared with metal:oxidizer ratios of 50:50, 55:45, and 60:40. Light output increased with increasing metal:oxidizer ratio and in subsequent work all flares were prepared with ratios of 60:40 or higher.

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[2] The Mk 21 flare case is 1 inch in diameter x 10 inches long and contains about 120 grams of flare mix.

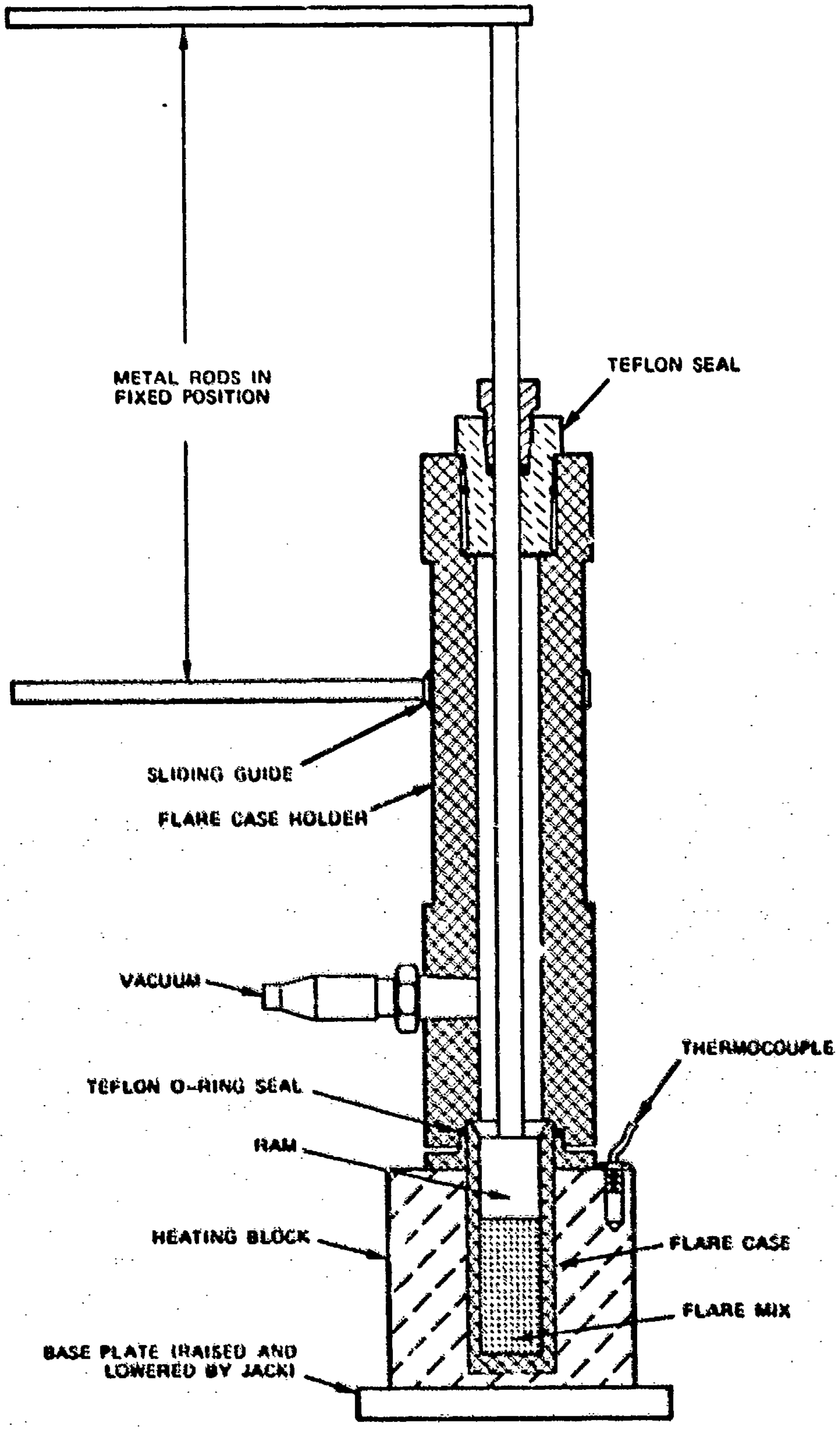

FIG. 1. Apparatus for Preparing Flares.

