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SMOKE/FLAME PYROTECHNIC MARKER COMPOSITIONS

WASATCH DIVISION
THIOKOL CHEMICAL CORPORATION

TECHNICAL REPORT AFATL-TR-73-199
SEPTEMBER 1973

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AIR FORCE ARMAMENT LABORATORY
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EGLIN AIR FORCE BASE, FLORIDA

Smoke/Flame Pyrotechnic Marker Compositions

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FOREWORD

This report was prepared by Thiokol Corporation, Wasatch Division, P.O. Box 524, Brigham City, Utah 84302, under Contract F08635-71-C-0136 with the Air Force Armament Laboratory, Eglin Air Force Base, Florida. This report covers work accomplished between May 1971 and June 1973. Lieutenant Russell A. Armstrong (DLIP) was the program manager for the Armament Laboratory.

Mr. Max Sears, Mr. Roy Minert and Mr. Peter Evanoff acted as Program Managers for the Wasatch Division while Mr. G. Shaw was the Principal Investigator who guided the composition development from program inception. This report has been given the corporation internal number designation. TWR-7776.

This technical report has been reviewed and is approved.

F Ramon Bonanno

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ABSTRACT

This report summarizes the work accomplished in the development of castable combined smoke/flame pyrotechnic compositions applicable to a wide variety of markers ranging from the 2.75-inch FFAR to the 4.87-inch LUU-1/B target marker. As a result of this investigation, three color combinations were selected for further development. They included red flame-white smoke, red flame-red smoke, and yellow flame-orange smoke compositions. With a view to an end-item product, the development program included a series of environmental and visibility tests for overall composition evaluation. The development of the red-white and yellow-orange compositions was successful, and these compositions show indication of satisfying the requirements of an operational combined smoke/flame target marker system. Unfortunately the red-red combination proved to be a more difficult problem, and although some promising approaches were generated, additional composition development is required to meet the ultimate marker objectives.

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TABLE OF CONTENTS

Figure LIST OF FIGURES Page

LIST OF TABLES

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SECTION I

INTRODUCTION

Current target and rescue markers utilize pyrotechnics which provide either day smoke or night flame signals but not both. From a logistics standpoint it would be highly desirable to replace the existing markers with pyrotechnic compositions which provide continuous simultaneous day and night capability. To qualify as an acceptable replacement, the compositions must provide flame intensities and smoke quantities, per unit volume, comparable to the conventional compositions currently in use.

The Air Force Armament Laboratory is actively engaged in the development of pyrotechnic compositions which produce a continuous source of colored flame and colored smoke. Several compositions simultaneously produce smoke and flame; however, white phosphorus munitions and magnesium/sodium nitrate flares are typical formulations which produce a yellow or white flame and white smoke. This combination is unsatisfactory since it is difficult to distinguish from the combustion of wood and vegetation which are typical features in combat areas. Virtually all colored smokes presently in use are produced by relatively low temperature vaporization and subsequent condensation of organic dyes. Unfortunately, the organic dyes are decomposed when subjected to the high temperature environment associated with pyrotechnic flames; hence, new mechanisms for smoke production must be identified to meet the requirements of single composition day-night markers. Although hybrid smoke-flame markers have been developed, they basically utilize separate compositions and exhaust ports which introduce added complexity in an end item assembly and reduce reliability in field applications.

The present inventory of markers imposes a wide variety of constraints on the development of a new pyrotechnic composition. Ideally, the composition should be consistent with markers ranging from the 2.75-inch FFAR to the 4.87-inch LUU-1/B target marker. To be compatible with this wide range of marking systems, the new compositions must be capable of surviving adverse environments such as high "g" loading induced by high velocity impact and be flexible enough to permit formulation adjustments to maintain a constant volumetric burn rate. With an end item in mind, the compositions should be relatively inexpensive, easy to prepare in a variety of shapes and sizes (i.e., castable, tampable, etc.), non-toxic, and safe to handle. Finally, the compositions must be capable of exposure to extremes in temperature, humidity, vibration, and long term storage without degradation in performance.

SECTION II

SUMMARY

The objective of this program was to develop new compositions capable of providing simultaneous smoke/flame signals comparable to existing flares and smoke grenades. To establish overall concept feasibility, the development program encompassed a three-phase effort which included Phase I, Composition Development; Phase II, Feasibility Demonstration; and Phase III, Methodology and Scale-up Testing.

A combined colored smoke/flame signal involves the voltilization of metals and metal derivatives to provide both color-emitting species for the flame and, by way of condensation, suitably colored reflecting inorganic pigments for the smoke. The smoke pigments can be either vaporized directly from the composition or be formed in the flame zone and eventually condensed to submicron sized particles suitable for the formation of a smoke cloud. The most successful clouds were obtained from materials which were comparatively volatile since nonvolatile pigments tended to form larger particles which rapidly fell out of the combustion zone producing an ash around the flare grain and a low density smoke cloud.

A large variety of metals were investigated, and it was observed that the metal halides and oxides were the best candidates for the colored smokes. The most vivid colors were produced by metallic iodides consisting of bismuth and lead followed by molybdenum and misch metal. To a lesser extent, other materials also gave colored smokes in small laboratory mixes but generally when a binder was added the color and density were markedly degraded. A summary of the smoke-producing metals that were considered in this study including the specific compounds which provide the color pigmentation are listed in Table I.

At program initiation the smoke/flame colors of interest to the customer were red, yellow, orange, and green. During the course of the development phase it was found that although small scale mixes in the laboratory using cobalt-based compositions gave good green smokes, scaled-up versions burned out of doors yielded smokes that rapidly faded to white or bluish white clouds. In addition, all attempts to produce a green flame with a green smoke failed. Technical difficulties were also encountered in the development of the red smoke/flame signal. Compositions were formulated that produced excellent red smokes using bismuth-iodine based formulations but when strontium oxidizers were added to provide a red flame the smoke quality was degraded and the flame was inadequate. An alternate approach

TABLE I. COLOR SMOKE PRODUCING COMPOUNDS

COLOR	HALIDES	OXIDES
Red	BiI_3, BiOI MoI_3 Misch metal iodides	
Orange	BiI_3 or BiOI with PbI_2	Fe_2O_3 Pb_3O_4
Yellow	PbI_2, $FeCl_3$ $CuCl_2$, $MnBr_2$	PbO or Pb_2O_3 V_2O_5
Green	$CoCl_2$, $CoBr_2$, VCl_2	

was considered in which separate flame and smoke compositions were cast as a double grain side-by-side in a single candle. This provided better performance than single grain compositions when tested under the low humidity conditions existing at the contractor test site, but when tested at Eglin AFB both the smoke and flame qualities were badly degraded. In any event the hybrid grain was not considered an acceptable concept since it would present a fabrication problem in an end item production unit. Both the orange and yellow compositions produced vivid colored smokes of excellent quality although the flame associated with the orange composition was yellow in color rather than the anticipated orange. When tested at Eglin, the yellow composition produced an orange-colored smoke similar to the orange candidate composition. The color change in the yellow smoke was attributed to the hydrolysis of the lead iodide pigment induced by the prevailing high humidity conditions. A summary of the composition evaluation is presented in Table II along with a cobalt/hexachloroethane composition which produced an excellent white smoke signal with a light red flame in tests at the contractor facility and a white flame at Eglin.

As a result of these tests and anticipated tactical usage, the program was redirected to develop red flame/white smoke, red flame/red smoke, and yellow flame/orange smoke marker compositions. Because of continued difficulties encountered with the red/red composition, the Air Force requested that primary consideration be given to the red/white and yellow/orange combinations in order to complete the Phase I task effort.

A number of metals form white-colored oxides which can be incorporated in the white smoke composition. The more promising materials included magnesium, titanium, zinc, aluminum, and cobalt. Of these materials only the aluminum compositions could accommodate high percentages of metal for smoke production and maintain a deep red flame.

The candidate formulations were tested at the contractor plant site, and a duplicate set of 2.25-inch-diameter by 3-inch-long candles were sent to the Air Force for evaluation. The test candles included two formula variations of the red/white composition and a typical yellow/orange composition. A list of the composition formulations, along with the linear burn rate characteristics, is presented in Table III.

One significant change which was incorporated in these compositions was the use of a Maleic Anhydride-Epon 812 binder system which provided better mechanical properties and improved pot life. Of the two red/white compositions, formulation 91-4 provided the best smoke/flame signal. The addition of the aluminum sulfate acted as a coolant and apparently stabilized the formation of the red emitting ($SrCl^+$) species and produced an excellent

TABLE II. PRELIMINARY DEMONSTRATION SMOKE-FLAME COMPOSITIONS

SMOKE COLOR	Orange	Red[1]		Yellow	White
FLAME COLOR	Orange	Red		Yellow	Red
COMPOSITION					
Fluoroalkyl acrylate binder[2]	-	6	-	-	-
Morestor 905 (Pfizer)	8	-	-	15	-
Hetron 92TG (Hooker)	-	-	-	-	7
Bismuth	18	24	-	-	-
Ammonium Iodate	18	28	-	-	-
Magnesium	2	2	12	2	5
Lead Iodide	33	30	-	63	-
Lead Iodate	21	-	-	-	-
Potassium Perchlorate	-	10	-	20	-
Cobalt	-	-	-	-	27
Hexachloroethane	-	-	-	-	26
Strontium Perchlorate	-	-	-	-	35
Strontium Perchlorate-Glycine	-	-	34	-	-
Strontium Nitrate	-	-	20	-	-
Dechlorane	-	-	7	-	-
Ammonium Perchlorate	-	-	12	-	-
Polyester F17-80 Binder (Witco)[2]	-	-	15	-	-
CONTRACTOR TESTS					
Smoke Color	Orange	Red		Yellow	White
Smoke Density	Very Good	Good		Very Good	Very Good
Flame	Yellow	Light Red		Yellow	Light Red
Burn Rate (ips)	0.045	0.046		0.022	0.043
EGLIN AFB TEST RESULTS					
Smoke Color	Orange	Violet Red		Light Orange	White
Smoke Density	Very Good	Fair		Very Good	Very Good
Flame	Yellow	White to Very Light Red		Yellow	Very Light Red to White

[1] Grain consisted of separated compositions cast side by side into one candle using 60% smoke and 40% flame comp.

[2] Binder includes curing agents; Morestor 905 included 1.8% PAPI and 0.002% FeAA; Witco F17-80 included 2.2% ERL-0510 and 0.05% chromium octoate; Fluoroacrylate contained 0.03% VAZO.

TABLE III. DEMONSTRATION SMOKE-FLAME COMPOSITIONS

COMPOSITION	087	94-11	91-4
Smoke Color	Orange	White	White
Flame Color	Yellow	Red	Red
Binder			
Epoxy/Anhydride	8.0	7.0	7.0
Aluminum	-	39.0	39.0
Strontium Nitrate	-	35.0	37.0
Strontium Chloride	-	19.0	15.0
Aluminum Sulfate	-	-	2.0
Ammonium Chloride	-	-	-
Bismuth	18.0	-	-
Ammonium Iodate	18.0	-	-
Lead Iodate	21.0	-	-
Lead Iodide	33.0	-	-
Magnesium	2.0	-	-
Burn Rate (ips) (typical)	0.053	0.048	0.046

red flame. The yellow/orange composition produced a high quality smoke signal, but the flame was partially obscured by the dense smoke. These compositions were exposed to both temperature shock and random vibration environments as specified by MIL-STD-810 without any visual effects, and subsequent testing indicated no discernible change in either the signal characteristics or burning rate.

Color value determinations were conducted by means of a rapid scan spectrophotometer, and the results show that both the red and yellow flames exhibited high color purity (> 90%) and the dominant wavelengths were in the desired visible spectral region.

During the Phase II feasibility effort further composition tailoring was completed to improve the flame characteristics of the yellow/orange composition and satisfy the specified volumetric burning rate of 5 cc/sec for both the 2.25-and 4.87-inch-diameter configurations. A detailed formulation of the final candidate compositions are presented in Table IV, along with the burning rate characteristics. All the compositions satisfy the burning rate requirements except for the slow burning red/white combination which is approximately 35 percent greater than specified. The burning rate of the red/white composition was reduced by adding ammonium chloride which acts as a burning suppressant. In the case of the yellow/orange composition, the flame output was improved by increasing the magnesium content and burning rate was adjusted by the addition of ammonium chloride and increasing the binder level. The compositions successfully withstood the 5000 "g" impact test and the 40-foot drop tower tests. Finally, the full scale candles (4.87-inch-diameter and 10-inch-length) did provide both day and night signals which were visible from an aircraft at a distance of 5 nautical miles at altitudes between 2000 and 4000 feet.

The red/white and yellow/orange compositions developed under this program verify that target and rescue markers which can provide simultaneous smoke/flame signals for day and night operation is feasible although complete flexibility of color combinations was not demonstrated as witnessed by the difficulties encountered with the red/red composition. Finally, the results of the impact, environmental, and visibility tests indicates that the compositions can be adapted to an operational system.

TABLE IV. FINAL CANDIDATE SMOKE-FLAME COMPOSITIONS

COMPOSITION	DL-Q131	DL-Q134	DL-Q135	DL-Q136
Smoke Color	White	White	Orange	Orange
Flame Color	Red	Red	Yellow	Yellow
Binder				
Epoxy/Anhydride	7.0	7.0	8.0	15.69
Aluminum	39.0	30.0	-	-
Strontium Nitrate	37.0	44.5	-	-
Strontium Chloride	15.0	14.5	-	-
Aluminum Sulfate	2.0	-	-	-
Ammonium Chloride	-	4.0	-	3.92
Bismuth	-	-	17.8	18.30
Ammonium Iodate	-	-	17.8	15.03
Lead Iodate	-	-	20.8	24.18
Lead Iodide	-	-	32.6	17.65
Magnesium	-	-	3.0	5.23
Burn Rate (ips) (typical)	0.046	0.022	0.058	0.016

SECTION III

TECHNICAL DISCUSSION

The objective of this program was to develop pyrotechnic compositions which will provide a simultaneous colored smoke and flame signal compatible with the requirements for day and night target and rescue marker systems. To accommodate these requirements, a variety of smoke/flame compositions are needed which can be readily adapted to markers ranging from 2.25 inches to 4.87 inches in diameter. In order to satisfy the requirements of operational marker systems, the smoke/flame compositions must provide the following capabilities:

(1) The quantity of colored smoke generated must be comparable to conventional smoke signals and provide five-nautical-mile visibility when five-mile-visibility conditions exist.

(2) The intensity and purity of the colored flame must be comparable to conventional flare signals and provide five-nautical-mile visibility when five-mile-visibility conditions exist.

(3) The composition formulations must be flexible enough to permit burn rate adjustment so that a volumetric burn rate of 5 cc/sec or less can be achieved for a range of candles varying from 2.25 (0.0768 ips) to 4.87 (0.0164 ips) inches in diameter.

(4) The compositions must be capable of withstanding a temperature shock environment (-65° F to +160° F) as specified by MIL-STD-810B without degradation in performance.

(5) The compositions must be capable of withstanding a random vibration environment specified by MIL-STD-810B without degradation in performance.

(6) The compositions must be capable of continued functioning after being subjected to 50-fps impact on hard ground.

(7) The compositions must be capable of withstanding a 5000-g deceleration load without degradation in performance.

The study consisted of a three-phase development program which included composition development, feasibility demonstration, and scale-up methodology and testing for final verification.

3.1 PHASE I - COMPOSITION DEVELOPMENT

The approach taken to generate a simultaneous colored smoke/flame composition involves the formation of color emitting species to provide the flame color and the vaporization and subsequent condensation of metal derivatives to produce the colored inorganic smoke particles. In general, the flame color and intensity is a function of the concentration of emitting species present which is directly related to the flame temperature, the concentration of specific radicals, and possible competing reactions. Flame color can therefore be tailored by controlling combustion and subsequent flame temperatures by use of burning suppressants and the quantity of binder.

The best quality smokes were obtained from materials which were readily volatilized or were formed in the vapor phase, thus leading to fine condensed particles. Less volatile materials generally formed larger particles and rapidly fell out of the combustion zone forming an ash around the flare grain instead of smoke. Of the many materials investigated, the metallic halides and oxides produced the best quality smokes being vaporized directly from the flame composition or forming in situ in the flame zone. Because of the method by which smokes are produced, the mechanism is relatively insensitive to flame temperature. This is a significant advantage since compositions can be tailored to optimize flame color by controlling combustion temperatures without appreciably affecting smoke quality. It should be pointed out, however, that the colored smoke pigments can be markedly influenced by atmospheric moisture since the complex metal halides are sensitive to hydrolysis reactions which can modify the smoke color.

This brief description of the mechanism of smoke/flame production represents a highly simplified model which can only be used as a guide for composition formulation. In reality, the mechanism is highly complex in nature and the optimum formulation of a specific color combination is very much dependent on the binder used, the liner composition, and the overall candle configuration and method of fabrication. Composition optimization is, to a large extent, empirical in nature, and experience was an important tool in guiding the composition development.

The formulation studies consisted of a series of screening tests using laboratory samples ranging from 1-to 100-gram mixes. These screening tests were used to select promising materials for the individual compositions and to assess the safety hazards associated with the processing and curing phases. During the course of the screening studies, material formulations were selected on the basis of visual observations as to flame and smoke quality. Test samples up to 20-gram mixes were burned in the laboratory fume hood while the larger sizes were tested out of doors. The promising candidate formulations were then cast in 2.25-inch-diameter sizes using the pint mixer, and these candles included both kraft paper-treated liners and aluminum cases. Because of the time and cost involved in conducting and reducing the data of the color purity tests, they were limited to the selected formulations which were based upon burn rate requirements and visual assessment of flame color and smoke density. These visual observations are somewhat subjective in nature and as such, various formulations appeared to give comparable smoke/flame signals that satisfied the maximum allowable 0.0768 ips burn rate requirement for the 2.25-inch-diameter candles. In these cases the final selection was based upon formulations which could be readily tailored for the 0.0164 ips burn rate requirement of the 4.87-inch-diameter candles. This approach provides a degree of commonality in composition formulation which is desirable for end item production markers.

