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EFFECTS OF ENVIRONMENTAL AND PROCESSING CONDITIONS ON COMPOSITION AND SENSITIVITY OF HC WHITE SMOKE MIX

by

J. F. Pankow
G. L. McKown

March 1975

NASA NATIONAL SPACE TECHNOLOGY LABORATORIES
General Electric Company
Engineering and Science Services Laboratory
Bay Saint Louis, Mississippi 39520

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DEPARTMENT OF THE ARMY
Headquarters, Edgewood Arsenal
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A series of experiments were performed to determine environmental condition effects of HC white smoke mix. Temperature, humidity level, blending rates and time were found to have minimal effect on input sensitivities and energy release. Significant findings were; gross sublimation of hexachloroethane from stored samples; large inhomogeneities in the blended samples; and inconsistencies in impact sensitivities of all samples compared to previous results.

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PREFACE

The work described in this report was authorized under Edgewood Arsenal MIPR Number B4030, PRON 81-4-B4030-01-F4-W5, AMCMS 4932.05.4099.0. It was performed at the NASA National Space Technology Laboratories (NSTL) for the Edgewood Arsenal Resident Laboratory (EARL) and NASA-NSTL by the General Electric Company under Contract No. NAS8-27750.

SUMMARY

A program was conducted to determine sensitivity and energy release of HC white smoke mixes prepared under a variety of environmental and blending conditions. The effects of temperature, humidity, mixing rate and time on moisture content, initiation sensitivity, homogeneity, output energy and reaction mechanism were investigated. Impact sensitivity, thermal stability, electrostatic sensitivity, chemical analysis, differential thermal analysis, and Parr bomb calorimetry results are reported on samples prepared within the following matrix of conditions:

- Temperatures of 24°C and 41°C
- Relative humidity of 35, 65, and 90 percent
- Two blending times
- Three sampling times
- Four HC mix compositions

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EFFECTS OF ENVIRONMENTAL AND PROCESSING CONDITIONS ON COMPOSITION AND SENSITIVITY OF HC WHITE SMOKE MIX

1.0 INTRODUCTION

1.1 Objective. The objective of this work is to provide the following information for HC white smoke mix compositions:

- To determine the effect of humidity and temperature on absorption of moisture during blending by the Jet Airmix(TM) Process.
- To determine the relationship between moisture content and initiation sensitivity.
- To determine the effect of mixing rate and time on the composition and homogeneity of the mixture.
- To examine changes in reaction processes by determination of the thermal decomposition and output energy variations with hexachloroethane concentration.

1.2 Authority. This work was authorized by Technical Work Request EA-4D41, dated September 1973, as amended on 21 June 1974.

1.3 Background. HC white smoke mix[1] is a commonly produced pyrotechnic composition used for numerous signal applications in the US Army. The mix nominally contains 46.5 percent ZnO, 44.5 percent hexachloroethane, and 9.0 percent aluminum powder by weight, although small adjustments in these percentages are permitted to control burning rate and ignition characteristics.

The reaction of HC smoke mix is presumed to involve formation of aluminum oxide and zinc chloride, which hydrolyzes in air to form a dense aerosol, and small amounts of free carbon. The percentage composition of the mix is not in simple stoichiometric ratios, and a complex reaction is predicted that is approximated by the equation

$$2Al + 7ZnO + 2C_2Cl_6 \rightarrow Al_2O_3 + 6ZnCl_2 + 3CO + C + ZnO \qquad \text{(Eq. 1)}$$

An excess of the diluent (coolant) zinc oxide is noted. The carbon monoxide and some of the carbon formed is expected to combine with atmospheric oxygen at the temperature of the reacting mass.

The input sensitivity and output energy of HC smoke mix has been determined,[2] resulting in an assignment of Class 2 (fire hazard) for the bulk composition. The classification data shows evidence of the rather inert nature of the standard mix toward all normal modes of initiation, and both starter and first fire initiators are required in end-item usage. An extensive evaluation program has recently been concluded that provided data for safety certification of Jet Airmix blending of HC smoke mix in quantities up to 2170 pounds.[3] Results of this project yielded no evidence of hazardous situations due to initiation stimuli levels found in the blending process, and showed critical (detonable) mass-diameter of the mix to be greater than 500 pounds at 3 feet diameter even under severe conditions of energy input. However, accidents involving production of HC smoke mix have been reported. It has been specifically determined that the presence of moisture in the composition can be potentially hazardous.[4] A total moisture content greater than 0.6 percent by weight has been observed to be extremely dangerous, and it is postulated that a decomposition process involving chloride ion is responsible.[5] The acidic chloride solution probably catalyzes reaction of the aluminum metal; i.e., acts as an etchant to expose fresh aluminum surfaces that can react with water in a highly exothermic manner:

$$2Al + 3H_2O \xrightarrow{Cl^-} Al_2O_3 + 3H_2 \qquad \text{(Eq. 1A)}$$

The hydrogen, released interstitially, is in intimate contact with the other mix components. At the elevated temperature of the initiation, a reduction of the hexachloroethane could be effected:

$$H_2 + C_2Cl_6 \longrightarrow HCl + C_2HCl_5, \underline{\text{etc.}} \qquad \text{(Eq. 1B)}$$