After development of the apparatus shown in Fig. 1, the Na/Mg nitrates eutectic was used in further work. The required fluidity was obtained at temperatures of 150-160°C. Vacuum of <1 mm, continuous vibration, and a heating period of 30-35 minutes was used for preparation of 30-35-gram flares in Micarta cases. Metal:oxidizer ratios of 65:35 were used for most of this work. The magnesium was gran 17, gran 18, and 1:1 mixtures of the two. Flares containing gran 17 magnesium reached a peak of 89,800 cd and had an efficiency of 31,200 cd-sec/g. Those containing gran 18 reached a peak of 29,000 cd and had an efficiency of 19,000 cd-sec/g. In the 1:1 mixtures, the metal of the smaller particle size appeared to govern burning rate; the peak was 57,500 cd and the efficiency was 21,300 cd-sec/g.

The first test flares (30 grams) made using dichromated magnesium and the Na/Mg nitrates eutectic were also made in Micarta cases. The greater ease of wetting the metal by the fuzed oxidizer facilitated flare preparation appreciably. Flares prepared with dichromated magnesium (gran 17) were burned under both ambient conditions and at simulated altitude. These flares were compared with the same type of flare prepared from untreated magnesium powder. Both types ignited readily up to 60,000 feet (limit of the test) and qualitative observations indicated no differences in ignition properties between the two types. However, flares made with dichromated magnesium powder consistently demonstrated a slightly shorter burning time, greater brightness, and higher efficiency. The data are given in Table 3.

TABLE 3. Performance of Binderless Flares at Simulated Altitude (65:35 metal:oxidizer ratio).

Altitude, feet	Magnesium	Burn time, sec	Light output, cd	Efficiency, cd-sec/g
Ambient	Untreated	11.9	89,800	31,200
	Dichromated	9.5	114,000	34,300
20,000	Untreated	10.0	49,600	16,400
	Dichromated	9.0	74,000	21,300
40,000	Untreated	13.5	20,200	8,800
	Dichromated	12.2	26,000	10,300
60,000	Untreated	21.6	7,700	5,300
	Dichromated	18.0	13,000	7,300

Initially, two approaches were used to scale up the binderless flares to Mk 21 size. One of these involved casting directly in the aluminum case, thus requiring an inhibitor which would be stable at high temperature. The other approach involved use of a split mold in which a flare candle could be prepared, then potted into the case with a suitable inhibitor material. After unsuccessful attempts to use several of the Sauereisen cements as inhibitors, the inhibitor problem was solved by anodizing the aluminum cases. The molten oxidizer wetted and adhered to this coating quite well, and work with the split mold was discontinued.

The first flares (50 grams) produced in the scale-up process were prepared in cut-down aluminum cases (1-inch x 6-inches, 0.035-inch wall). The Na/Mg nitrates eutectic was used as the oxidizer with gran 17 magnesium powder. Subsequent scale-up work to 75 and 105 grams utilized the Na/Mg/Ca nitrates eutectic. This oxidizer was equal to the binary eutectic in light output and also gave a slightly more fluid melt at the temperature used for flare preparation (150-160°C, heating time 20 minutes). Dichromated magnesium powder was used in all of the flares prepared in the aluminum cases. The metal:oxidizer ratio was 65:35. Better wetting of dichromated metal powder by molten oxidizer allowed very coarse oxidizer to be used in the dry mixes, and the prefused oxidizer was ground only fine enough to pass a 14-mesh sieve.

In preparing 50-gram flares, the entire weight of dry mix was added to the case in one portion. When this procedure was used for 75-gram flares, excessively rapid burning rates occurred, probably due to poor compaction. Consequently, the full-sized flares (105 grams, case 1 inch x 8 inches) were prepared by gently tamping the dry mix into the case in four or five increments prior to fusion of the oxidizer. A total of 24 Mk 21-sized binderless flares were prepared containing gran 17 magnesium; four were prepared using gran 18 magnesium. These flares were tested in the light tunnel along with six NOTS 701A flares (same size, case, and composition as the Mk 21) for comparison. Test data are given in Table 4. The average output of the 701A flares was somewhat higher than that of the binderless flares containing gran 17 magnesium; however the 701A burning was erratic and one especially high value raised the average output considerably. (Tests on more 701A flares would have been desirable if more had been available.) Burn times of the binderless flares containing gran 18 magnesium were appreciably longer than those of the flares made from gran 17 magnesium; however the average efficiency (cd-sec/g) was approximately the same.