During the initial phase of the composition development the smoke/flame colors of interest were red, yellow, orange, and green. As a result of this early effort the program was redirected to only develop red flame/white smoke, red flame/red smoke, and yellow flame/orange smoke color combinations. This change was requested for several reasons which included difficulties in developing a green smoke/flame signal; the orange and yellow compositions did not provide enough of a difference in signal characteristics, especially at the higher humidity conditions; and customer assessment of priorities and anticipated field application. However, the material presented in this section summarizes the results of all the color combinations which were investigated because the information acquired during the initial development phase guided the follow-on program.

3.1.1 Red Flame/White Smoke

The simultaneous red flame/white smoke signal is generated by red emitting species which provides the flame color and white reflecting condensed metal combustion products which provide the smoke cloud. A number of metals such as aluminum, magnesium zinc, titanium, and cobalt were considered and although they all generated good smoke signals only the aluminum compositions provided a simultaneous high color purity red flame.

A comparison of the different metal compositions are summarized in Table V, along with qualitative observations of the burning characteristics.

Of the metals considered, cobalt produced the most impressive white smoke clouds and had no gray tint which is exhibited by the current MK-25 smoke grenade. The cobalt containing compositions required the use of a chlorine source such as hexachloroethane to produce the cobalt oxide or possibly oxychloride salts which generate the smoke cloud. In all cases (27-2, 27-3, 27-4), the flame color was an unacceptable light red color. The cobalt compositions, in general, formed pastel green and blue smokes in the stem of the smoke cloud indicating that cobalt chloride formed in the flame zone and then further oxidation or hydrolysis yields the white oxide or oxychloride in the hot expanding cloud. It appears that the cobalt competes with the strontium in the oxidizer for the chlorine, thus limiting the formation of the red emitting $SrCl^+$ species and producing a light red flame.

The zinc compositions (31-7, 31-8, 32-1) produced good white smokes which consist of zinc oxide particles; however, the flames were white in color. This occurred regardless of the oxidizer or binder used, and it appears that the high flame temperatures prevent the formation of the red emitting species.

The magnesium and titanium fuels produced fair to good smoke signals and flame colors varying from yellow to light red. These compositions also exhibited high burning rates and did not appear as promising as the aluminum fuels for the slow burning rate compositions.

As shown in Table V, the aluminum based compositions produced the best red color flames in conjunction with a good smoke signal. Although the early formulations (44-1, 45-4) exhibited high burning rates, these studies indicated that the aluminum compositions offered the best potential for a red/white marker, and it was selected for further investigation.

In the formulations considered during the course of this investigation, the oxidizers were selected to not only provide oxygen for sustaining combustion but also to supply the basic source of the red flame emitting species. With this in mind, the oxidizer materials were limited to strontium and lithium derivatives. Early in the study it was found that lithium chlorate and perchlorate oxidizers did not produce as good red flames as the strontium compounds, and they were eliminated from further consideration.

A review of the literature indicates that the characteristic red color associated with strontium is attributed to SrO, SrOH, and $SrCl^+$ species with the strontium chloride ion providing the primary emission. Therefore,

TABLE V. RED FLAME - WHITE SMOKE COMPOSITION SCREENING TESTS

COMPOSITION	44-1	45-4	27-2	31-5	31-7	31-8	45-1	45-3	27-3	27-4	32-1
Binder											
Oxygenated Polyeste-[1]	5	5	-	-	10	10	5	5	-	-	-
Hetron 92TG	-	-	7	10	-	-	-	-	5	5	10
$Sr(ClO_4)_2$	50	61	35	-	-	50	61	46	47	47	40
$Sr(NO_3)_2$	-	-	-	45	45	-	-	-	-	-	-
$SrCl_2$	-	-	-	20	15	-	-	-	-	-	-
Al (5 micron)	45	34	-	-	-	-	-	-	-	-	-
Mg (50/200 mesh)	-	-	5	25	-	-	-	-	-	-	-
Co	-	-	27	-	-	-	-	-	24	33	-
Hexochloroethane	-	-	26	-	-	-	-	-	24	15	-
Zn	-	-	-	-	30	40	-	-	-	-	50
Ti	-	-	-	-	-	-	34	24	-	-	-
TiO_2	-	-	-	-	-	-	-	25	-	-	-
APPEARANCE											
Flame	Good Red	Very Good Red	Light-Red	Light-Red	White	White	Light-Red	Yellow	Light Red	Light Red	White
Smoke Quantity or Density	Good	Good	Very Good	Fair	Fair to Good	Fair to Good	Good Very Rapid	Good Rapid	Poor	Fair	Good
OTHER COMMENTS	Not as fast burning as 45-1 and 3	Faster burning than 44-1; best Flame									

[1] Binder consists of 39 parts maleic anhydride, 60 parts Epon 812 and 0.01 parts ferric acetonylacetonate.

two oxidizers were considered, as a chlorine source for color intensification: strontium perchlorate and strontium nitrate with strontium chloride. The strontium perchlorate oxidizer provides an excellent red color flame as indicated in Table V; however, these compositions exhibit high burning rates which cannot be readily adapted to long burning marker systems. During this screening phase it was found that the strontium nitrate/strontium chloride oxidizer system produced as good or even better red flames than was obtained with the perchlorate. The advantage of the nitrate oxidizer is a lower burn rate which provides much greater flexibility in tailoring the composition for different burn rates and lower materials cost. When the sodium nitrate compositions were scaled up to 2.25-inch-diameter grains, the flame colors faded somewhat to a lighter color; however, the addition of small amounts of aluminum sulphate which act as a coolant improve the flame quality in these full diameter candles.

Although the binder is primarily used to enhance processibility and provide the necessary material properties to satisfy environmental constraints, it was found that the binder has a marked effect on smoke quality. During the screening evaluation, essentially two basic binders were used which included a chlorinated polymer to provide a source of chlorine and a high oxygen content binder which would replace some of the oxidizer and thus add more of the smoke producing metals. The Hetron 92T6 chlorinated binder mixes processed easily; however, the cured grains were hard and brittle and did not provide the necessary material properties to withstand the environmental constraints. Primary emphasis was placed on oxygeneted polyester binders which enabled higher smoke producing metals to be used by reducing the oxidizer content. Various binders were investigated which included a Witco carboxyl terminated polyester, Morester 905 polymer, polybutadiene polymers and a maleic anhydride/Epon-812 polyester. The carboxyl terminated polyester provided a good cured grain; however, it exhibited poor pot life of the order of 30 minutes, which of course affects processing. The Morester polymers exhibited curing difficulties while the polybutadiene binders degraded the smoke quality. As a result of these studies, the Maleic Anhydride-Epon 812 polyester proved to be the best binder for the red/white composition and it was selected for further composition development.

Having selected aluminum as the fuel, strontium nitrate/strontium chloride as the oxidizer, and Maleic Anhydride/Epon-812 polyester as the binder, further composition tailoring was conducted to adjust the burn rate and improve the smoke quality.

As discussed previously, the higher burning rate compositions (94-11, 90-1) shown in Table VI produced very good red flames in small test samples but when scaled up to 2.25-inch-diameters the color often faded to light red probably due to higher temperatures in the flame core which was also evidence of increased burn rates. The addition of small amounts of aluminum

TABLE VI. RED FLAME- WHITE SMCKE FAST BURNING COMPOSITIONS

COMPOSITION	90-1	91-1	91-4	91-5	91-6	91-7	94-11
Binder Maleic Anhydride 39.4 parts Epon 812 60.6 parts	7.0	10.0	7.0	7.0	7.0	7.0	7.0
Sr $(NO_3)_2$ (200 micron)	37.0	45.0	37.0	35.0	35.0	33.0	35.0
Sr $(NO_3)_2$ (30 micron)	0	0	0	0	0	0	0
$SrCl_2$	15.0	10.0	15.0	15.0	15.0	15.0	19.0
Al (60 micron)	0	0	0	39.0	39.0	39.0	0
Al (15 micron)	41.0	35.0	39.0	0	0	0	39.0
$Al_2 (SO_4)_3$	0	0	2.0	0	0	0	0
TiO_2	0	0	0	4.0	0	0	0
Al_2O_3 (12.5 micron)	0	0	0	0	4.0	6.0	0
$Sr(ClO4)_2$	0	0	0	0	0	0	0
OBSERVATIONS							
Burn Rate, IPS	.039	.040	.046	.030	.024	.037	.052
Cloud Density	Good	Fair-Good	Good	Fair-Good	Fair-Good	Fair-Good	Good
Flame Quality	Poor Red	Good	Best Flame	Good	Good	Good	Fair
		Moderate Residue		High Residue Remaining 63 to 73%			Moderate Residue

sulphate which acts as a coolant improved the flame color as is evident in composition 91-4 in Table VI. Other coolants were tried such as titanium oxide, aluminum oxide, and magnesium carbonate but as shown by compositions 91-5, 91-6, and 91-7, the flame colors were adequate but the smoke density was reduced and the residual ash content was as high as 73% of the original weight. Formulation 91-4 was selected as the candidate fast burning rate composition (2.25-inch), and it provided the best compromise for both flame and smoke signals. This composition also yields residue content as high as 50 percent; however, a reduction in aluminum content with a corresponding increase in oxidizer to reduce the residue does not increase the smoke density. In fact, the smoke density was somewhat reduced apparently due to the lower concentration of combustion products.

To meet the burning rate requirements of the large diameter candles (0.0164 ips), ball-milled ammonium chloride which ranged from 1 to 15 microns in size was added to provide burning rate suppression. The effectiveness of ammonium chloride as a suppressant is clearly indicated by compositions 9-2, 9-4, 9-5, 9-6, and 9-7, as shown in Table VII. Reduction in burn rate is also accomplished by increased binder content; however, this resulted in a degradation of the smoke quality and in some cases, the flame color purity. Ammonium perchlorate was added to improve combustion of the aluminum fuel, and although the smoke output was increased the burn rate also increased. Of the formulations shown in Table VII, composition 9-11 appeared to exhibit the best combination of smoke/flame signals and burn rate and was delivered to the Air Force; however, the burn rate of 0.022 ips is 35% higher than the specified requirement for the 4.87-inch-diameter candles.

3.1.2 Red Flame/Red Smoke

A number of materials have been found which produce red colored smokes, and of the metals considered the more intense colors were obtained from bismuth, molybdenum, and misch metal with an iodine source. The red color is attributed to the formation of condensed particles of metallic iodides and oxyiodides. The smokes produced from these materials were degraded both in density and color when a binder and strontium oxidizers were added to provide the red flame. Compositions containing a binder tended to produce a red-violet smoke whose quality was independent of the metal fuel. It was found that the smoke quality, color, and density could be improved by the addition of lead iodide, and this synergetic effect of the color intensifier was most pronounced with bismuth-derived smokes.

During the early part of the composition screening the effort was primarily directed toward the formation of good red smokes. The best red smoke composition (066) produced a yellow flame and, as shown in Table VIII, this composition contained a fluorocarbon binder, bismuth and magnesium fuels, ammonium iodate to provide the iodine source and oxidizer

TABLE VII. RED FLAME-WHITE SMOKE SLOW BURNING COMPOSITIONS

COMPOSITION	9-1	9-2	9-4	9-5	9-6	9-7	9-8	9-9	9-11
Epon 812-Maleic Anh.	15.0	20.0	20.0	20.0	20.0	20.0	15.0	7.0	7.0
Aluminum	36.0	33.9	33.0	33.0	3[illegible].0	32.2	34.3	37.7	30.0
Strontium Chloride	12.0	11.3	11.0	11.0	11.0	10.7	11.4	12.6	14.5
Strontium Nitrate	37.0	34.8	33.9	33.9	33.9	33.1	35.3	38.7	44.5 [1]
Aluminum Sulfate	-	-	2.0	-	-	-	-	-	-
Ammonium Chloride	-	-	-	2.0	-	4.0	4.0	4.0	4.0
Magnesium Carbonate	-	-	-	-	2.0	-	-	-	-
Flame	Good	Good	Small	Good	Good	Soft	Good	Fair	Good
Smoke	Fair	Fair	Fair	Fair	Fair	Poor	Poor	Fair Good	Good
Residue 2.25 in dia wt %	43	51 Hollow [2] Core	49	51 Solid Core	48	66 Solid Core	59 Solid Core	72	51
Burn Rate (ips)									
2.25 in. dia	.038	.031	.025	.018	.026	.016	.020	.02[illegible]	.022
1.75 in. dia [1]	-	.028	-	.017	-	.013	.017	-	-

[1] Grain was wrapped with masking tape instead of using a liner and burning inside of an Al canister.

[2] Residue formed a cylinder same configuration as original candle.

requirements, potassium perchlorate as additional oxidizer, and lead iodide as a color intensifier. The data in Table VIII indicates that substitution of a lower oxygen content binder as compared to premix A (49%) degraded the smoke color and density. The smoke varied from lighter reds to light pinks or yellowish orange depending on the composition variations. The fluorocarbon binder appears to provide a halide oxidizing environment in the flame zone which tends to stabilize the bismuth colored pigments. In addition, the CF_2 radicals formed from the pyrolysis of the fluorocarbon remove water present in the flame zone according to the following reaction:

$$CF_2 + H_2O \longrightarrow CO + 2\,HF$$

This removal of water prevents the hydrolysis of the red bismuth compounds to other less intense colored derivatives.

The addition of strontium perchlorate to provide the red emitting $SrCl^+$ species for flame coloring compromised the smoke color and, as shown in Table VIII, formulation 34-4 provided the best combination of smoke and flame; however, neither signal was comparable to the conventional red flare or organic dye smoke. In tailoring the composition for flame color, the fluorocarbon binder must be replaced by an oxygenated polyester because the fluorine competes with the chlorine to form strontium fluoride which emits in the shorter wavelength region.

As discussed previously, molybdenum and misch metal were other promising materials which provide red-colored smokes when burned with a source of iodine. The colors obtained were similar to the bismuth compositions although the flames produced were much more intense.

A summary of some of the molybdenum screening compositions which were investigated is presented in Table IX. The data shows that the flame colors are primarily yellow and in those cases where the smoke clouds did provide some red color, the densities were not comparable to equivalent bismuth-derived smokes.

The misch metals exhibited burning characteristics similar to the molybdenum-based compositions, and a summary of the better smoke producing formulations is presented in Table X. One interesting observation which may prove significant in further investigations is the formation of a light red flame with a fluorocarbon binder exhibited by composition 85-7. This indicates the possibility that the misch metal is a good scavenger of the fluorine in the binder allowing the formation of the red emitting $SrCl^+$ species. The addition of misch metal to the bismuth/fluorocarbon formulations which provided the best red smoke could possibly stabilize the formation of the $SrCl^+$ species to provide a red flame.

TABLE VIII. RED FLAME - RED SMOKE COMPOSITIONS

COMPOSITION	066	29-2	29-6	2-1	37-4	34-5	14-2	44-6	21-2	98-3
Premix A[1]	6.0						6.6			
Polyester[2]		6.0	10.0		6.0	6.0		10.0	15.0	
Sylgard 182				6.0						12.0
Bismuth	24.0	24.0	30.0	24.0	22.0	14.0	27.1	17.0	12.0	15.0
Ammonium Iodate	28.0	28.0		28.0	17.0	16.0		34.0	24.0	38.0
Lead Iodide	30.0	30.0		30.0	14.0	17.0	33.7			
Lead Iodate			33.0							
Potassium Perchlorate	10.0	10.0	10.0	10.0			11.0			
Iodoform			15				20.8			
Magnesium	2.0	2.0	2.0	2.0	1.0	2.0	0.8	4.0	4.0	5.0
Strontium Perchlorate					40.0	45.0		35.0	45.0	38.0
Flame Color	Yellow	Yellow	Yellow-White	Yellow-White	Light Red	Light Red	Yellow	Light Red	Good Red	Light Red
Smoke										
Color	Good Red	Orange Red	Light Orange	Pinkish Orange	Light Red	Light Pink	Light Red	Very Light Red	Very Light Red	Light Magenta
Density	Good	Good	Good	Good	Fair	Fair	Good	Poor to Fair	Poor to Fair	Fair to Good
COMMENTS	Best Red Smoke				Best Combination of Smoke and Flame					

[1] C_7 fluoroalkyl acrylate - Viton A binder containing 9% Viton A and cured with benzoyl peroxide.

[2] The polyester binder consisted of Morester 905 (90%), isopherone diisocynate (9%) and Ferrous acetyacetonate (1%). Later it was found that Maleic Anhydride and Epon 812 gave better cures.