The acid formed promulgates further reaction resulting in production of highly flammable partially hydrogenated chlorocarbons and hydrogen gas. The sensitivity of these products to initiation by electrostatic, thermal, or electromagnetic stimuli is obvious.

It is known that a least one previous accident involved extended blending of HC smoke mix under hot, humid environmental conditions, and initiation mechanisms such as that postulated are suspect. The present study was undertaken to determine the influence of environmental and processing parameters with respect to safety of HC smoke mix manufacturing operations.

A factor that potentially could create abnormally high hazard levels is the sublimation rate of hexachloroethane. The cubic crystalline form of this compound exhibits a sublimation pressure of 1.6mm at 41°C.* Thus significant removal of this constituent from a mixture, particularly during blending, is expected even at normal ambient temperatures.

It is reasonable to assume that the reaction process will depend on the constituency of the mix. For the case with no zinc oxide present, the following reaction is expected:

$$2Al + C_2Cl_6 \longrightarrow 2AlCl_3 + 2C \qquad \text{(Eq. 2)}$$

A composition with excess aluminum might follow the equation:

$$2Al + 3ZnO + C_2Cl_6 \longrightarrow Al_2O_3 + 3ZnCl_2 + 2C \qquad \text{(Eq. 3)}$$

Finally, total absence of hexachloroethane permits only the well-known thermite-type reaction:

$$2Al + 3ZnO \longrightarrow Al_2O_3 + 3Zn \qquad \text{(Eq. 4)}$$

* For hexachloroethane (cubic form), $\log P(mm) = 8.731 - 2677/T(°K)$

An investigation of the reaction energy depending on hexachloroethane concentration was attempted to determine whether this situation could be a relevant safety factor.

2.0 TECHNICAL APPROACH

Experiments were performed for determination of chemical analysis and input sensitivities of HC smoke batches blended within a matrix of environmental and process parameters. Blending of standard formula HC smoke mix was accomplished in a bench model Jet Airmix (TM) blender, details of which have been described previously. Four hundred gram batches were blended in the mixer under a variety of conditions, as follows:

- Temperatures of 24° ± 3°C and 41° ± 3°C
- Relative humidities of 90 ± 5%, 65 ± 5%, 35 ± 5%
- Blending repetitions of five (5) and two (2) two-second blend/four-second pause sequences.

Appropriate sample sizes were removed from the blender and packaged in sealed containers (polyethylene bags) to aid in preservation of the original material condition.

Impact sensitivity,[6] thermal stability[6] and electrostatic sensitivity[7] tests were performed on each of the samples. Chemical analysis was accomplished as follows:

- Determination of moisture content by a desiccation method.[7]
- Determination of chemical composition; a known quantity of the mixture was eluted with isopropyl alcohol and filtered. The residue was dissolved in nitric and hydrochloric acid solutions and the resulting solution diluted to one liter. Aliquots were further diluted and introduced into a Perkin-Elmer Model 403 atomic absorption spectrometer fitted with appropriate lamps. The percentages of zinc and aluminum were determined by comparison to known standards; the percentage of hexachloroethane was determined by difference. Inherent experimental accuracy of this method was calculated to be better than three percent of the composition for any component; i. e., for the percentages in standard HC smoke mix:

  Aluminum ± 0.08%

  Zinc Oxide ± 1.0%

  Hexachloroethane ± 1.0%

The investigation of reaction process was accomplished as follows:

- HC smoke mix samples were prepared with varied composition as shown in table 1.
- Weighed samples of each mix were conditioned for 24 hours at constant temperatures in desiccators containing H_2SO_4 solutions of concentrations appropriate for maintenance of 35, 65, and 90 percent relative humidities. Other samples were

ovendried or maintained at low humidity, and control samples were taken immediately after blending. Details are given in table 2. Samples were re-weighed after the 24 hour period to determine weight loss in each of the environments.

- Differential thermal analysis of 50 milligrams of each sample was performed on a Fisher Thermalyzer(TM). All isotherms were recorded over the range from ambient temperature to beyond the melting point of aluminum.