TABLE 4. Performance of Mk 21-Size Flares.

Flare type	Burn time, sec	Light output, cd	Efficiency, cd-sec/g
Binderless, gran 17 Mg	22.6	153,000	32,900
NOTS 701A[a]	24.6	188,000	42,400
Binderless, gran 18 Mg	36.6	92,000	32,200

[a] Mg (gran 15)	56%
$NaNO_3$	34%
Polyvinyl chloride	2%
Laminac-Lupersol	4%
Styrene monomer	4%

The performance specifications for Mk 21 flares require an output of 150,000 cd and a burn time of 25 seconds (sea level). These figures are approximated by the binderless flares containing gran 17 magnesium, although the burning rate tends to be slightly higher.

MELT-CAST PHOTOFLASH COMPOSITIONS

BACKGROUND

Photoflash cartridges and bombs used for high-altitude aerial reconnaissance photography normally contain a loose-power pyrotechnic charge consisting of fine aluminum powder and finely ground oxidizer. Such compositions show a high sensitivity to impact, friction, and static electricity. Thus, there are hazards associated with both mixing these compositions and handling devices containing them.

The concept of using a fusible inorganic oxidizer and a metal powder to produce a binderless cast flash charge was an outgrowth of the previously discussed work on binderless cast illumination flares and similar work on hybrid propellant grains. During this earlier work, it was observed that such mixtures were not excessively sensitive. Therefore, in an effort to increase the safety of flash charges, exploratory development was carried out on melt-cast compositions as a possible replacement for the hazardous conventional loose-powder charge.

SELECTION OF OXIDIZER

A literature search produced melting point/composition data for a number of eutectic systems composed of perchlorates, nitrates, and nitrate/perchlorate mixtures. Seven of these oxidizer systems were selected for testing; all eutectic mixtures were prepared from reagent grade chemicals. To select the oxidizer having the best performance, cast compositions were fired in small steel-cased test cartridges (1 1/4 inch diameter x 3 3/8 inch long x 0.035 inch wall thickness). These charges (120-130 grams) were prepared by fusing the oxidizer (60%), stirring in 20μm aluminum (40%) by hand, then pouring the mix into the steel cases around a 1/4-inch-diameter Teflon mandrel extending the length of the case. The well formed by removal of the mandrel was filled with high explosive (tetryl pellets) to actuate the charge. The explosive core was initiated with an Engineers Special blasting cap.

Light output measurements (Appendix) were made on six or more firings of each of the seven oxidizer systems. Highest peak cd was obtained from the devices containing the Li/Na perchlorates eutectic; it was assigned a "relative efficiency" of 1.00 for comparison with the other oxidizers. All the oxidizers are listed in Table 5 in the order of decreasing "efficiency". The small test devices showed a rapid rise to peak candlepower (1-3 msec) and a comparatively rapid decay. The bulk of the light was produced during the first 10-15 msec.

TABLE 5. Eutectic Oxidizers for Photoflash Compositions.

Composition	Wt., %	Melting point, °C	Relative efficiency	Source
$LiClO_4$ $NaClO_4$	68.6 31.4	207	1.00	Ref. 6
$LiClO_4$ $NaClO_4$ $Ca(ClO_4)_2$	57.0 21.6 21.4	202	0.94	Ref. 6
$LiClO_4$ $LiNO_3$	64.0 36.0	172	0.71	Ref. 2
$LiClO_4$ $NaNO_3$	70.0 30.0	180	0.62	[a]
$LiClO_4$ NH_4ClO_4	66.0 34.0	182	0.61	Ref. 7
$LiClO_4$ $KClO_4$	70.8 29.2	207	0.58	Ref. 8
$LiNO_3$ $NaNO_3$ KNO_3	23.5 16.3 60.2	120	0.26	Ref. 1

[a] U. S. Naval Ordnance Test Station. Unpublished data. Approximate eutectic composition and melting point.