TABLE IX. MOLYBDENUM CONTAINING COMPOSITIONS

COMPOSITION	90-1	90-2	40-1	90-5	90-7	91-1	97-5	21-5	21-3	23-1	23-4	35-1	35-3
Polyester[1]	20	20		20				15	15				
Sylgard			23				11			15	15		
Molybdenum	22	30	40	22	22	20	18	22	27	27	17	24	24
Ammonium Iodate	58			50	58	30	48	54				29	
Lead Iodate			30						20	20	12		
Iodoform									33	33	20		29
Potassium Perchlorate		20		8		15		5					
Strontium Perchlorate							20				36	11	
Magnesium (-325 mesh)			7					4	5	5			
Hexachlorothane		30											
Flame Color	No Flame	Orange-Yellow	Yellow	Yellow	Yellow	Yellow	Yellow	Soft Red	Yellow	Orange Yellow	White	Orange Yellow	Yellow
Smoke													
Color	Orange	Yellow	Yellow	Pink	Violet	Darker Pink	Pink to Magenta	Brown-Red	Orange	Dark Orange	Red-Violet	Orange	Pink
Density	Very Good	Fair	Good	Fair to Good	Fair to Good	Good	Fair to Good	Good	Good	Good	Fair	Fair to Good	Fair to Good

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[1] WITCO F17-80 (85.3%) and ERL 0510 (14.7%) polyester binders.

TABLE X. MISCH METAL CONTAINING COMPOSITIONS

COMPOSITION	82-2	82-3	82-4	82-6	85-1	85-7	88-1	88-3
Polyester (same as Table VIII)	15	15	15	15			15	15
C_7 Fluoroacrylate					15	15		
Misch Metal	30	40	30	35	35	35	25	20
Ammonium Iodate	45						35	30
Iodoform		10	30	30	30	30		
Potassium Perchlorate	10	35	25	20	20			
Strontium Perchlorate						20	25	20
Lead Iodide								15
Flame Color	yellow-orange	yellow-orange	yellow-orange	yellow-orange	bright white	light red	reddish orange	orange
Smoke:								
Color	pink red	light pink	light pink	pink	pink red	light orange	pink red	pink
Density	good	good	good	good	very good	fair	fair	good

Another concept which was considered used two separate compositions molded side by side into one grain. The bismuth/fluorocarbon composition (066) was used for red smoke production, and a variety of strontium-based formulations was considered for the flame composition. These dual systems worked fairly well in dry atmospheric conditions experienced at the contractor's facility; however, the smoke compositions interfered with the flame, reducing its color saturation to a light red flame. When these compositions were tested under the higher humidity and atmospheric pressure conditions at Eglin AFB, the smoke and flame qualities were markedly degraded. The smoke appeared lower in density due to its more transparent violet-red color, and the flame color was predominately white with only a light red tint. A summary of some of the dual grains which were studied are presented in Table XI. The candles shipped to Eglin AFB for these tests were 2.5 inches in diameter and 3 inches in length. The smoke producing grains consisted of the red smoke composition (066) which used a bismuth base. The primary flame color-producing ingredient is a complex of strontium perchlorate and glycine which was first reported by Douda of NAD Crane, and it burns with a high color purity at a dominate wavelength of 625 nanometers. This concept, however, is not very attractive for an end item production.

Use of a pressed grain concept without binder material was a third approach considered. Only a limited number of 1/2-inch pellets were tested, and the data is summarized in Table XII. Composition 043-8 which contains the red flame ingredient strontium perchlorate appeared promising although the flame was still comparatively light in color. A reduction in the magnesium content could improve the flame color. Since these compositions contain no binder, it appears that they may be susceptible to the environmental test required, especially temperature shock. However, because these compositions burn at essentially atmospheric pressure and are designed for relatively low burn rates, the increased burning surface exposed by grain cracking (primary failure mode) may not significantly affect overall performance.

3.1.3 Yellow Flame/Orange Smoke

The development of the yellow/orange combination was guided by the information obtained from the red and yellow smoke compositions. The orange colored smoke is produced by a mixture of red bismuth iodide and yellow lead iodide condensed phase particles.

During the composition screening effort it was found that the best orange smokes were generated by formulations containing ammonium iodate, lead iodide, bismuth, magnesium, potassium perchlorate oxidizer, and an oxygenated polyester binder in place of the fluorocarbon binder used in the red smoke. The addition of lead iodate, along with the oxygenated binder, increased the optical density and decreased the red tint of the orange smoke.

TABLE XI. DUAL GRAIN RED FLAME COMPOSITIONS[1]

COMPOSITION	23-7	23-8	23-9	23-10	23-11[2]	23-12	23-13	23-14	23-15
Witco F17-80	12.79	12.79	12.79	12.79	12.79	12.79	12.79	-	12.79
ERLA 0510	2.20	2.20	2.20	2.20	2.20	2.20	2.20	-	2.20
Iron Octoate	0.01	0.01	0.01	0.01	0.01	0.01	0.01	-	0.01
Strontium perchlorate glycine adduct	46.00	46.00	42.00	38.00	34.00	-	-	100.00	85.00
Strontium nitrate	30.00	20.00	20.00	20.00	20.00	47.00	47.00	-	-
Dechlorane 510	9.00	7.00	7.00	7.00	7.00	14.00	14.00	-	-
Ammonium perchlorate	-	12.00	12.00	12.00	12.00	10.00	-	-	-
Magnesium (-325)	-	-	4.00	8.00	12.00	14.00	14.00	-	-
Potassium perchlorate	-	-	-	-	-	-	10.00	-	-
COMMENTS									
Flame Color	Orange	Orange	Light Red	Light Red	Good Red	Good Red	Good Red	Very Good Red	Yellow
Tests with Red Smoke	-	-	-	-	Red[3]	Orange[4] Yellow	Orange[4] Yellow	Intense coloration	Flame was too cool for red emission

[1] Red flame composition used with red smoke dual grain configuration.

[2] Used in conjunction with composition 066; results shown in Table II.

[3] The flame appeared red with, as expected, some decrease in the density of the red smoke produced.

[4] The flare burned red alone but combined with a red smoke grain appeared more yellow or orange.

TABLE XII. PRESSED[1] GRAIN RED SMOKE FLAME COMPOSITIONS

COMPOSITION	043-1	043-2	043-3	043-5a	043-6	043-8
Bismuth	40.0	40.0	40.0	33.0	30.0	24.0
Iodoform	35.0	35.0	-0-	0	26.0	0
Ammonium Iodate	25.0	20.0	60.0	57.0	19.0	30.0
Kaolin	0	5.0	0	5.0	0	0
Lead Iodide	0	0	0	0	25.0	0
Strontium Perchlorate	0	0	0	0	0	36.0
Magnesium (-325 mesh)	0	0	0	5.0	0	10.0
OBSERVATIONS						
Flame	Orange	Orange	None	Yellow	Orange	Red
Smoke	Violet-Red	Rust-Red	Violet	Light Red	Dark Red-Violet	Violet-Pink
Smoke Density	Very Good	Very Good	Poor	Good	Good	Good

[1] Dry blended and pressed into pellets @ 30,000 psi (1/2-inch-diameter and 1/2-inch-length)

Table XIII presents a summary of these composition screening tests. The results of these tests seemed to indicate that the best orange smokes were obtained when both lead iodide and lead iodate were used, and composition 25-9 provided the best orange smoke signal. This composition was selected for the fast burning rate marker with one change, the Morester 905 binder was replaced by another oxygenated polyester, maleic anhydride/Epon-812 which provided better grain curing and pot life with essentially no change in burning characteristics.

To satisfy the low burning rate characteristics of the large diameter candles, further composition tailoring was necessary. With the fuel, color intensifiers, and oxidizer selected, the burning rate is influenced by binder level, particle size of the ingredients, and the addition of a coolant or burning rate suppressant. Burning rate could also be adjusted by variations in the material proportions; however, the optimum levels were controlled by the color and quality of the smoke and flame. At the time the materials were purchased there was little choice in particle size of the lead and ammonium iodate oxidizers. These materials were available in only fine powders ranging from 2 to 30 microns and so particle size variations for composition tailoring could not be implemented. Instead, emphasis was placed upon increasing binder level and adding burning rate suppressants.

Rather than directly increase the maleic anhydride/Epon-812 binder level, DER 732, an epoxy terminated polypropylene glycol was added which provided characteristics particularly adaptable to a castable grain. The methyl substituted groups attached to the carbon atom containing the tertiary hydrogen in the DER 732 polymer results in a more stable epoxy compared to Epon-812 which tends to reduce the burning rate. The decreased oxygen content and the increased binder level degraded the flame size and the smoke color. The data given in Table XIV summarized the effort expended on the burning rate adjustment. Compositions 20-1, 20-2, and 20-3 represent formulations with increased binder levels from 8 to 15 percent and a decrease in magnesium content which reduced the burn rate from about 0.05 ips to rates between 0.025 to 0.035 ips. These compositions required an increase in the lead iodide content to give the orange smoke quality. The data also shows the effect of increasing the particle size of the bismuth on burn rate, and although the burn rates were reduced by a factor of 2, further tailoring was necessary to meet the 0.0164 ips requirement. This was accomplished by adding about 4% ammonium chloride as a coolant, and the effect is clearly shown in the 21 series compositions given in Table XIV. In addition, the magnesium content was increased to a 5% level to improve the flame quality. Formulation 21-6 gave the best combination smoke/flame signal, and it was selected for scale-up and environmental testing.

TABLE XIII. ORANGE SMOKE-FLAME COMPOSITIONS

COMPOSITION	25-7	25-8	25-9	25-10	25-11	25-12
Morester 905	8	8	8	8	8	8
Bismuth	23	23	18	23	23	23
Ammonium Iodate	20	23	18	23	23	37
Magnesium (-325 mesh)	2	2	2	2	2	2
Lead Iodide	36	33	33	34	22	-
Lead Iodate	11	11	21	-	-	30
Potassium Perchlorate	-	-	-	10	22	-
COMMENTS						
Smoke Color	Good Light Orange	Light Orange	Very Good Orange	Light Orange	Reddish Orange	Reddish Orange
Density	Good	Good	Very Good	Good Less Than No. 8	Good	Good
Flame	Yellowish Orange	Yellowish Orange	Yellowish Orange Best Orange Smoke Observed	Yellowish Orange	Yellowish Orange	Yellowish Orange

TABLE XIV. SLOW BURNING RATE[1] YELLOW FLAME - ORANGE SMOKE COMPOSITIONS

COMPOSITION	21-1	21-2	21-3	21-5	21-6	20-1	20-2	20-3
Total Binder (wt %)	16.00	15.8_	15.19	16.00	15.67	15.00	15.00	15.00
DER-732	8.80	8.70	8.35	-	8.63	4.99	4.99	4.99
Epon-812	4.40	4.35	4.18	6.30	4.31	4.98	4.98	4.98
Maleic Anhydride	2.80	2.7	2.66	9.70	2.75	5.03	5.03	5.03
Magnesium (100/200 mesh)	5.30	5.24	5.03	5.30	5.23	2.00	2.00	2.00
Bismuth (140/325 mesh)	16.00	15.82	17.76	16.00	18.30	16.70	-	-
Bismuth (70/140 mesh)							16.70	
Bismuth (-325 mesh)								16.70
Ammonium Iodate	15.40	16.34	17.67	15.40	15.03	16.70	-	16.70
Lead Iodide	25.30	25.02	23.46	25.30	17.65	30.30	30.30	30.30
Lead Iodate	18.00	17.80	17.09	18.00	24.18	19.30	19.30	19.30
Ammonium Chloride	4.00	3.96	3.90	4.00	3.92	-	-	-
MAXIMUM VISCOSITY (KPS AT 74°F)	21	28	26	Wet, Sandy Appearing	24	-	-	-
BURNING OBSERVATIONS								
Burn Rate, ips	0.0152	0.0152	0.0127	0.0150	0.0146	0.025	0.028	0.03[illegible]
Flame[2]	Good, slight pulsing	Fair	Marginal small	Good but pulsed	Good	Small	Small	Small
Smoke	Light Yellow to Pinkish Orange	Pinkish Orange	Light Orange	Light Orange	Pinkish[3] Orange Best color of group	Orange	Orange	Orange

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[1] Burning rate requirement 0.0164 ips for 4.87-inch-diameter.

[2] All flames were yellow in color.

[3] Color saturation was low, since the candle was burned in the 2.25-inch-diameter, giving a sparse or low density cloud.

3.1.4 Yellow Smoke/Yellow Flame

Yellow smokes with good quality color and density were obtained from formulations containing lead iodide, a polyester binder,and potassium perchlorate. The combustion of the magnesium and binder with potassium perchlorate provides the energy to vaporize the lead iodide,and the subsequent condensation produces a dense cloud of yellow smoke similar to the yellow M-18 grenade. When similar compositions in 2.25-inch-diameter grains were burned at Eglin AFB under higher humidity conditions the smoke color was altered to a yellow orange. It appears that high moisture content partially hydrolyzes the lead iodide to the orange or red colored lead oxyiodide or oxide (Pb_3O_4) which would produce the observed color change. To overcome this difficulty, an alternate formulation was considered in which the lead iodide is replaced with powdered lead and lead nitrate or lead oxide. In this composition the yellow smoke is generated by the formulation of the yellow lead oxide (PbO) which is not as highly colored as the lead iodide but does provide an adequate signal. The lead oxide particles would be expected to provide a more stable color under varying atmospheric conditions and this was verified by limited laboratory tests; however, the program was redirected to emphasize other color combinations and so this effort was discontinued.

The binder producing the best smoke colors were the higher oxygen content polyesters such as Witco F17-80 cured with ERL-0150, or its hydroxyl terminated equivalent M8-13 cured with isophorane diisocyanate using trimethylolpropane as a crosslinker. Polybutadiene binders resulted in a denser cloud or a dark yellow color which appeared to be due to carbon particles that were not fully oxidized in the flame. Silicone binders such as Sylgard 182 produced lighter colored smokes similar to those obtained from the aforementioned lead/lead oxide compositions.

The yellow flame color is attributed to the magnesium oxide particles which emits at a wavelength of 500 nanometers and gray body radiation which provides a predominate yellow spectral distribution at the temperatures associated with typical flares. Sodium impurities which are present in many of the materials could also contribute to the yellow flame color. As the magnesium content is increased to provide a more intense flame, the color saturation of the smoke decreased. At a 10 percent magnesium content the smoke cloud was a much lighter yellow color and less dense even though the burning rate was increased. The use of sodium nitrate appeared to be a better method of increasing flame luminosity, but the smoke output decreased when the sodium nitrate content was greater than five percent. Formulations containing 5 percent sodium nitrate and less than 5 percent magnesium provided best smoke/flame signals (Table IX compositions). A summary of the data for the yellow/yellow compositions is presented in Table XV and includes the formulations using lead iodide as the smoke pigment.

TABLE XV. YELLOW SMOKE FLAME

COMPOSITION	1[1]	2	3	4	5	6	7	8	9	10
Ingredient (wt %)										
M8-13 Polyester	8.68	8.68	8.68	8.68	8.68	-	8.68	-	-	.01
Trimethylol propane	3.72	3.72	3.72	3.72	3.72	-	3.72	-	-	14.00
Isopherone diisocyanate	2.59	2.59	2.59	2.59	2.59	-	2.59	1.11	-	.99
Sylgard 182	-	-	-	-	-	-	-	-	13.6	-
Sylgard 182 catalyc.	-	-	-	-	-	-	-	-	1.4	-
R45M Polybutadiene	-	-	-	-	-	-	-	13.88	-	-
Iron acetyl acetonate	0.01	0.01	0.01	0.01	0.01	-	0.01	0.01	-	-
Witco F17-80	-	-	-	-	-	11.94	-	-	-	-
ERL-0510	-	-	-	-	-	2.05	-	-	-	-
Chromium Octoate	-	-	-	-	-	0.01	-	-	-	-
RS 410 surfactant	-	-	-	-	-	1.00	-	-	-	-
Mg (-200 +325 mesh)	2.00	4.00	6.00	8.00	10.00	5.00	2.00	10.00	2.00	-
PbI_2	63.00	63.00	61.00	59.00	57.00	55.00	63.00	55.00	63.00	60.00
$KClO_4$	20.00	18.00	18.00	18.00	18.00	20.00	15.00	20.00	20.00	25.00
$NaNO_3$ (100-140 mesh)	-	-	-	-	-	5.00	5.00	-	-	-
COMMENTS										
Smoke Color	Yellow	Yellow	Light Yellow	Light Yellow	V. Light Yellow	Pale Yellow	Yellow	Dark Gray (sooty)	Light Yellow	Dark Yellow
Density	Very Good	Good	Fair	Fair	Fair	Good	Very Good	Very Good	Good	Very Good
Flame	Fair to Good	Good	Good	Good	Very Good	Very Good	Very Good	Fair	Fair to Good	Fair
Burn Rate (ips)	0.012	0.021	0.024	0.029	0.031	0.025	0.020	0.027	-	-

[1] Flame is smaller than #7 but is acceptable for large diameter candle and exhibits required burn rate.

3.1.5 Green Smoke/Green Flame

A green smoke was obtained using small scale mixes in the laboratory, but scaled-up versions of these compositions when burned outdoors rapidly faded to white or bluish white clouds. A green flame, along with a green smoke, was never obtained with any of the test compositions.

The basic approach consisted of laboratory testing of small mixes containing a metal, halogen source oxidizer, and additional fuel such as magnesium if needed to support combustion; the most promising formulations were then combined with a binder for further evaluation.

Light green, turquoise, and aqua blue smokes believed to be cobalt chloride, accompanied by yellow/orange flames, have been obtained by burning compositions containing cobalt powder, hexachloroethane (HCE), and potassium perchlorate. In the absence of a binder, wide variations in the ratio of HCE to cobalt produced good density clouds of smoke in the pastel blues and greens. The addition of binder such as the polyester, Morester 905, greatly decreases the amount of smoke produced which suggests that hydrogen-containing species produced from pyrolysis of the binder are competing with the cobalt for the chlorine or are dehalogenating the cobalt chloride. It was also observed that combustion of larger samples outdoors at comparatively low relative humidity (30% or less) gave a good green smoke that soon faded in color giving dense white clouds, an effect which may be due to the hydrolysis of the cobalt chloride by atmospheric moisture. This hypothesis was strengthened when samples burned at humidity levels near 80% lost all indication of color in the smoke.