- Oxygen-bomb calorimetric measurements were made on one gram sample of each batch using a standard Parr(TM) bomb calorimeter. The heat of combustion in calories per gram, H_g was obtained from the equation:

$$H_g = \frac{tW - e_1 - e_2 - e_3}{g}$$

Where: t is the temperature rise

W is the energy equivalent of calorimeter (1386)

e_1 is the correction for heat of formation of HNO_3 in calories, which was used as an estimation for acidity of combustion residue due to formation of amphoteric metal chlorides

e_2 is the correction for heat of formation of H_2SO_4 in calories, given by (14) x (% sulfur in sample) x (weight of sample in grams)

e_3 is the correction for heat of combustion of firing wire in calories; 2.3x centimeters of chromel C wire consumed;

and

g is the weight of sample in grams

3.0 RESULTS AND DISCUSSION

3.1 Experimental Data. Experimental results are given in tables 3 through 8.

3.2 Discussion of Results.

3.2.1 Input Sensitivity vs Mixing Parameters. A serious anomaly exists in the results shown in table 3 for the impact sensitivity tests. These results indicate decomposition in 39 percent of all tests using drop heights from 9.5 to 25.4 cm and in 59 percent of the tests at 25.4 cm (10-inch drop height). These observations contrast strikingly with those obtained in previous classification tests for HC white smoke mix[2] which showed no apparent reaction at any drop height. Based on the results of this project, the classification of HC white smoke mix as Class 2 is highly suspected.

There does not appear to be any significant correlation between the mixing parameters (temperature, humidity, airmix sequence) and any of the input sensitivity tests; internal comparisons of the impact sensitivity results are erratic. The mix prepared at a temperature of 41°C and 90 percent relative humidity gave some detectable evidence of decomposi-

Table 1. Composition of Samples

Mixture	Constituent	% Composition	Mole Composition	Rationale
1	Aluminum	5.0	1	Standard Mix
	Zinc Oxide	48.6	3.5	Equation 1
	Hexachloroethane	46.4	1.1	
2	Aluminum	18.6	2	No diluent;
	Hexachloroethane	81.4	1	Equation 2
3	Aluminum	10.0	2	No excess diluent;
	Zinc Oxide	46.0	3	Equation 3
	Hexachloroethane	44.0	1	
4	Aluminum	18.1	2	No oxidizer; Thermite
	Zinc Oxide	81.9	3	reaction; Equation 4

Table 2. Conditioning Parameters for Samples

Relative Humidity %	Temperature	Desiccant	Period
0	24.7°C	Drierite$^{(TM)}$ ($CaSO_4$)	24 hours
35	24.7°C	50.0% H_2SO_4	24 hours
65	24.7°C	35.8% H_2SO_4	24 hours
90	30.0°C	18.6% H_2SO_4	24 hours
-	40.5°C	Oven Dried	24 hours
Control		None	Immediately after mixing

Table 3. Test Results, Sensitivity of Mixes

Sample Number	Mixing Parameters				Thermal Stability Test				Electrostatic Sensitivity				Impact Sensitivity Tests*				
	Temp. (°C)	R.H. (%)	No. of Pulses	Time Lapse	Wt. (g)	Wt. (g)	Loss (g)	Loss (%)	Wet Mix		Dry Mix		Height of Drop (cm)				
									Pos	Neg	Pos	Neg	9.5	19.0	22.2	25.4	38.1
24-35-5-5	25	32	5	5 min	165.3	85.2	80.1	48.5					0-0-10	1-4-5 1-3-6	3-2-5 2-6-2	2-4-4	1-3-6
24-65-5-5	21	62	5	5 min	165.3	87.5	77.8	47.1	0	5			1-0-9	0-2-8	0-1-9	0-4-6	1-4-5
24-90-5-5	21	90	5	5 min	165.3	85.7	79.6	48.2					0-0-10	0-3-7	0-4-6	0-4-6	0-3-7
41-35-5-15	43	34	5	15 min	165.3	88.4	76.9	46.5					0-0-10	2-3-5	0-4-6	0-7-3	0-1-9
41-65-5-5	39	65	5	5 min	165.3	89.3	76.0	46.0					0-2-8	0-2-8	0-4-6	0-5-5	0-5-5
41-90-5-5	40	90	5	5 min	165.3	88.3	77.0	46.0	0 0	5 5	0	5	0-1-9	3-6-1	4-3-3	0-7-3	1-4-5
Mix from Stock					165.3	90.8	74.5	45.1	0	5	0	5	0-0-10			2-6-2	

* Results reported as number of trials exhibiting explosion/flame/noise-decomposition/smoke/no noise-no reaction/no smoke/no noise.

tion in 58 percent of the tests at all drop heights, compared to an average of 34 ± 8 percent for all other samples tested (table 4). Otherwise, there is no statistically significant difference in the percentage of samples showing any form of decomposition upon impact. Furthermore the agreement between impact results at different drop heights for any given batch is extremely poor. Thus for batch number 41-35-5-15 the results show serious decomposition (50 percent) at 19 cm. drop height, but only 10 percent decomposition at twice that impact energy (38 cm.). Similar discrepancies exist throughout the rather voluminous quantity of results, leading to the conclusion that very little information of a quantitative nature can be derived from the results of impact sensitivity testing when small differences are probable.