TESTS ON 100 GRAM CAST FLASH CHARGES

Further work with small devices was done on cartridges containing 100 grams of 20μm aluminum and Li/Na perchlorates eutectic. These were made by two methods. The first involved loading a mixture of coarsely ground oxidizer and aluminum into the metal charge case (with an extension to accomodate the loose mix), heating the oxidizer until it was fused, then compacting the mixture by vibration. As metal content was increased, the mixtures became less fluid and it was necessary to modify the procedure. For this second method, a small pressure (< 100 psi) in addition to vibration was applied to the mixture during fusion. The essential parts of the arrangement are shown in Fig. 2. The loaded charge case and extension, wound with a heating tape, was mounted on a jack that could be operated remotely. The Teflon ram was anchored in a fixed position. When the oxidizer reached the desired fluidity (at about 10-15°C above its melting point), the vibrator was turned on and the heated charge case assembly was raised against the fixed ram by means of the jack. This procedure gave well-compacted flash charges.

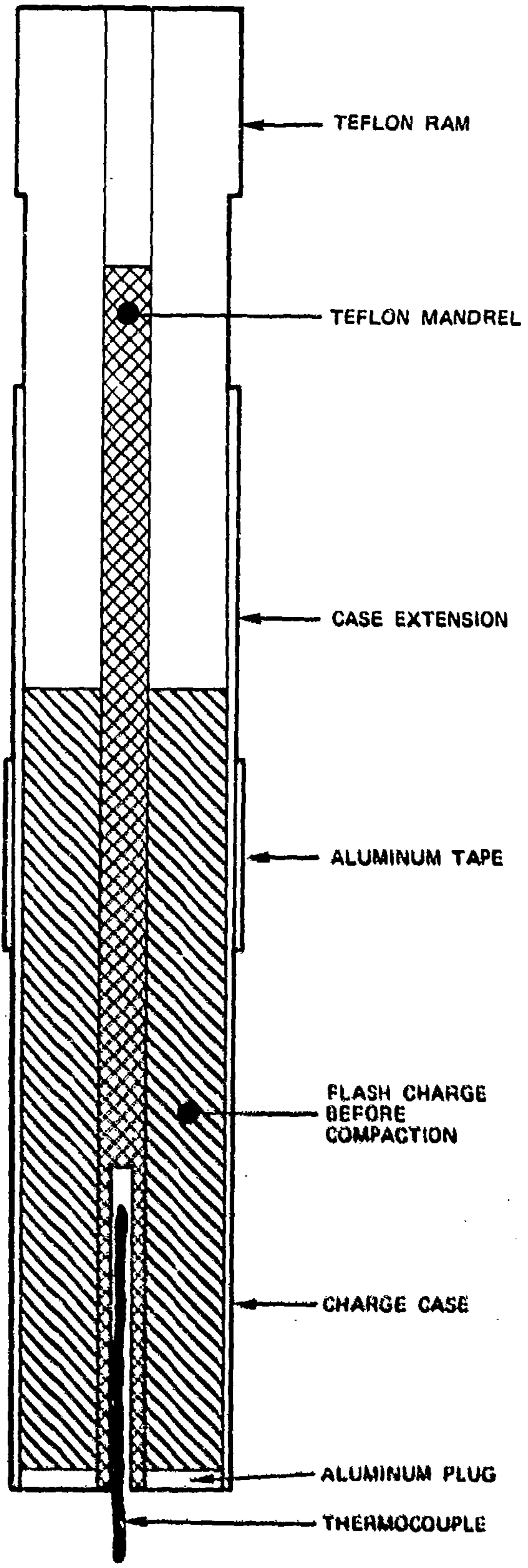

FIG. 2. Apparatus for Preparing Photoflash Charges.

Effect of Varying Metal:Oxidizer Ratio

To test the effect of metal:oxidizer ratio on light output, a series of small charges was prepared in which the percentage of 20μm aluminum was varied from 40 to 70%. Light output measurement (Table 6) showed that the peak increased from 42.7 x 10^6 cd at 40% aluminum to 53.3 x 10^6 cd at 55% aluminum, then decreased. Based on these tests, peak brightness was obtained in the 50-60% aluminum range.