The use of chlorinated polyesters, Hetron 92TG, 2891, or 2892 (containing 30% chlorine) from Hooker Chemical, with approximately 30 percent cobalt and HCE with 25 percent oxidizer generated good density smoke clouds of a light green color. The best green smoke was obtained by decreasing the polymer content to 11 percent in the presence of 32 percent cobalt and HCE (composition 92-7) as shown in Table XVI, along with typical compositions tested. A brominated epoxy resin (DER 599) from Dow Chemical gave the same grayish clouds as those obtained from the high oxygen content polyesters as Morester 905. Attempts to use either the brominated epoxy resin or chlorinated polyester as the only source of halogen resulted in dark black or gray smokes, probably due to its stripping of the hydrogen and halogen from the polymer backbone leaving a carbonaceous residue. Substitution of dechlorane, a less volatile source of chlorine for the HCE, also produced gray to black clouds. Dehalogenation of these organic chlorine derivatives yields solid carbon which contributed to the gray color, an effect which can apparently be overcome by using HCE which has a higher Cl/C ratio 2, as compared to 1.2 for dechlorane. The carbon can probably be oxidized to some extent at least by water and other oxidizing agents.

The addition of barium perchlorate to the cobalt compositions generally produced poorer quality smoke than potassium perchlorate. A green flame was

TABLE XVI. GREEN SMOKE COMPOSITIONS

COMPOSITION	53-1	35-3	35-4	35-5	35-7	55-2	56-1	56-2	56-3	65-1	65-2	65-3	65-4	92-7	5-3	5-3a
Morester binder	10				10											11
DER 599 binder				10												
Triethyl borate							15	10	10							
Hetron 92IG binder							30		30	15	15	15	15	11		
Hetron 2891 binder						15										
Cobalt	30	55	60	32	30	30	30	32	30	30	25	25	30	32	29	26
Hexachlorethane	29	20	15	32	30	30		32		30	25	25		32		
Potassium perchlorate	25	25	25	26		25	25	26			25		25	25	25	22
Barium perchlorate					30				30	25		25				
Tetrabromobutane															46	41
Copper powder											10	10				
Dechlorane 510													30			
Smoke Color	Green Gray	Turquoise	Light Blue	Dark Green Gray	Light Brown	Light Green	Gray	Gray	Gray	Dark Gray	Gray Green	Black	Black	Best Light Green	Dark Turquoise	Gray
Smoke Density	Fair	Very Good	Very Good	Good	Fair	Good	Good	Poor	Poor	Good	Fair	Good	Good	Good	Good	Fair
Flame Color	← Yellowish Orange →					Orange Yellow	← Orange →									

not obtained in any of the cobalt compositions even when the amount of barium perchlorate was increased to 45 percent and the binder eliminated. The addition of copper to the compositions had no effect upon flame color which was not unexpected since the green flame from both the copper and barium halide flames are easily masked by other emitters in the flame. The addition of triethyl borate to the cobalt compositions, either alone or with the chlorinated polyester binder, resulted in orange-colored flames when the samples were burned in long grains. The high temperature of the sustained combustion zone apparently decomposed the oxyalkyl radicals which normally combine with the boron from the green emitting species.

Attempts to produce cobalt bromide smokes were less successful using tetrabromobutane with fluorocarbon, Sylgard and polyester binders. These compositions yielded black and blue-gray smokes probably due to incomplete combustion of the carbon contained in the binder. Increased oxidizer levels only succeeded in producing a light gray smoke.

Various other metal fuels were used to produce green smokes; however, they all provided to be unsuccessful. These materials included nickel, vanadium, chromium, and tungsten, which were burned with various oxidizers and halogen compounds.

3.1.6 Preliminary Smoke/Flame Composition Evaluations

During the course of this program a number of smoke-producing materials other than those previously mentioned were investigated. In general, these materials exhibited a significant reduction in smoke quantity when sufficient binder was added to provide a castable mix. This reduction is attributed to changes in the character of the combustion zone which is induced by the presence of the binder. Hydrocarbon binders, for example, require several times their weight in oxidizer to sustain oxidation or decomposition into gaseous species. This results in either a highly reducing atmosphere or a high concentration of water vapor in the combustion zone which can promote secondary reactions to continue in the hot expanding gases. These secondary reactions have a pronounced effect on both the color and density of the smoke signal.

(a) Copper-Based Compositions (Yellow Smoke)

Mixtures of Cu powder, hexachloroethane (HCE), and oxidizers such as ammonium perchlorate (AP) (014-6, 7) gave bright yellow smokes of good density and a yellow/orange flame as shown in Table XVII. The yellow smoke is presumably due to the formation of $CuCl_2$ which is a bright yellow solid decomposing to the white CuCl at 993°. When the hexachloroethane was removed, lighter yellow and orange smokes were produced with fair density (014-5 and 014-3, respectively). This composition burned with an orange flame while giving a yellow smoke of good density. The compositions without magnesium burned with difficulty while replacement of KP with AP caused little change.

TABLE XVII. COPPER CONTAINING COMPOSITIONS

COMPOSITION	14-3	14-4	14-5	14-6	14-7
Barium Dichromate	-	30	-	-	-
Magnesium (-325 mesh)	-	5	-	-	-
Copper Powder (100/120 mesh)	70	30	75	50	30
Hexachloroethane	-	30	-	25	45
Potassium Perchlorate	-	5	-	-	-
Ammonium Perchlorate	30	-	25	25	25
Smoke Color	Light Orange	Yellow	Light Yellow	Yellow	Yellow
Smoke Density	Fair	Good	Fair	Good	Good
Flame	Orange	Orange	Orange	Orange	Orange

The addition of various binders (polyester, fluorocarbon, and chlorinated polyesters) at levels as low as 8 to 10% destroyed the yellow smoke, and only a white cloud of low density was produced. This result may have been due to the higher flame temperatures caused by the combustion of the binder. Since the yellow smoke flame composition containing lead oxidizer iodide is much superior, copper and hexachloroethene systems were not pursued further.

(b) Iron Based Compositions (Yellow and Orange Smoke)

The use of iron powder with a source of chlorine such as hexachloroethane (HCE) and with potassium perchlorate as an oxidizer produced colored clouds ranging from a light yellow to burnt orange, depending upon the amount of oxidizer present. When a binder was added to the powdered composition, the amount of smoke produced was decreased and the intensity of the smoke coloration was decreased to pale or smoky gray/orange colors. Generally, the better quality smoke color was obtained when the ratio of iron to HCE was near a 1 to 2 weight ratio with sufficient oxidizer to prevent the formation of carbon from the binder. When ammonium perchlorate was substituted for the potassium perchlorate, the smoke density was somewhat poorer, due perhaps to the lower available oxygen content, an effect which resulted in the formation of a carbonaceous residue. Typical examples of compositions tested are shown in Table XVIII.

Iron pentacarbonyl, a toxic, flammable liquid was briefly evaluated by burning small samples. A very dense opaque light brown smoke was produced, but no flame was observed. In view of its hazardous properties the use of this carbonyl is not feasible. Moreover, the smoke was not a vivid color and would be difficult to recognize under tactical conditions.

Larger mixes were made using iron powder and HCE (Table XVIII) and burned outdoors. The results were disappointing in that the yellow orange clouds seen in the laboratory hood tests rapidly faded to a greenish-gray even when compositions with lower levels of binder were burned (i.e., 10 to 15% polyester 14-1A to 6A). The yellow ferrous chloride may be hydrating to yield the light-colored green hydrates; oxidation to the dark brown ferric chloride may also be responsible for the fading of the yellow cloud since ferrous salts are oxidized when exposed to the air.

(c) Manganese Based Compositions (Yellow and Red Smokes)

A manganese iron alloy was evaluated as shown in Table XIX, and in the presence of HCE and tetrabromobutane (TBB) these manganese halides are pink and rose-red, respectively. White to yellowish-white smokes were produced by formulations 016-20 to 016-23 using HCE. The TBB compositions gave brown smokes as typified by 016-24 and 016-25. Other variations

TABLE XVIII. IRON CONTAINING COMPOSITIONS

COMPOSITION	078-2	078-3	078-4	079-1	079-2	079-4	079-5
Binder Type							
Witco F17-80 ERL 0510	20	20	20	15	15	15	
Iron Powder (120/170 mesh)	13	20	13	30	25	55	
Hexachloroethane	27	40	27	30	40		
NH_4ClO_4 (70/80 mesh)	40						
$KClO_4$		20	40	25	20	30	
$Fe(CO)_5$[1]							100
COMMENTS							
Smoke Color	Orange	Smoky Orange	Orange Gray	Pale Orange	Gray Orange	Gray	Light Brown
Smoke Density	Poor	Poor to Fair	Good	Good	Fair	Poor	Very Good
Flame Color	Yellow/ Orange						No visible flame

[1] $Fe(CO)_5$ was burned as a liquid

TABLE XVIII.   IRON CONTAINING COMPOSITIONS (CONCLUDED)

COMPOSITION	14-1A	-2A	-3A	-4A	-5A	-6A
Hexachloroethane	40	45	49	41	41	40
Potassium Perchlorate (170/325 mesh)	25	24	24	24	24	25
Ammonium Perchlorate	-	-	-	-	-	-
Witco M8/TMP Biner	15	10	10	10	10	15
Iron Powder (120/170 mesh)	20	21	17	25	-	-
Carboxyl Iron Powder (-325 mesh)	-	-	-	-	25	20
Smoke Color	Brown Gray	Greenish Gray	Greenish Gray	Greenish Gray	Greenish Gray	Greenish Gray
Smoke Density	Good	Good	Good	Good	Good	Good
Flame	Yellowish/Orange					

TABLE XIX. MANGANESE-IRON ALLOY COMPOSITIONS

COMPOSITION	-20	-21	-22	-23	-24	-25
Manganese Iron Alloy	50	45	40	25	40	25
Hexachloroethane	30	25	25	40	-	-
Tetrabromobutane	-	-	-	-	25	40
Potassium Perchlorate	20	30	30	30	30	30
Magnesium	-	-	5	5	5	5
Smoke Color	White	White	Slight Yellowish White	White	Brownish White	Brown
Flame Color	None	Intermittent White	White	White	White	White
Smoke Density	Fair	Fair	Fair	Fair	Fair	Fair

gave similar results and in all cases the flames were largely white in color. The use of bromine and chlorine donors to produce colored manganese halides does not seem to be a feasible means of attaining brightly colored smokes.

(d) Vanadium Based Compositions (Yellow and Orange Smokes)

Since some vanadium halides are deeply colored and volatile, an attempt was made to form these by reaction of the metals with hexachloroethane (HCE) and tetrabromobutane (TBB). The tetrachloride VCl_4 (red liquid) boils at 149°C, bromide VBr_3 boils at 3000°C, oxybromide $VOBr_3$ at 130° (100 mm), oxychloride (yellow/orange) $VOCl_2$ at 127°C, and oxytrichloride (yellow) liquid boils at 126.7°C. While these may be hydrolyzed, the resulting hydrated oxides are also colored. Vanadium and the less costly ferro-vanadium alloy was used as the metal. With HCE, KP, and vanadium powder (016-9), a yellow/green smoke and yellow flame was produced with fair density. When the vanadium was decreased and the HCE increased (016-10), the light yellow smoke was contaminated with some gray (presumably carbon formed by dehalogenation of the HCE), and the density was decreased; further decreases in vanadium and increases in HCE gave a similar cloud, but the mixtures burned with difficulty (016-11 and 016-12). When the HCE was replaced by TBB (016-13), an orange smoke of fair to good density was attained; the flame was yellow. Again, increasing the TBB at the expense of the vanadium was deleterious to smoke color and density. When magnesium was added, light yellow and orange/yellow smokes were produced by 016-7 and 016-8, respectively. The magnesium improved the luminosity of the flame, particularly in the case of 016-7.

Addition of a fluorocarbon binder to a mixture of vanadium and KP did not produce a cloud of the yellow or green fluorides, but instead a gray smoke resulted. The behavior of typical compositions is illustrated by 016-17 and 016-18.

A ferro-vanadium alloy was evaluated since the greater enthalpy release of the iron may facilitate the reaction of the more inert vanadium. Yellow smokes of good density were obtained in the presence of HCE, KP, and low levels of magnesium (016-6 and 016-7). Tetrabromobutane replacing HCE gave a brownish/yellow smoke. Addition of the polyester binder resulted in a yellowish gray smoke of poor density, an effect which may be due to hydrolysis (016-12). The chlorine-containing polyester produced a light yellow smoke of fair density (016-13). The silicone binder gave a composition producing a pale yellow smoke of fair density; the polyester binder gave a white smoke, a result again indicating hydrolysis of the colored halides. Polybutadiene binder (R-45) gave a slightly yellow smoke of poor density (016-16). Pale yellow smokes were produced from composition containing the chlorinated polyesters (016-17 and 016-18). It would seem that the vanadium halides can form colored smokes but that they are incapable of producing useful smokes in the presence of minimum levels of binders; hydrolysis of the halides is believed to be causing the fading of the smokes. The results of this study are summarized in Table XX.

TABLE XX. VANADIUM CONTAINING COMPOSITIONS

COMPOSITION	016-9	016-10	016-11	016-12	016-13	016-14	016-15	016-16	016-17	016-18	016-7	016-8
Premix A[1]	-	-	-	-	-	-	-	-	20	25	-	-
Vanadium	45	35	25	15	45	35	25	15	50	45	43	33
Hexachloroethane	25	35	45	55	-	-	-	-	-	-	-	-
Tetrabromobutane	-	-	-	-	25	35	45	55	-	-	24	34
Potassium Perchlorate	30	30	30	30	30	30	30	30	30	30	29	29
Magnesium	-	-	-	-	-	-	-	-	-	-	4	4
Smoke Color	Yel Grn	Lt Yel Gray	Lt Yel Gray	Lt Yel Gray	Lt Org to Org	Lt Brn	Sl Grn Gray	Gray	Gray	Gray	Lt Yel	Org Yel
Smoke Density	Fair	Poor	Poor	Poor	Fair to Good	Fair	Poor	Fair	Fair	Fair	Fair-Good	Good
Flame	Yel	Yel	Would not support comb.		Yel slow burning	Yel	Yel slow burning	Yel	Yel	Yel	Bright Yel	Yel

[1] 7% Viton A dissolved in C_7 fluoroalkyl acrylate cured with benzoyl peroxide.

TABLE XX. VANADIUM CONTAINING COMPOSITIONS (CONCLUDED)

COMPOSITION	17-6	17-7	17-8	17-9	18-1	18-2	18-3	18-4	18-5	18-6
Vanadium Iron Alloy	40	40	40	36	37.5	37.5	35	37.5	35	37.5
Hexachloroethane	30	30	-	-	27.5	27.5	25	27.5	30	27.5
Tetrabromobutane	-	-	30	27	-	-	-	-	-	-
Potassium Perchlorate	30	28	30	27	30	30	30	30	30	30
Sodium Nitrate	-	2	-	-	-	-	-	-	-	-
Binder[1]	-	-	-	10	5	5	10	5	5	5
Binder Type[1]	-	-	-	M-8	TG 92 Hetron	Sylgard	M-8	R-45	TG 92 Hetron	28092 Hetron
Smoke Color	Yel	Yel	Brn Yel	Yel Gray	Lt Yel	Pale Yel	White	Sl Yel	Pale Yel	Pale Yel
Smoke Density	Good	Good	Fair	Poor	Fair	Fair	Fair	Poor	Poor	Poor
Flame	Yel	Yel	Yel-White	Yel	White	White	White	White	White	White

[1] M-8, Witco hydroxyl terminated polyester isocynate cured; Hetron, Hooker proprietary chlorinated polyester, Sylgard, Dow silicone polymer; R-45, Arco hydroxyl terminated polybutadiene cured with isopherone diisocynate.

3.1.7 Color Value Determination

A detailed discussion of color value determination is beyond the scope of this report, and interested readers are referred to the Handbook of Colorimetry by A. C. Hardy and the Development of Improved Visible Marker Compositions, AFATL-TR-69-159, by J. Roberts and G. Shaw.

The International Commission on Illumination (CIE) has adopted a system of characterizing color in terms of three parameters:

(1) luminous intensity (brightness)

(2) dominant wavelength (hue)

(3) color purity (saturation)

In brief, the color value determination is based upon the tristimulus color system (three primary colors). Any color can be reproduced by mixing varying amounts of the three primary colors or mixing white with a specific spectrum color which defines the dominant wavelength. The tristimulus colors are arbitary to some extent, and the CIE has selected a set of standards for color value determination. The proportions of the individual tristimulus colors which produce a specific color (wavelength) were determined by a comparison method using photometric techniques and averaging the values of a number of acceptable observers. This data has been compiled and published in tables from 400 to 700 nanometers and the values are referred to as the tristimulus coefficients. A color determination is obtained by measuring the spectral distribution of the emitted energy from the signal of interest using a rapid scan spectrophotometer which has been calibrated against a standard CIE reference source. The recorded data is combined with the tabulated tristimulus coefficients to generate the tristimulus values and the chromaticity coordinates which define the color purity and the dominant wavelength. Color intensity is determined by comparing the energy output with the standard reference source.