TABLE 6. Effect of Metal Content on Peak Light Output (Untreated Aluminum).

Metal:oxidizer ratio	Number of tests	Average peak, cd x 10^6	Average time to peak, msec	Aveage time to decrease to 10% of peak, msec
40:60	3	42.7	0.8	12.0
50:50[a]	6	50.2	1.1	15.2
55:45	7	53.3	1.9	17.8
60:40	5	52.4	2.0	19.8
65:35	6	37.2	3.6	21.8
70:30	6	37.3	3.5	24.7

[a] 120-130-gram charges, all other 100-gram charges.

Use of Surface-Treated Aluminum Powder

It did not appear to be feasible to remove the last traces of moisture from the Li/Na perchlorates eutectic, therefore, it seemed likely that this moisture would react with the aluminum during storage. Consequently, coated aluminum powder was tested as a replacement for untreated powder. Dichromated aluminum powder, the first material tested, could not be used because it caused decomposition and frothing of the perchlorate melt. Aluminum treated with an acidic phosphate solution was satisfactory, however, and was more easily wetted by the fused oxidizer than was the untreated powder. In addition, it gave a more thermally stable mixture. There was no appreciable difference in light output between mixtures containing phosphated and untreated aluminum. Light output data from a series of devices containing phosphated aluminum powder are given in Table 7. Peak candlepower was obtained in the 55-60% metal range.

Effect of Charge Orientation. The effect of charge orientation on light output of the 100-gram devices was found to be small. Six tests were conducted with the devices in vertical and horizontal positions (three each). For these tests the charges were fired in front of a metal framework having vertical and horizontal members marked at 1-foot intervals. Fireball size and shape were recorded from the front with a Hycam camera operating at 5,000 frame/sec. Light output was measured by a photocell to the rear directly opposite the camera. (Obstruction of light by the framework resulted in somewhat lower outputs than were previously recorded for devices of this size; however, since this was a constant factor, comparative measurements between vertical and horizontal firings were still possible.) The data are given in Table 8 in the order in which the charges were fired.

TABLE 7. Performance of 100-Gram Flash Charges With Phosphated Aluminum.

Metal:oxidizer ratio	Number of tests	Average peak, cd x 10^6	Average time to peak, msec	Average time to decrease to 10% of peak, msec
40:60	4	34.3	0.8	12.3
50:50	4	48.3	1.1	15.0
55:45	4	50.5	1.4	17.0
57.5:42.5	5	53.2	1.8	19.3
60:40	5	47.4	2.0	19.9
62.5:37.5	4	46.3	2.7	22.0
65:35	3	42.7	2.4	22.5

TABLE 8. Performance of 100-Gram Flash Charges in Vertical and Horizontal Positions.

Charge position	Peak cd x 10^6	Time to peak, msec	Time to decrease to 10% of peak, msec
Vertical	34	2.0	18.4
Horizontal	36	2.0	21.4
Vertical	33	2.0	18.4
Horizontal	39	2.0	20.8
Vertical	37	2.0	19.0
Horizontal	36	2.2	18.8
Average	35.8	2.0	19.7

High-speed camera coverage of the tests showed little difference in size or shape of the fireball between vertical and horizontal positions of the charge. A fairly uniform fireball approximately 4 feet in diameter was obtained in all tests. Photocell measurements showed a slightly higher output for the devices when they were fired in the horizontal position, i.e., with the photocell directed toward the functioning end of the charge. However, this amounted to only 6.4% based on average values for the two positions.

Non-Metallic Case Materials

In a preliminary test, two of the small cast charges in aluminum cases (charge weight 365 grams) underwent partial deflagration when struck by a 30 caliber bullet. Since the use of a soft case material might be expected to reduce bullet impact sensitivity (on the basis of past experience with explosives), it was decided to explore the use of such a material for cast flash charges. Accordingly, cast 100-gram charges (55:45 metal:oxidizer ratio) were prepared in a mold from which they could be removed. They were then encased in three layers of 3M No. 69 glass cloth tape. Test firings showed that the average light output was as good as that obtained from charges of the same composition in steel cases. Unlike loose-powder charges, which require a rigid case for proper performance, the cast charges functioned satisfactorily with much less confinement.

TESTS ON MELT-CAST M123-SIZE CHARGES

The M123A1 photoflash cartridge is fired from an outer-case type dispenser. The charge case contains 1.75 pounds of photoflash powder (as well as delay pellets) and produces 260 x 10^6 candlepower for 40 msec. For the work on cast photoflash compositions, standard M123 aluminum charge cases were used. Cast charges were prepared directly in the cases and measured approximately 2 1/2 inches in diameter by 5 1/2 inches long.

Flash charges of this size were prepared remotely using a procedure similar to that followed for preparation of high-metal-content charges in the small steel cases. A mixture of coarse oxidizer and aluminum was loaded into a charge case (with extension) and heated with electrical heating tape. The temperature was regulated with a Honeywell recorder controller. The case contained a Teflon mandrel which, after removal, formed the burster well. After heating the mixture to 245°C (well above the melting point of the oxidizer) and holding the temperature there for at least 1 hour, the mixture was compacted by vibration. Attempts to aid compaction with low pressure from a Teflon-faced ram (as was done with small charges) failed because of heat losses to the ram. For some castings, two separately controlled shorter heating tapes were used, making it possible to cool the castings progressively from bottom to top. This reduced cavity formation at the top of low-metal-content charges and also reduced the size of oxidizer crystals formed on cooling. However, it had no effect on performance of the flash charges.

All of the work on M123-size charges was done using untreated 20μm aluminum powder. An order for phosphate-treated 20μm powder arrived too late for use in the larger charges.

The first M123-size charges contained 55% aluminum and 45% Li/Na perchlorates eutectic. Initially, four charges with a 3/4-inch-deep burster well were cast. The charge weight was 1,000 grams; burster weight was 80 grams (tetryl). These were fired 10-12 feet above ground level in a vertical position. One phototube directed toward the side of the devices was used to measure light output. The charges gave an average peak candlepower of 175 x 10^6. Average time to peak was 2.3 msec and time to decrease to 10% of peak averaged 33.3 msec. High-speed photography showed that the fireball of these charges was spherical during the early stages of growth, and that it had become somewhat spheroidal (approximately 8 x 10 feet) by the time peak brightness was reached.

The next cast charges were made with a 1-inch-deep burster well (charge weight 950 grams; burster 116 grams tetryl) and at aluminum contents of 40, 45, 50, and 55%. All of these were fired on a fixture that permitted positioning them horizontally 14 feet above ground. Two photocells were used for light measurements. One was directed toward the end and one toward the side of the devices. The data are shown in Table 9. Unlike the small charges, peak candlepower did not increase with increasing metal content up to 55%. Integral light output increased, however. This increase was slight over the first 10 msec, but more marked over a 40 msec period. The average peak measurement from the end of the charge was 293 x 10^6 candlepower; from the side, the peak was 214 x 10^6 candlepower. The time-intensity curves showed multiple peaks, with the maximum being reached most rapidly on the phototube toward the side of the device. The first peaks were probably produced by the primary oxidizer/metal reaction, while the second peaks resulted from a secondary reaction of metal powder with air.

A further increase in burster size to 1 1/4 inches (charge weight 854 grams) resulted in a drop in peak candlepower. The average of four devices was 244 x 10^6 candlepower measured toward the end of the charge and 149 x 10^6 toward the side of the charge. The low output from the side of the devices was probably due to an increase in the lenticular shape of the fireball with the larger burster.

It was possible to obtain better fluidity of the mix and make charge fabrication easier if spherical instead of atomized aluminum powder was used. Combustion was poorer, however, and a decrease in average peak candlepower occurred. The data from four such charges fired with a tetryl burster are given in Table 10.

COMPARISON OF M123A1 CHARGES WITH MELT-CAST CHARGES

Standard M123A1 charges were fired for comparison with M123-size melt-case charges. Four were tested with a phototube directed toward the end of the devices; no measurement was made from the side. An average peak candlepower of 261 x 10^6 was obtained, compared to 293 x 10^6 candlepower for melt-cast charges fired in the same way.