The color value of three flame compositions which were sent to Eglin AFB for evaluation was determined spectroscopically using a Perkin Elmer rapid scan Model 108 spectrophotometer. Because of the difficulties encountered with the red/red, an additional red/white composition was requested by the customer as a replacement for color value determination. The detailed technique for determining the color characterization is described in AFATL-TR-69-159.

Very high color purities were reported, and the results of these tests are summarized in Table XXI. Eglin AFB personnel also obtained the spectral data on the red flame compositions and, within experimental error, verified the results shown; however, they were unable to obtain data on the yellow flame at the time of testing. The results obtained indicate that composition 91-4 containing the aluminum sulfate suppressant gave a deeper red flame at a dominant wavelength 625 nanometers with a color purity of 95 percent.

TABLE XXI. COLOR VALUE DETERMINATIONS

COMPOSITION	Red/White 091-4	Red/White 094-11	Yellow/Orange 087
Maleic anhydride	4.24	4.24	4.85
Epon 812	2.76	2.76	3.15
$Sr(NO_3)_2$ (Coarse 250)	37.0	35.0	0
$SrCl_2$(10-120)	15.0	19.0	0
Al (15)	39.0	39.0	0
Al_2SO_4 (anh.)	2.0	0	0
Bismuth	0	0	18.0
NH_4IO_3	0	0	18.0
Mg (-325 mesh)	0	0	2.0
PbI_2	0	0	33.0
$Pb(IO_3)_2$	0	0	21.0
BURNING DATA			
Color Purity	95	96.6	89.1
Wavelength Nanometers	625	616.5	593
Chromaticities			
x	0.6812	0.6709	0.5774
y	0.3042	0.3160	0.4004
Burn Rate (ips)	0.046 to 0.054	0.048 to 0.081	0.052 to 0.054

Composition 94-11 had a slightly higher color purity of 96.6 percent and within the data scatter is similar to the previous composition. The dominant wavelength, however, was a lower value of 616.5 nanometers which verified a previous supposition that a higher flame temperature obtained without a suppressant reduces the concentration of the primary $SrCl^+$ red emitting species.

The orange smoke-yellow flame gave a dominant wavelength of 594 nanometers and purity of 89 percent which is slightly higher than the major sodium emission lines at 558.9 and 589.5 nanometers. When viewed at night from a distance the yellow flame looked identical in color though not nearly as intense as the sodium vapor lamps lighting highway intersections.

3.1.8 Environmental Tests

Although end item development is outside the scope of this program, certain design goals had to be considered in selecting optimum marker compositions. These design goals include the capability of withstanding specific environmental conditions to which an operational system can be exposed. Specifically, one is interested in composition response to temperature shock, vibration, and humidity. In simulating operational environment conditions, one should not lose sight of the fact that the final end item configuration can play an important role, especially in the case of vibration, where component packaging and mounting are primary factors affecting ultimate system response. This section presents a brief description of the test facilities and procedures utilized in implementing the tests specified by the contract.

3.1.8.1 Temperature Shock

Four candles of each color combination, which included the red/white and yellow/orange compositions, were fabricated for the temperature shock test. The candles were cast in aluminum cases 2.25 inches in diameter by 3 inches long with approximately a 4-mil-thick kraft paper liner for the individual compositions. Masking tape with an overlay of waterproof Teflon® tape was used to seal the ends of the candle, and the first fire propellant was not included. Three candles of each composition were exposed to the temperature cycling environment, and one was retained as a control for post-test inspection and functional operation. The candles tested represent the higher burning rate red/white and yellow/orange compositions, designated as DLQ-131 and DLQ-135 in Table IV; however, the results of these tests should apply to the lower burning rate compositions since they reflect only minor formulation tailoring.

The temperature cycling was accomplished by using two constant temperature controlled environmental chambers. The -65°F chamber was continuously conditioned with liquid CO_2 while the 160°F chamber was controlled by means of electric heaters. The candles were temperature cycled in accordance with MIL-STD-810B, Method 503, Procedure I and the cycling operation is

TABLE XXII. TEMPERATURE CYCLING OPERATION

CYCLE	TEMPERATURE	160 + 5°F	-65 + 5°F
1	Start	5/31/73 @ 06:00	5/31/73 @ 10:05
	Stop	5/31/73 @ 10:00	5/31/73 @ 14:15
	Transfer Time	2 min	5 min
	Time Conditioned	4 hrs	4 hrs 10 min
2	Start	5/31/73 @ 14:20	6/01/73 @ 06:06
	Stop	6/01/73 @ 06:00	6/01/73 @ 10:10
	Transfer Time	5 min	5 min
	Time Conditioned	15 hrs 40 min	4 hrs 5 min
3	Start	6/01/73 @ 10:15	6/01/73 @ 14:20
	Stop	6/17/73 @ 14:15	6/02/73 @ 06:00
	Transfer Time	5 min	N/A
	Time Conditioned	4 hrs	15 hrs 40 min

presented in Table XXII. The 15-hour conditioning in cycles 2 and 3 is consistent with the requirements of MIL-STD-810B, and it was cycled in this manner to avoid the expense of employing off-hour working shifts. No observable anomalies occurred during the course of the test.

The candles were inspected before and after cycling, and no visual changes were observed as can be seen from the photograph shown in Figure 1. Results of the post-test burning are presented in Table XXIII.

TABLE XXIII. BURNING RESULTS FROM TEMPERATURE SHOCK UNITS

Smoke Color	Flame Color	Burn Rate, ips
Orange (control)[1]	Yellow	0.066
Orange	Yellow	0.071
Orange	Yellow	0.066
Orange	Yellow	0.066
White (control)[1]	Red	0.048
White	Red	0.067
White	Red	0.054
White	Red	0.047

[1] The control units were cast from the same mix but not temperature cycled.

These candles were burned during the day and within the scatter of experimental data it appears that the burning characteristics are not affected by exposure to temperature shock except for one red/white sample. This sample exhibited a 40-percent increase in burning rate which is probably due to liner separation resulting from either the test and/or defective fabrication.

The yellow/orange compositions exhibited a 10 percent increase in burn rate over the selected fast burning compositions of the same formulation shown in Table IV. The ultimate reduction in burn rate was accomplished by improved tamping procedures and the use of a thicker liner which provides better case insulation, thus inhibiting side burning.

3.1.8.2 Vibration Tests

Three candles of each color combination were fabricated, and two of each were exposed to the random vibration environment while one was retained as a control for post-test inspection and functional operation. The compositions tested included the higher burn rate red/white and yellow/orange formulations designated as DLQ-131 and DLQ-135. To partially simulate an end item assembly, the vibration test candles were fabricated from existing in-house hardware which consisted of 2.75-inch-diameter aluminum tubing with matching aluminum bulkheads. The bulkheads were crimped in place, the kraft paper liners were inserted, and the candles were then cast to provide a 3-inch composition length.

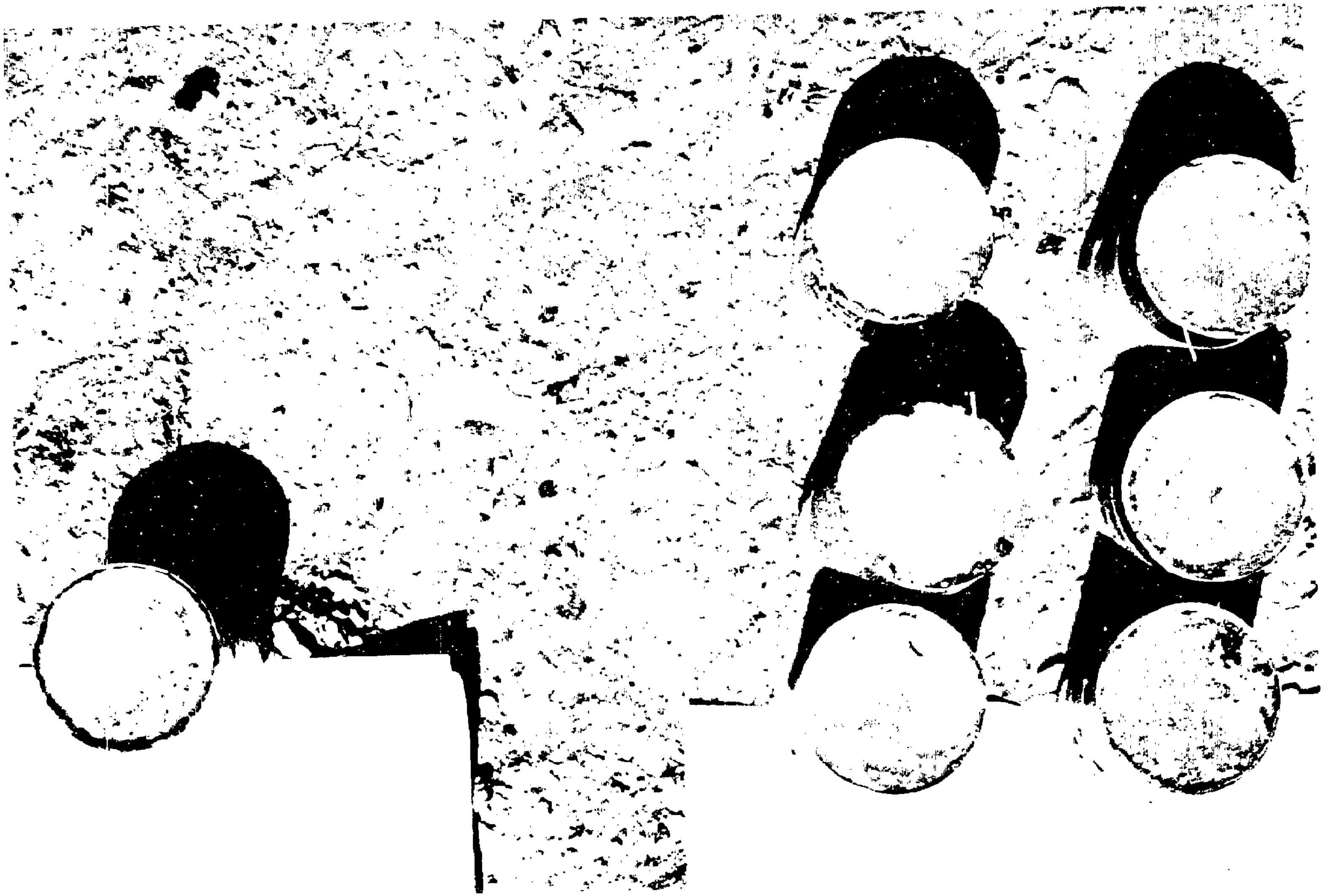

Figure 1. Temperature Shock Test Specimens

All four samples were attached to a single 1-inch-thick aluminum plate which was fitted with four individual contoured saddles and bolt-down straps to provide a uniformly oriented rigid mounting. The assembly was then bolted securely to the existing slip plate fixture which provides the coupling to the LING 249 Electro Dynamic Shaker. The input vibration profile is controlled through a random vibration console.

The test candles were subjected to the random vibration environment along the three mutually perpendicular principal axes as specified by MIL-STD-810B, Method 514.1, Procedure II, Part 3, Curve AH. The time duration of 30 minutes per axis is in accordance with Table 514-1-IV given in Part 3 of Procedure II. The specified random vibration profile consists of the following:

20-100	Hz with a + 6db/octave rise from $0.004g^2$/Hz
100-1000	Hz at $0.10g^2$/Hz flat
1000-2000	Hz with a = 6db/octave roll off

The candles were inspected before and after testing, and no discernible changes were noticed. A photograph of the test candles and the controls prior to post-test burning is shown in Figure 2. Results of the post-test burning are presented in Table XXIV.

TABLE XXIV. BURNING RESULTS FROM RANDOM VIBRATION UNITS

Smoke Color	Flame Color	Burn Rate, ips
Orange (control)[1]	Yellow	0.060
Orange	Yellow	0.057
Orange	Yellow	0.058
White (control)[1]	Red	0.0440
White	Red	0.0423
White	Red	0.0417

[1] The control units were cast from the same mix but not vibrated.

Again, within the scatter of the experimental data it is apparent that these compositions are not affected by exposure to a random vibration environment.

3.1.8.3 Humidity

Past experience has shown that smoke color, depending upon the smoke generating process, can be sensitive to the prevailing humidity conditions. In the case of the red/white combination the smoke consists primarily of Al_2O_3

Figure 2. Random Vibration Test Specimens

particles, and one would not expect a humidity sensitive smoke as has been observed by tests. However, in the case of the yellow/yellow and red/red compositions, the smoke color is generated by chemical species which can be readily hydrolyzed in humid atmospheres, and this had a pronounced effect on the color when tested at the high humidity conditions at Eglin AFB, as compared to tests conducted at the contractor test site.

The contractor operates an on-site weather station, and local temperature and relative humidity are monitored continuously and recorded on a 24-hour basis. By checking with the station periodically, tests were schedules to cover a range from 20 to 85 percent relative humidity. It should be pointed out that the high relative humidity conditions at the contractor site usually occurs at low temperatures when the absolute humidity is low and so results can be misleading when compared with conditions at Eglin AFB.

In performing the humidity tests, there was no dry air reference condition available and so a direct or side-by-side comparison was not possible when the higher humidity tests were conducted. The results of these tests which were conducted on a day-by-day basis were reported from visual observations, and unfortunately the comparisons are somewhat subjective.

The red/white and the yellow/orange compositions which were finally selected after the Phase I effort showed no observable changes in smoke color when burned at varying humidity conditions at either the contractor plant site or customer location at Eglin AFB. The yellow smoke produced from lead iodide showed a definite color change when burned at higher humidities producing a light orange smoke probably due to the formation of lead oxyiodides or oxides by hydrolysis. The red/red composition was also affected by high humidity conditions which is probably due to the hydrolysis of the red bismuth iodide to less intense colored pigments. This effect was much more pronounced when the red smoke compositions were tailored with red flame additives because of the reduced concentration of smoke-producing ingredients and the higher oxidizing environment.

3.2 PHASE II - FEASIBILITY DEMONSTRATION

The objective of the Phase II effort was to demonstrate the concept feasibility of incorporating the smoke/flame compositions into an operational marker system. To accomplish this goal, a series of tests were conducted which included both a low and high velocity ground impact evaluation and day and night visibility tests viewed from an aircraft at altitudes between 1000 and 5000 feet.

As mentioned previously, the tests were limited to the red/white and yellow/orange compositions which were selected after completion of the Phase I effort. The results of these tests indicate that the compositions developed under the current program will survive typical environmental conditions experienced by operational systems. These operational conditions include loads imposed by high velocity impact associated with the 2.75-inch FFAR and the parachute descent of the 4.87-inch LUU-1/B. The visibility tests indicated that the compositions provide good day and night signals; however, as might be expected, the day smoke signals are affected by the background terrain.

3.2.1 Visibility Tests

Visual ground observations of the smoke/flame signals are subject to individual interpretation. Although spectrophotometric flame color purity tests and smoke color and density photographic comparisons with conventional grenades can be used as a form of standard, final verification testing was conducted at the contractor plant site using a leased aircraft with two company observers on board for a qualitative evaluation of the signal characteristics.

The five-mile visibility tests were made by observing each of the burning candles from an aircraft at elevations from 2500 to 4000 feet above ground level. The smoke from all the test grains burned in the day time were observable from the air from a distance of at least five miles. In general, the white smokes were less visible than the orange, and the slower burning 4.8-inch diameter candles were more visible than the smaller 2.5-inch-diameter candles.

The daytime tests were influenced by the prevailing winds and the terrain which included a gravel road bed and background sagebrush and June grass. Initiation of the candles were visible from the air; however, in the case of the small diameter white smoke candles, the signal was not visible for some time after ignition. Communication with ground personnel indicated that the smoke clouds were directed down the gravel road bed, and because of the lack of contrast, these signals could not be detected from the air. With the changing wind direction, the smoke clouds drifted into a field of sagebrush and were then detectable from a distance of 5 miles. The orange smoke cloud could be seen more easily than the white smoke cloud; however, the winds did blow these smokes into an area of June grass and then they became very difficult to detect. The orange smoke appeared low in color saturation at the 5-mile distance. It should be pointed out that the daytime visibility tests are somewhat biased, since the observers did have information on candle location which would not be available during actual search and target marking operations.

The nighttime visibility tests were made under calm conditions where the smoke from the candles formed large slow drifting columns. The flames from all the compositions were easily observed. The red flames formed an intense red spot which was still observable when the white smoke was between the aircraft and flame as a diffused red glow. The yellow flames, obtained from both of the large and small diameter yellow flame/orange smoke candles appeared the same color as sodium vapor lamps on nearby highways. These highway lamps were visible from the aircraft during the tests at approximately the same five-mile distance, and the light from the candles was less intense. When the smoke column was between the aircraft and flame, the light from the flame was blocked momentarily from view. This difference is a result of the increased smoke density and also decreased luminosity of the yellow flame/orange smoke compositions, as compared to the red flame/white smoke compositions.

The observed smoke and flame output is essentially that expected from a comparison of the volumetric output of each composition. It can be observed from Table XXV that the volumetric output of this smaller diameter candles was approximately one-half of the larger units. An increase in the burning rate of the smaller units would improve their visibility. The larger diameter units tested were fabricated with a styrofoam plug at the closed end, allowing some preignition and burning at both ends near the end of burn. This decreased the burning time to some extent, and the candles which were prepared for shipment to Eglin AFB had the styrofoam removed and the end closed with an epoxy plug to prevent this condition from recurring.