SAFETY CHARACTERISTICS OF MELT-CAST MIXTURES

Impact, Friction, and Electrostatic Sensitivity

Thin sheets of cast material broken into small bits were used for these routine safety tests. Mixtures of the Li/Na perchlorates eutectic and 20μm aluminum were tested for impact sensitivity over a 10-50% metal range. The mixture having a metal:oxidizer ratio of 40:60 was the most sensitive. This may be due to the fact that it is near to stoichiometric proportions. The data are shown in Table 11. Phosphate treatment increased sensitivity slightly. Impact sensitivites of mixtures containing phosphated aluminum were determined over the 40-60% metal range. Values of 50 cm for 40%, 60 cm for 50%, 64 cm for 55%, and 81 cm for the 60% aluminum mixtures were obtained.

TABLE 9. Performance of M123-Size Flash Charge (1-Inch Burster Charge).

Test No.	Metal:oxidizer ratio	Peak cd x 10^6	Time to peak, msec	Time to decrease to 10% of peak, msec	cd-sec x 10^3[a]	cd-sec x 10^3[b]
9	40:60	260	3.5	31	2,015	3,410[c]
		210	2.0	32	1,500	2,730[d]
10	40:60	295	2.5	33	2,445	4,295[c]
		230	1.0	28	1,810	3,605[d]
11	40:60	335	3.5	33	2,720	4,465[c]
		220	1.5	33	2,085	4,100[d]
12	40:60	320	4.0	33	2,660	4,690[c]
		220	1.0	28	1,805	3,210[d]
13	45:45			Missed oscilloscope trace		
		220	1.0	33	1,935	3,970[d]
14	45:55	310	3.4	34	2,550	4,855[c]
		220	1.0	33	1,900	3,960[d]
15	45:55	240	3.0	38	2,025	3,786[c]
		190	1.0	36	1,375	2,946[d]
16	45:45	[illegible]5	3.0	32	2,090	3,683[c]
		200	1.0	33	1,420	2,883[d]
17	50:50	340	3.0	41	2,880	5,758[c]
		225	1.0	40	1,985	4,476[d]
18	50:50	285	2.0	40	2,470	5,064[c]
		190	1.0	43	1,700	3,814[d]
19	50:50	310	3.0	38	2,725	5,819[c]
		220	1.0	42	1,890	4,276[d]
20	50:50	255	2.0	43	1,945	3,943[c]
		215	1.0	38	1,765	3,986[d]
21	55:45	300	2.0	40	2,565	5,789[c]
		200	1.0	47	1,822	5,065[d]
22	55:45	2[illegible]	2.5	42	2,212	4,591[c]
		220	1.0	52	2,001	5,312[d]
23	55:45	290	2.0	45	2,517	5,762[c]
		210	1.0	52	1,799	4,480[d]
7	55:45	315	2.5	48	2,770	5,430[c]
		230	5.0	42	2,300	5,405[d]

[a] Integral cd-sec for first 10 msec.

[b] Integral cd-sec for first 40 msec.

[c] Phototube toward initiator end of device.

[d] Phototube toward side of device.

TABLE 10. Performance of Flash Charges Containing Spherical Aluminum.

Test No.	Peak cd x 10^6 (end on)	Peak cd x 10^6 (side on)
27	230	160
28	165	105
29	195	140
30	180	120
Average	193	131

TABLE 11. Impact Sensitivity of $LiClO_4$–$NaClO_4$–20μm Al Mixtures.

Metal:oxidizer ratio	50% point, 2 1/2 kg wt.
10:90	246 cm
20:80	126 cm
30:70	79 cm
40:60	47 cm
50:50	96 cm

ABL sliding friction tests (10 ZIL) on a mixture containing 40% untreated aluminum powder and the Li/Na perchlorates eutectic gave a value of 260 pounds. The same mixture containing phosphated aluminum gave no fires at 1,000 pounds.

Tests for electrostatic sensitivity were made on all the above mixtures up to 0.25 joule. No fires were obtained in 10 tests.

For comparison, a loose-powder mixture of 20μm aluminum (40%) and potassium perchlorate (60%) was prepared. This mixture had an impact sensitivity of 18 cm, a friction sensitivity of 72 pounds, and no fires in 10 tests for electrostatic sensitivity.