3.2.2 40-Foot Drop Test

The tower drop test simulates the environment associated with the delivery of a signal marker by parachute descent which generally results in impact velocities between 30 and 50 fps. In operation the candles are ignited during descent, and the purpose of dropping the flares at various orientations is an attempt to simulate conditions which may occur because of candle separation due to premature case burn-through or structural failure of the parachute attachment.

To provide the required 50 fps impact velocity, the candle must be dropped from a height of approximately 40 feet which can be readily verified from the well-known expression, $h = v^2/2g$.

These conditions are consistent with an existing contractor tower facility which is located over a concrete lined pit suitable for testing the burning candles.

TABLE XXV. BURN RATES OBTAINED FROM VISIBILITY TESTS

COMPOSITION	DIAMETER	CANDLE COLOR	BURN TIME					
			DAY OBSERVATIONS			NIGHT OBSERVATIONS		
			Seconds	In/Second	CC/Second	Seconds	In/Second	CC/Second
DLQ 136	4.78	Yellow Flame - Orange Smoke	450	0.022	6.23	593	0.017	4.81
DLQ 135	2.25	Yellow Flame - Orange Smoke	220	0.045	2.68	199	0.050	2.98
DLQ 134	4.78	Red Flame - White Smoke	367	0.027	7.64	434	0.023	6.51
DLQ 131	2.25	Red Flame - White Smoke	194	0.052	3.09	210	0.048	2.86

Burn Rates obtained from 10-inch length candles.

The facility includes a manual hoist, harness for supporting the candle, and a remote-controlled quick-release mechanism. The impact surface in the existing facility is a 3-inch-thick steel plate and so a wooden box 6 feet by 6 feet and 4 inches in depth was positioned in the pit and filled with dirt, which was conditioned to simulate hard ground. Photographs of the tower facility during operations, showing the harness and quick-release mechanism, and an ignited candle prior to release are presented in Figures 3 and 4. The wire leads extending from the candle are a part of the remote-controlled hot wire ignition system.

The candles for the drop tower test were 4.87 inches in diameter, and 10 inches long and were cast with the slow burning rate red/white and yellow/orange compositions designated as DLQ-134 and DLQ-136, respectively. The candles were ignited remotely and allowed to stabilize for about 30 seconds prior to initiating the release mechanism. As specified, the candles were dropped in the vertical flame up, 45°, and horizontal attitudes for each color combination.

In all cases except one, the candles continued to burn after impact and gave reproducible burn rates. The flame and smoke output generally decreased on impact but then rapidly recovered. Failure of the red/white composition in the vertical drop mode was caused by a release malfunction which caused the candle to tumble, and it impacted in a flame-down position at approximately 35° to the vertical. This caused dirt to be pushed into the burning surface resulting in flame extinguishment. A summary of these drop tests is presented in Table XXVI.

3.2.3 High Speed Impact

The forces associated with high speed impact impose severe shock loads on both the overall ordnance delivery system and subsystem components. In general, the complexities of the shock phenomenon and related coupled loading effects preclude analytical assessment, and one must resort to testing under a simulated loading environment. The actual loading simulation is dependent on both the imposed shock pattern induced by the decelerating impact process and the location and method of component internal mounting. Shock testing for final product acceptance requires sophisticated equipment and instrumentation; however, during the development stages simplified test procedures can be implemented to provide at least first order simulation of the expected environment.

Although various techniques were considered, in the interest of expediency an aircraft drop from an altitude of 2500 feet was selected as the test procedure to simulate the 5000 "g" impact loading requirements. The test was facilitated by the availability of in-house 2.75-inch warhead assemblies

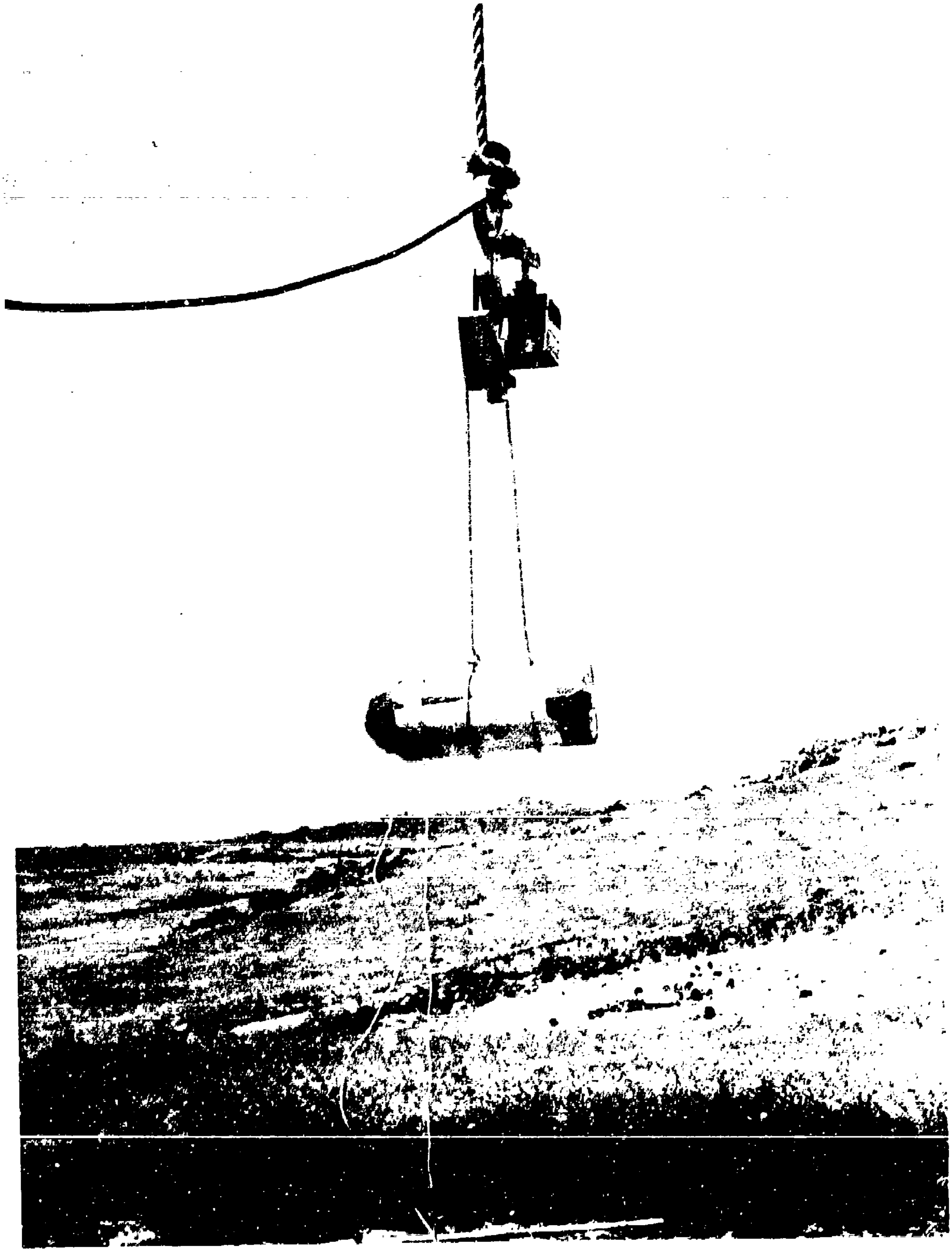

Figure 3. Drop Tower Test Harness and Quick-Release Mechanism

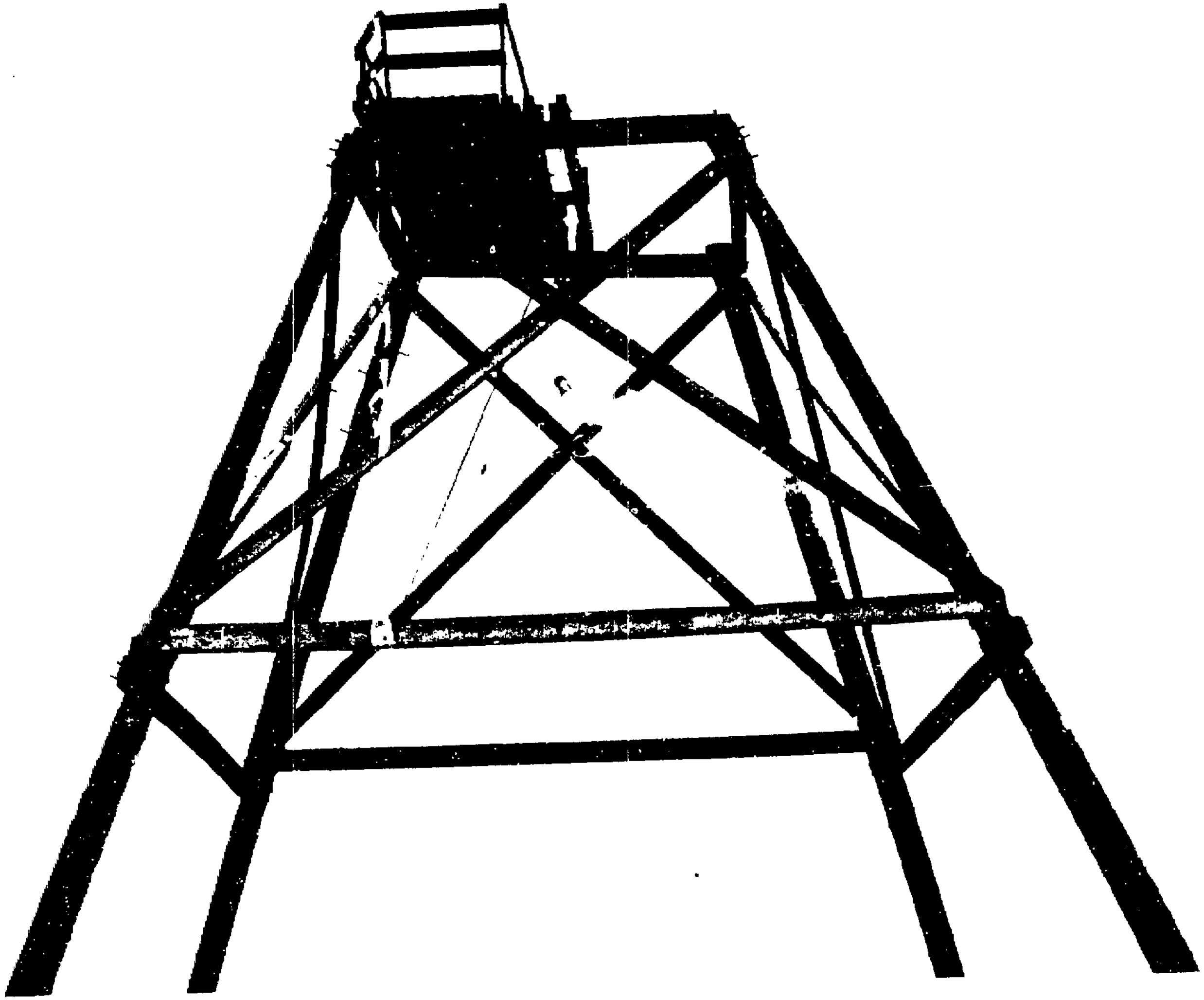

Figure 4. Drop Tower Test After Ignition

TABLE XXVI. BURNING CHARACTERISTICS FOR TOWER DROP TESTS

SMOKE COLOR	FLAME COLOR	DROP ATTITUDE	BURN RATE	COMMENTS
White	Red	45° Flameup	.0253	Upon impact burning was reduced but recovered.
White	Red	Vertical Flameup	-----	Candle tumbled @ 125° hit with flame into dirt, extinguished flame.
White	Red	Horizontal	.0250	Burning continued.
Orange	Yellow	45° Flameup	.0168	Burning continued.
Orange	Yellow	Vertical Flameup	.0185	Output decreased upon impact but recovered.
Orange	Yellow	Horizontal	.0163	Continued burning.

which house both the test candle and a smoke grenade (red) to aid in recovery. The warhead assemblies were modified by the addition of lead to the plastic nose cone section and a cruciform fin configuration to provide aerodynamic stability. A schematic of the final assembly is shown in Figure 5 and a weight breakdown of the individual red/white and yellow/orange configurations is given in Table XXVII. The 2.25-inch-diameter by 3-inch-long candle was placed against the nose cone backing plate and held in position by a forced fit induced by a kraft paper liner. One sheet each of felt and cardboard was placed between the candle and a M-18 grenade which was pinned in place at the open end.

The results of the impact analysis indicate that the projectile experiences a monotonic deceleration time profile with a peak loading of approximately 4700 g's at initial impact, and an effective pulse duration of about 5 milliseconds. Although the analysis presented herein is admittedly based upon a simplified mathematical model, it is felt that the 2500-foot drop simulates the required shock loading environment.

3.2.3.1 Earth Impact Analysis

The phenomenon of earth penetration is highly complex in nature and is directly dependent on soil rheology which is difficult to characterize. For the current impact analysis the mathematical model assumes that vehicle deceleration is induced by direct momentum transfer to the displaced soil and shear stresses acting on the projectile sidewalls. With these assumptions in mind, the dynamics of earth penetration can be described by the following differential equations:

$$\frac{d}{dt}\left[(M_p + \rho_e Ax)v\right] = \pi D f_s x \qquad x < L \qquad (1)$$

$$\frac{d}{dt}\left[(M_p + \rho_e Ax)v\right] = \pi D f_s L \qquad x > L \qquad (2)$$

where,

M_p = Mass of projectile lbm

A = Projected area of projectile ft^2

D = Diameter of projectile ft

f_s = Shear stress lb_f/ft^2

x = Depth of penetration ft

L = Length of projectile ft

v = Velocity of projectile ft/sec

ρ_e = Density of earth lb_m/ft^3

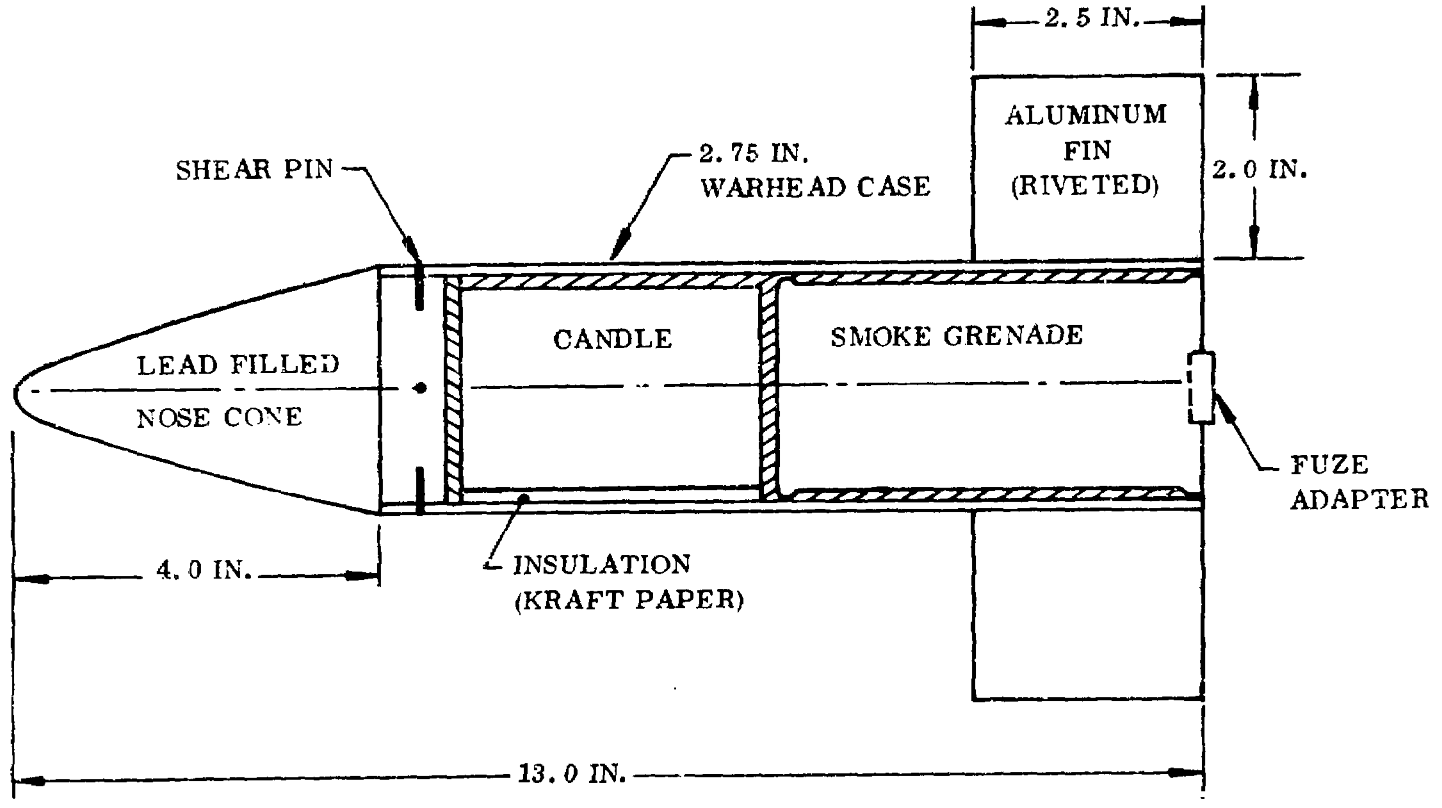

Figure 5. Projectile Assembly for 2,500-Foot Drop Test

TABLE XXVII. 2.75-INCH WARHEAD WEIGHT STATEMENT

COMPONENT	WEIGHT
--	(lbm)
Cylinder and Fin Assembly	1.0
Nose and Lead Ballast	2.94
Smoke Grenade and Fuse	1.31
TOTAL	5.25
Red/White Candle	0.845
Yellow/Orange Candle	1.58
Red/White Assembly	6.10
Yellow/Orange Assembly	6.83

Differentiating equations (1) and (2) and rearranging yields the following:

$$a = \frac{dv}{dt} = - \frac{\rho_e Av^2 + \pi Df_s x}{M_p + \rho_e Ax} \qquad x < L \tag{3}$$

$$a = \frac{dv}{dt} = - \frac{\rho_e Av^2 + \pi Df_s L}{M_p + \rho_e Ax} \qquad x \geq L \tag{4}$$

Equations (3) and (4) describes the deceleration profile as a function of penetration depth. These equations can be integrated directly by making use of an integrating factor $(M_p + \rho_e Ax)^2$ and noting that,

$$\frac{dv}{dt} = \frac{dv}{dx} \cdot \frac{dx}{dt} = v \frac{dv}{dx} \tag{5}$$

the resulting integration yields,

$$v = \sqrt{\frac{M_p^2 v_o^2 - \pi D f_s (M_p + \frac{2}{3} \rho_e Ax) x^2}{M_p + \rho_e Ax}} \qquad x < L \tag{6}$$

$$v = \sqrt{\frac{(M_p + \rho_e AL)^2 v_L^2 - \pi Df_s L (M_p + \frac{1}{2} \rho_e Ax) x}{M_p + \rho_e Ax}} \qquad x \geq L \tag{7}$$

v_o = Velocity at impact ft/sec

v_L = Velocity for $x = L$ ft/sec

For given values of "x" the corresponding values of the velocity (v) can be computed from the appropriate equation (6) or (7) and then substituted into (3) or (4) to yield the deceleration profile as a function of penetration depth. The overall penetration depth can be determined by setting the numerator of either (6) or (7) identically equal to zero ($v = 0$) and solving for the independent variable (x_δ).. Further examination of equations (3) and (4) indicates that the maximum deceleration occurs at the instant of impact and then falls off monotonically. The results of this analysis for the current test is summarized in Figure 6 , with penetration distance as the independent variable. To convert to time as the independent variable, the following numerical integration was carried out:

$$t = \int_o^x \frac{dx}{v} \tag{8}$$

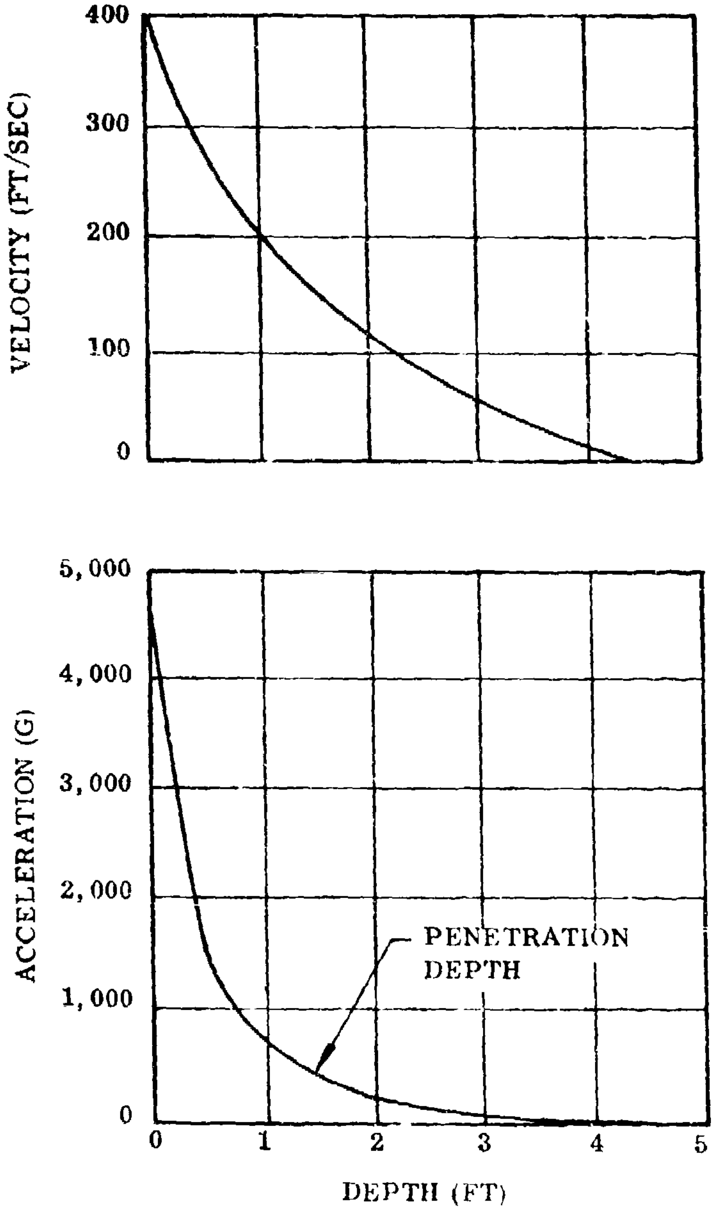

Figure 6. Earth Penetration Profile

From Figure 6, which gives velocity as a function of penetration depth, the numerical integration of equation (8) was carried out to yield the independent variable change giving the deceleration rate as a function of time as shown in Figure 7. The analysis indicates that the effective shock pulse width is approximately 5 milliseconds,

3.2.3.2 Vehicle Ballistics

The motion of a point mass under the influence of a gravitational field, including the effects of aerodynamic drag, can be described by the following equation:

$$\frac{dv}{dt} = \frac{\rho}{2\beta} v^2 - g \tag{9}$$

$$\beta = \frac{m}{C_D A} \tag{10}$$

where,

C_D = Drag coefficient

β = Ballistic coefficient $\quad$ lbm/ft^2

ρ = Air density $\quad$ lbm/ft^3

g = Gravitational constant $\quad$ ft/sec^2

A = Base area $\quad$ ft^2

Assuming constant density, equation (9) can be integrated to yield,

$$v = \sqrt{\frac{2\beta g}{\rho}} \cdot \frac{1 - e^{\sqrt{\frac{2\rho g}{\beta}} \cdot t}}{1 + e^{\sqrt{\frac{2\rho g}{\beta}} \cdot t}} \tag{11}$$

The term $\sqrt{\frac{2\beta g}{\rho}}$ in equation (11) is the terminal velocity of the projectile. Equation (11) can be further integrated to determine the altitude for a given impact velocity as follows:

$$h = \frac{2\beta}{\rho} \ln \frac{1 + e^{\sqrt{\frac{2\rho g}{\beta}} \cdot t}}{2} - \sqrt{\frac{2\beta g}{\rho}} \cdot t_I$$

t_I = impact time

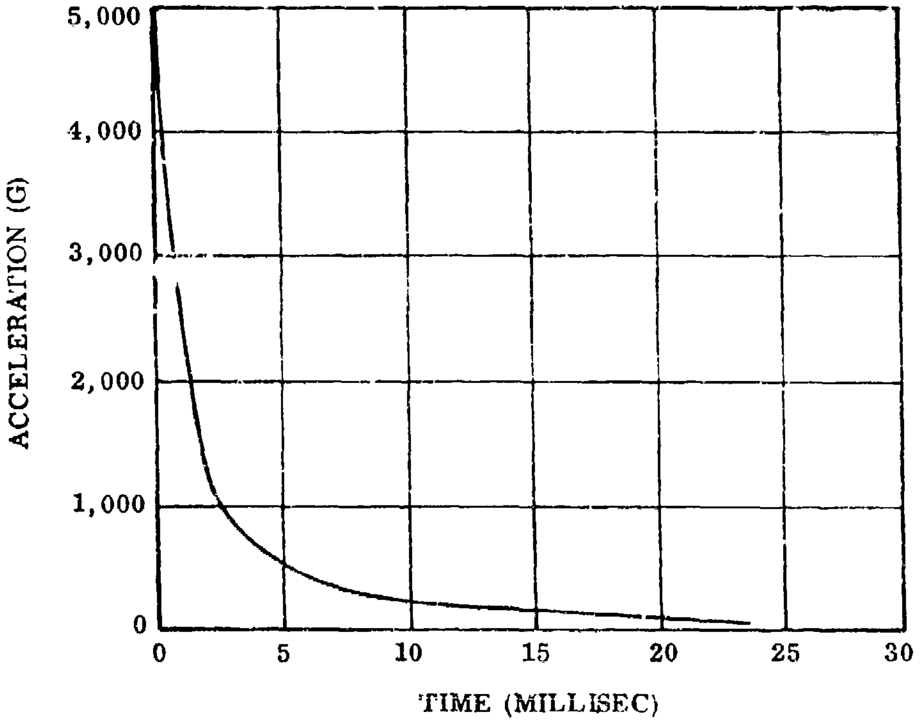

Figure 7. Shock Pulse Width

The cone cylinder configuration with a drag coefficient (C_D) of the order of 0.2, a base diameter of 2.75 inches, and the mass properties of the individual projectiles, yields the following,

$$\beta_{R/W} = 725 \text{ lbm/ft}^2$$

$$\beta_{Y/O} = 825 \text{ lbm/ft}^2$$

Using these values for β and equations (11) and (12), the impact velocity as a function of altitude was computed and the data is summarized in Figure 8. It is apparent that at the altitude being considered (2500 ft), the impact velocity of both vehicle types are essentially identical and they differ very little from the infinite ballistic coefficient ($C_D = 0$) value. Therefore, under these conditions drag has very little effect, and the resultant impact velocity should include the vectorial addition of the aircraft speed (100 knots)

Impact velocity, $V_I = \sqrt{168^2 + 375^2} = 410 \text{ ft/sec}$

Impact angle, $\gamma = \tan^{-1} \dfrac{375}{168} = 65°$

3.2.3.3 Test Results

The candles tested were the high burn rate red/white DLQ-131 and the yellow/orange DLQ-135 compositions. A photograph of the candles after the test is shown in Figure 9. One red flame/white smoke unit could not be located after a thorough search, and it was assumed that the projectile penetrated the ground (4 to 5 feet) and a grass fire resulting from the ruptured smoke canister obscured the entry point. The second red/white unit unfortunately struck a large rock with a glancing impact. The side of the nose cone was heavily damaged and the backup plate was also bent. The candle, designated No. 1 in Figure 9 was compressed nearly 1/4 inch on the end of one side and sustained a small crack across the diameter and approximately 1/4 inch deep. In addition, the case suffered severe crimping at both ends. One of the yellow/orange units tumbled during its free fall and appeared to land on its side. This candle, designated No. 4 in Figure 9, shows no apparent grain damage. The second yellow/orange unit descended properly. However, the unit impacted a gravel road bed producing a 3 to 4-inch-deep crater, rebounded and was recovered lying on its side. Calculating an average deceleration rate, $a = v^2/2x$, this results in a value of approximately 7500 g's with a peak value of greater than 10,000 g's. The recovered candle, designated No. 3 in Figure 9, showed no observable grain damage and minor case crimping on the end which interfaced with the M-18 grenade.

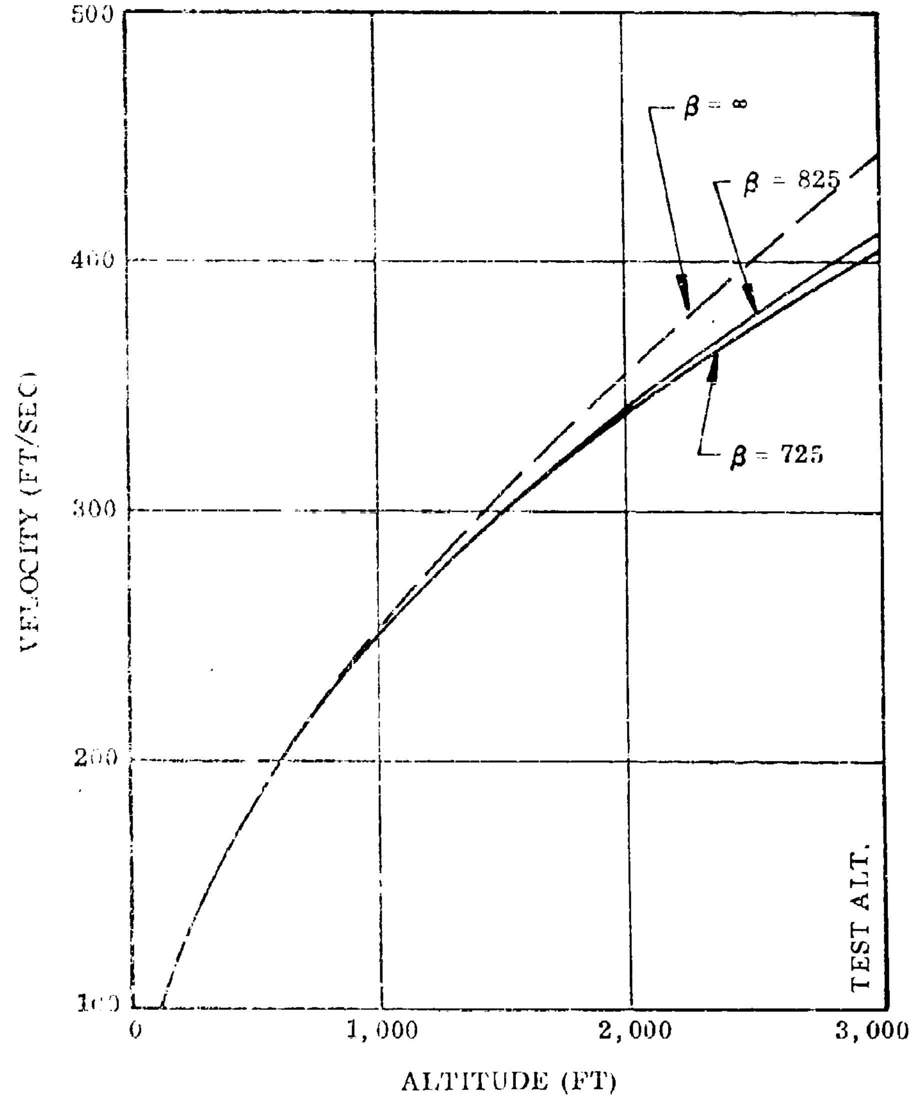

Figure 8. Impact Velocity Altitude Profile

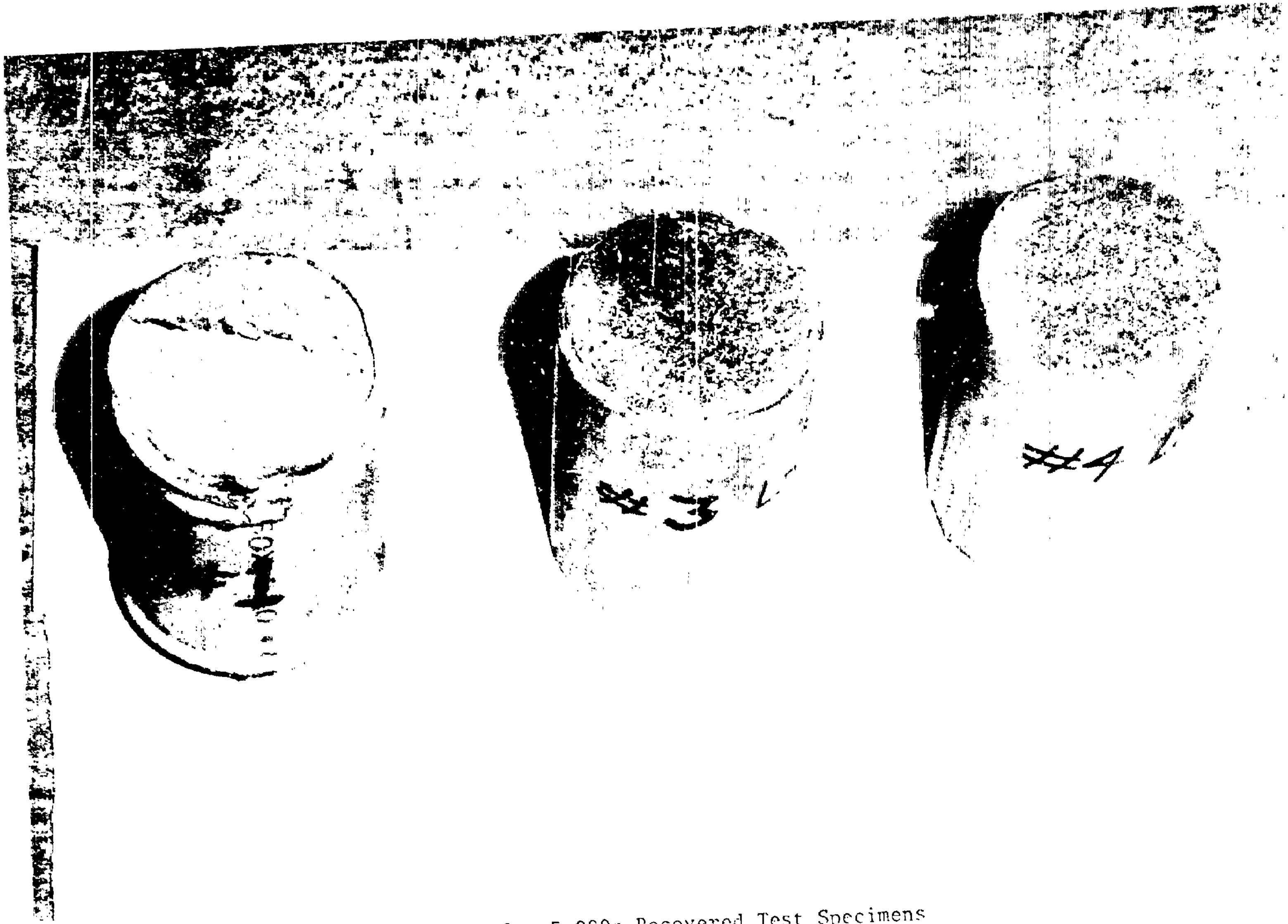

Figure 9. 5,000g Recovered Test Specimens

The high velocity impact units were burned after recovery, and their performance showed no discernible change in color and smoke quality. Despite the crack and severe case crimping, the red/white composition had a burn rate of 0.045 ips which is identical to the regular high burn rate formulations. The two yellow/orange units showed consistent burn rates of 0.036 and 0.038 ips which is slightly lower than comparable units tested previously. These variations are attributed to differences in batch mixing and tamping rather than the consequences of the shock loading.