Differential Thermal Analysis

Differential thermal analyses were made on mixtures containing 40% 20μm aluminum and 60% Li/Na perchlorates eutectic. A mixture containing untreated aluminum powder showed two exotherms in the 450-525°C region. Thermograms of the same mixture, but containing phosphated aluminum, showed a marked reduction of the first peak (almost to the point of disappearance) and also a slight reduction of the second peak.

Cook-Off Tests (Controlled Heating to Decomposition)

Mixtures weighing 600 grams were used in these tests. With the larger sample size, the onset of exothermic reaction occurred earlier than in the DTA runs. However, increased stability of the mixtures containing phosphated aluminum was noted. A mixture containing 50% untreated aluminum and 50% eutectic oxidizer showed the onset of a strong exotherm at about 300°C. Heating was continued up to the melting point of the metal (660°C) but no deflagration took place. A similar mixture containing phosphate-treated aluminum did not show a strong exotherm until a temperature of 390°C was reached.

Bullet Impact Tests

Tests were made on the effect of a 30 caliber AP projectile fired at the flash devices from 25 yards. Initial tests were made on 375 gram charges in aluminum cases that approximated a M112A1 photoflash cartridge in size and shape.[3] Partial deflagration occurred. Tests on M123-size cast charges, both with and without a burster (Composition C-3), produced explosions. High-speed photography indicated a much faster reaction with the larger M123-size charges. Standard M123A1 charges (loaded charge case only) also exploded on bullet impact, as did a cast charge encased in glass cloth. Light output measurements were made of the explosions of the larger devices at bullet impact. The values obtained approximated those measured during normal firing of the devices.

Tests With Blasting Cap

In an effort to better define the sensitivity of the aluminum and Li/Na perchlorates eutectic castable flash compositions, tests were made in which blasting caps of different sizes were fired on castings of the mixture. Using a mixture containing 40% aluminum (20μm), caseless cylindrical castings 3/4 x 3/4 inch, 1 x 1 inch, and 1 3/16 x 2 1/2 inches were made. The blasting caps were taped to the castings end to end and fired. All the caps had "shaped-charge dimples" in the end of their metal cases. No explosion of the castings were obtained with No. 6 caps (base charge 317 mg PETN) or No. 8 caps (base charge 447 mg PETN). An Engineers Special cap (base charge 875 mg PETN) gave explosions with all sizes of castings. With the two smaller castings, some unreacted material was found at the firing site, indicating that the explosion had not propagated completely.

It was also possible to cause explosion of a cast M123-size charge (without burster) in a standard aluminum case by firing an Engineers Special taped to the outside of the case. In the same type of test, a standard M123A1 charge was exploded with a much smaller detonator, the Mk 71 Mod 0 (base charge 120 mg lead azide/PETN). Although a direct comparison between cast and loose-powder charges is not possible because the latter can not be tested except in the confinement of a case, the above experiments indicate that the cast charges require a much greater stimulus to produce an explosion.

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[3] The M112A1 aluminum case is 1.57 inches in diameter x 7.73 inches long.

SUMMARY AND CONCLUSIONS

It was demonstrated that cast photoflash charges can be made from aluminum and an alkali metal perchlorate eutectic. The best of these give performances as good, on a volume basis, as conventional photoflash powders. The new types of charges do not deflagrate on slow cook-off and are less sensitive to impact and friction than conventional charges. However, M123-size charges are sensitive to bullet impact. In view of the anticipated high cost of developing safe and efficient production facilities for the melt-cast material, and the uncertainty of future photoflash requirements, further work is not contemplated.

Appendix

LIGHT OUTPUT MEASUREMENTS

Candlepower measurements were made using a GL 1672 phototube in conjunction with a cathode follower and a balance bridge. The bridge is used for balancing the output to zero and for setting a known calibration in candlepower referenced to a bulb calibrated by the National Bureau of Standards, Washington, D.C. The phototube is referenced to the visible spectrum by using a C.I.E. standard filter. The response time of the phototube is about 1 msec. This was calibrated against a stroboscope using an oscilloscope.

During a light output measurement the oscilloscope trace was recorded with a Polaroid camera.

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