3.3 PHASE III - METHODOLOGY AND SCALEUP TESTING

On completion of the Phase I and Phase II investigations, development of the red/white and yellow/orange compositions was completed, including the necessary burning rate adjustment for both the 2.25-and 4.87-inch-diameter candles. Since full scale candles were fabricated for the Phase II feasibility demonstration tests and the program objectives were satisfied, the final phase of the study was devoted to candle fabrication of 24 full scale units for delivery to the Air Force and composition hazards classification. The candles delivered to the customer were 10 inches in length and consisted of both the 2.25-inch and 4.87-inch-diameter configuration. The shipment included seven 2.25-inch and four 4.87-inch candles for both the red/white and yellow/orange compositions and two red/red units of the 2.25-inch configuration. The 2.25-inch-diameter candles included the red/white DLQ-131, yellow/orange DLQ-135, and the red/red DLQ-137 flame/smoke compositions. The 4.87-inch-diameter candles included the red/white DLQ-134, and the yellow/orange DLQ-136 flame/smoke compositions.

This section presents a detailed methodology of full scale candle fabrication including liner preparation. In addition, the results of the hazards classification tests which were monitored by a Department of Transportation inspector are presented for each of the compositions.

3.3.1 Composition Mixing, Casting and Safety Data

The compositions selected for scale-up testing in 2.25- and 4.8-inch-diameter candles were mixed in one of three different mixers, including a 1-pint and a 1-gallon vertical blade Baker-Perkins mixer and a horizontal blade 2-1/4 gallon mixer. The pint and gallon mixers were located in dehumidified bays which are kept at a nominal 1 percent relative humidity at 70° F. However, there were no adverse effects found upon the mixes, or candles tamped from mixes made and cast in non-humidity-controlled areas.

The only control of humidity or moisture found necessary was in the storage of the raw materials. The shipping containers were normally adequate for storage purposes; however, the lead iodide, lead iodate, and ammonium iodate arrived in fiber packs without a liner. After the moisture content was verified to be less than 0.1 percent, the materials, if necessary, were sealed in polyethylene bags before being replaced into the fiber packs. The lead iodate arrived with a moisture content of 3 percent. This moisture content was sufficient to catalyze an exothermic reaction between lead iodide and magnesium when the three compounds were mixed. There was no immediate reaction between the wet lead iodate and magnesium. The strontium chloride purchased as the anhydrous was hydrated to the dihydrate in an oven at 170°F. It is more convenient to use in that form; also, it has less effect upon the cure reaction of the binder used in the flare compositions. The materials used in the following mixes are shown in Table XXVIII along with particle size, purity, and vendor.

The mix procedures used in the mixes of the compositions were essentially the same and are as follows.

The binder ingredients were premixed to obtain a homogeneous solution. The binder containing only Epon 812 and maleic anhydride required heating and stirring on a magnetic hot plate and then temporary storage at 135°F just prior to being used in the mixer to keep the anhydride in solution. When the aluminum powder, for example, was added to the binder, part of the anhydride precipitated out into fine crystals which was used in the mixes without further modification or heating.

The red flame and yellow flame compositions using 7 to 8 percent binder gave a wet sandy nearly dry appearing mix which was tamped as previously described. The DLQ-135 composition containing approximately 16 percent binder gave viscosities of 2,100,000 centipoise (21 kps) in the one-pint vertical mixer and 6,000,000 centipoise (60 kps) in the horizontal 2-1/4-gallon mixer. This difference was likely due to the greater efficiency in cooling and mixing action in the smaller mix. The cure reaction of this composition caused an increase in mix temperature in the 2-1/2-gallon mixer, and it was found to cast more readily if the last 10-minute mix cycle was omitted in the larger mixes. Aliquots of the DLQ-136 mix were placed into the candles and either allowed to flow into place or tamped lightly with the aid of the impact hammer. The use of a vibration table was also used in place of the tamping to make the higher viscosity (60 kps) mixes flow into the candles. There was no difference noted in the candles cast by either method.

The orange smoke/yellow flame composition DLQ-135, containing 8 percent binder, was mixed more readily in a horizontal blade mixer than one having vertical blades such as the pint and gallon mixers. The closer blade tolerances and greater shear forces produced in the vertical blade mixers caused the composition to wet together, forming a very high viscosity material which tended to pack along the sides and bottoms of the mixers. In the larger mixer this tended to overload the motor, and the additional energy absorbed tended to heat the composition and resulted in a decrease in the composition pot life. The length of the mix cycle in the pint mixer was therefore cut to 6 to 8 minutes per cycle, resulting in a total mix time of 20 to 24 minutes.

(1) The binder was weighed into the mixer bowl.

TABLE XXVIII. RAW MATERIALS

MATERIAL	DESCRIPTION OR PARTICLE SIZE (microns)		PURITY	VENDOR
Aluminum	Atomized	15 to 30	98	Valley Met.
Aluminum Sulfate	Anh. Powder	6 to 80	Reagent Grade	Baker & Adamson
Ammonium Iodate	Powder	7 to 80	99 + %	ROC/RIC
Ammonium Chl	Ball-Milled	1 to 15	Reagent Grade	Wasatch Chemical
Bismuth	Ball-Milled	40 to 70	99 + %	Griff Williams Co., & ROC/RIC
Lead Iodate	Powder	2 to 30	99 +[1]	ROC/RIC
Lead Iodide	Powder	2 to 25	99 +	ROC/RIC
Magnesium	Spherical	75 to 150	99 +	Reed
Strontium Nitrate	Crystalline	150 to 300	98. 5 +	Barium Chemicals
Strontium Chloride	Powder	10 to 80	98. 5 +	Barium Chemicals
DER 732	Liquid	-	-	Dow Chemical
Epon 812	Liquid	-	-	Shell Chemical Co.
Maliec Anhydride	Lumps	-	Reagent Grade	Baker & Adamson Aldrich Chemical

[1] Contained 3% moisture which required drying the material.

(2) Metallic fuels such as aluminum, bismuth, magnesium, etc., were then added and wet down with the binder. This generally required 1 to 5 minutes mixing, depending upon mix size. Any material on the mixer bowl sides or blades was scraped down.

(3) Approximately two-thirds of the remaining solids, such as the strontium nitrate and chloride or lead iodate and lead iodide, were added and mixed for 5 minutes and scraped down. The temperature of the mix was kept below 80°F.

(4) The remaining solids (generally, the lower bulk density materials as ammonium chloride, or ammonium iodate) were added and mixed 10 minutes, then scraped down again to insure proper mixing of all materials.

(5) The mix was continued 10 minutes and scrapped down, followed with a final 10 minute mix cycle.

The compositions DLQ-131, DLQ-134, DLQ-135, and DLQ-137 shown in Table XXIX, were cured at 135°F for 18 to 36 hours. When cured, the candles were all tough with comparatively little flexibility and Shore A Hardness above 90. DLQ-136 candles were given an 18 to 24 hour ambient pressure precure to allow dissipation of a cure exotherm and then placed in an oven at 120 to 130°F for 48 to 72 hours. The cured candles had elastomeric properties resembling composite propellant compositions with an estimated modulus of approximately 1000 psi with a Shore A Hardness of 50 to 60.

The compositions selected for the high and low burning rate candles for demonstration units are shown in Table XXV, along with safety data obtained. The demonstration compositions passed the DOT safety requirements and were assigned the hazardous classification of "smoke signals Class C explosive."

TABLE XXIX. CANDIDATE SMOKE-FLAME COMPOSITIONS AND SAFETY DATA

COMPOSITION DESIGNATION	DL-Q131	DL-Q134	DL-Q135	DL-Q136	DL-Q137
	(Red/White)	(Red/White)	(Yellow/Orange)	(Yellow/Orange)	(Red/Red)
Binder					
Premix A					6
Epoxy/Anhydride	7.0	7.0	8.0	15.69[1]	
Aluminum	39.0	30.0	-	-	-
Strontium Nitrate	37.0	44.5	-	-	-
Strontium Chloride	15.0	14.5	-	-	-
Aluminum Sulfate	2.0	-	-	-	-
Ammonium Chloride	-	4.0	-	3.92	-
Bismuth	-	-	17.8	18.30	24.0
Ammonium Iodate	-	-	17.8	15.03	28.0
Lead Iodate	-	-	20.8	24.18	-
Lead Iodide	-	-	32.6	17.65	30.0
Magnesium	-	-	3.0	5.23	2.0
Potassium Perchlorate	-	-	-	-	10.0
SAFETY DATA					
Impact (inches)	46	46	28.6	34	22
Electrostatic (J. W. /.01 mfg)	8	8	8	8	8
Friction	64	64	46	64	64
Detonability	None	None	None	None	
No. 8 Blasting Cap	No ignition	No ignition	No ignition	1 of 5 ignited	
Pentalite Booster	No propagation				
Burn Rate (typical ips)	0.050	0.022	0.050	0.016	
Autoignition (48 hr)	300°F	300°F	300°F	300°F[2]	
Sawdust-kerosene flame	Would not burn within 10 minuts	Would not burn within 10 minutes	Burned in less than 1 minute	Burned in less than 1 minute	

[1] Binder contained DER-732. The ratios of Epon-812 to maleic anhydride for other binders was the same as composition 21-5, cf. Table I.

[2] Uncured sample ignited within 24 hours at 225°F.

In addition to the DOT regulations the contractor conducted further safety tests which included impact, friction, electrostatic autoignition, and shock from a No. 8 blasting cap. The red flame/white smoke compositions gave no reaction to any of the safety, impact, friction, electrostatic autoignition, or ignition by a No. 8 blasting cap. The yellow flame/orange smoke composition, DLQ-136 containing ammonium chloride with the increased amount of lead iodate, was more sensitive to the impact and autoignition tests and the shock from a No. 8 blasting cap. The impact sensitivity was greater than 46 inches in the uncured state, but when cured, the 50 percent fire point was 34 inches, using a 5-pound weight. The uncured AIT (autoignition) was less than 225°F; however, when cured it did ignite at 300°F over a period of 48 hours. When a No. 8 blasting cap was placed on a 2-inch cube, one of five samples ignited and burned. The higher burning rate orange smoke, Composition DLQ-135, exhibited a 50 percent impact point of 38 inches with a 5-pound weight when cured. The test results from friction, AIT at 300°F, and the shock from a No. 8 blasting cap were all negative, giving no indication of reaction under those conditions.

3.3.2 Liner

It was observed early in the investigation into colored flares which were to burn through the case that the liner material could greatly affect the color of the operational flare.

The main function of the liner is to minimize the interaction between the composition and the flare case. In order to accomplish this, the liner must do the following:

(1) Allow the flare case to be consumed or melted away to prevent chimney effects.

(2) Prevent side burning by providing an inhibiting layer between the composition and case wall.

(3) Insulate the composition from heat feedback from the hot flare case. This can cause a form of side burning where the flare composition becomes preheated by heat conduction down along the aluminum case, and the hot flare composition becomes the burning rate determining factor.

The type of liner that has given the best performance in the LUU-2/B colored flame configuration is one which contained an oxidizer. The oxidizer would prevent the liner from forming a char layer that protects the aluminum housing from the flame and preventing burn-through of the case.

Since an oxidizer is placed in the liner in red flares, it was found advantageous in the red flare to use the same combination of strontium nitrate and chloride as found in the flare. This tended to improve the color quality of the flare by eliminating smaller, less intense yellow flames from the liner appearing around the side of the case.

Some of the orange smoke flame compositions have shown an effect of the interaction with the liner, and a smoke of a different orange color was emitted from the area of the pyrolizing liner composition interface. It appeared that the increased concentration of pyrolized organic fragments from the liner was interacting with some of the condensing smoke. Although this interaction was not extensive enough to change the overall color of the smoke cloud formed by the burning of a full-scale orange smoke flame unit, it could be further minimized by increasing the oxidizer content of the liner.

The liners consisted of the high oxygen content prepolymer, Witco F17-80, and was cured with an epoxy EFL0510 or Epon 812. The oxidizer and a filler which can be either Cab-O-Sil fumed silicon dioxide or Aerocel (aluminum oxide) increased the viscosity of the liner material so that it would not flow after it was spread onto a sheet of kraft paper. The amount of filler was adjusted to give the most convenient viscosity for the method of application, and the amount often ranged from 2 to 4 percent. The liner compositions are given in Table XXX. The catalyst level was varied to obtain the desired cure time which ranged from 12 to 64 hours. Generally, it is recommended that the lowest practical catalyst level be used to prevent the possibility of its acting as a burning rate catalyst in the liner or at the interface of the liner and flare composition.

In the Development of Improved Visible Marker Compositions program the liner for yellow flame compositions containing potassium perchlorate instead of sodium nitrate gave more reproducibility in the burning rate of test candles, and its use was carried over into this program.

Either of the epoxy curatives listed in Table XXX could be used with the yellow flame compositions; however, the ERL 0510 epoxy is degraded by the presence of strontium chloride and it should not be used in the red flame compositions. It was found that the ERL 0510 gives a tighter crosslinking density than does the Epon 812, and so the liners using the ERL 0510 should not be fully cured. The liners were generally removed from the oven while the surface was still tacky so that a good bond between the liner and flare was obtained. If the liner was insufficiently cured, it would extrude away from the composition by cast into the liner case.

The amount of the liner composition applied to a sheet of kraft paper was adjusted to give a nominal thickness of 0.04 inch ± 0.10 inch. This

TABLE XXX. LINER COMPOSITIONS

COMPOSITION	RED FLAME COMPOSITIONS		YELLOW FLAME COMPOSITIONS	
	071	082	069	070
Witco F17-80	41.8	42.0	71.23	71.04
Epon 812	13.7	13.5	-	-
ERL-0510	-	-	15.00	15.00
$Fe(AA)_2$	-	-	00.01	-
Chromium Octoate	00.5	00.02	-	00.24
Strontium Nitrate	28.0	28.0	-	-
Strontium Chloride	14.0	14.0	-	-
Potassium Perchlorate	-	-	11.76	11.76
Aerocel (aluminum oxide)	2.0	2.0	2.0	2.0
CURE (HOURS AT 135°F)	12	48 - 64	48 - 64	12

amounts to approximately 33 g liner for a 7.5 x 10-inch sheet. The liner was applied by placing a sheet of kraft paper on a flat surface and placing an excess of liner near the top edge of the paper, and a scraper, slotted along the bottom edge to leave the desired thickness of liner behind, was pulled over the paper removing the excess liner material. The coated sheets were then placed flat in an oven for curing.

A series of flares containing the red flame/white smoke composition DLQ-131 were burned with varying thicknesses of liners. The results shown in Table XXXI indicate that a liner thickness of 0.03 inch was approaching the minimum thickness which would give adequate insulation between the flare case and composition to prevent side burning. The tests also show that wrapping the flare grain with masking tape provides one of the best inhibiting materials for burning rate tests.

TABLE XXXI. COMPARISON OF LINER AND TAPE INHIBITION OF 2.25 AND 1.8 INCH CANDLES

COMPOSITION NO.	INHIBITOR THICKNESS, (10^{-3} Inch)	INHIBITOR	FLARE SIZE (INCH)	ALUMINUM CAN	BURN RATE (IPS)
1	80	Liner	2.25 x 3	Yes	0.052
2	50	Liner	2.25 x 3	Yes	0.053
3	50	Liner	2.25 x 3	Yes	0.051
4	30	Liner	2.25 x 3	Yes	0.055
5	20	Masking Tape	2.25 x 3	No	0.054
6	50	Masking Tape	2.25 x 3	No	0.050

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Naval Ammn Depot (Code 5041)	1
TRADOC/ADTC-DO	1
Edgewood Ars (SMUEA-MT-CM)	
Picatinny Ars (SMUPA-VL1	
Picatinny Ars (AMCDM-RK2)	

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13. ABSTRACT

This report summarizes the work accomplished in the development of castable smoke/flame pyrotechnic compositions applicable to a wide variety of markers ranging from the 2.75-inch FFAR to the 4.87-inch LUU-1/B target marker. As a result of this investigation, three color combinations were selected for further development. They included red flame-white smoke, red flame-red smoke, and yellow flame-orange smoke compositions. With a view to an end-item product, the development program included a series of environmental and visibility tests for overall composition evaluation. The development of the red-white and yellow-orange compositions was successful, and these compositions show every indication of satisfying all the requirements of an operational smoke/flame marker system. Unfortunately the red-red combination proved to be a more difficult problem, and although some promising approaches were generated, additional composition development is required to meet the ultimate marker objectives.

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2.75-Inch FFAR						
4.87-Inch LUU-1/B Target Marker						
Pyrotechnic Composition Evaluation						
Smoke/Flame Marker System						