Table 4. Summary Results, Impact Sensitivity

Mixing Parameters		% Samples Showing Decomposition at all drop heights
Relative Humidity (%)	Temperature (°C)	
35	24	46
35	41	34
65	24	26
65	41	36
90	24	28
90	41	58
Factory Premix		40

The Class 2 designation for the mix is also in question upon perusal of the thermal stability data, which shows an average of 47 ± 1 percent weight loss at 75°C/24 hours. The thermal stability test results show little variation with mixing parameters, and all results are contained within the range of 45 to 49 percent weight loss, regardless of the conditions under which the mix was blended. Within experimental errors, these weight losses are equivalent and tantamount to complete loss of hexachlorethane from the samples.

All results of the electrostatic sensitivity tests performed were negative; i.e., no evidence of sample decomposition or reaction was observed in a total of 30 trials. For this reason, tests on a number of the batch samples were omitted and no comparisons can be made. It appears that HC white smoke mix samples used in these tests are not overly sensitive to electrostatic energy input.

In summary, very little significant differences in input sensitivities of samples prepared under a variety of environmental conditions were observed in this experiment. The possibility that higher sensitivity for mixes prepared under conditions of high temperature and high humidity was indicated, albeit based upon shallow evidence. The most striking observation was the overall input sensitivity results and the magnitude of weight loss in the thermal stability test, a result expected in view of the probable extent of hexachloroethane sublimation from samples maintained at 75°C for a period of 24 hours.

3.2.2 Variances in Moisture Content and Chemical Composition. Determination of the percentage moisture in batches of HC smoke mix was inconclusive, due primarily to the experimental method (desiccator) employed and the overwhelming interference of hexachloroethane sublimation on sample weight losses with time. As shown in table 5, approximately one percent loss in weight of all samples was observed within a period of 72 hours and the loss rate continued until the experiment was terminated after 15 days. The average weight loss rate was 0.21 ± .04 percent-per-day over the period of observation, even in the closed vessel conditions of the desiccation method.[7]

An attempt was made to obtain percentage moisture content of the samples by extrapolation of the weight loss/time data backward to time zero. It was assumed that sublimation of the hexachloroethane would proceed at a constant rate and that moisture loss would cease after some initial period of time. Nonlinear variations in the loss/time curve near time zero could be attributed to the loss of moisture. Straight-line extrapolation of the curves from regions of constant loss rate to zero time would yield the percent weight loss not attributable to sublimation; i.e., the percent of moisture in the original sample. These attempts were eventually abandoned for the following reasons:

- It was required to use several different desiccators in the experiment, and weight losses for both water and hexachloroethane are expected to be strongly dependent on the physical characteristics, e.g., tightness of cover and percent of desiccant expended, of a particular desiccator system. This situation was in fact observed during the experiment.
- There is no reason to believe that sublimation rate from a 10 gram sample would be constant, particularly at the start of the experiment, since material-air and material-material interface partition functions would be different.
- The desiccators were opened periodically for weighing of samples and consequently the closed system environment was altered.
- Several samples were maintained in each desiccator, and complex partition functions, upon which weight loss rates depend, would be involved.

Despite the failure to obtain reliable moisture content information, the weight loss measurements provide valuable gross sublimation rates for hexachloroethane from HC smoke mix under semiconfined conditions.

The chemical analysis data shown in table 5 appears to be inconsistent in several ways:

- The variation in percentage composition for samples taken from a particular batch at different times is much larger than both the expected effect and the inherent analytical reliability. The expected variation would be due entirely to changes in moisture content with sampling time, which effect should not exceed

Table 5. Chemical Analysis Data

SAMPLE NUMBER	MIXING PARAMETERS				CHEMICAL COMPOSITION			WEIGHT LOSS, %, IN DESICCATOR (ELAPSED TIME)					
	TEMP (^{o}C)	RH (%)	NO. OF PULSES	TIME LAPSE (MIN)	% Al	% ZnO	% HC	24 HRS	48 HRS	72 HRS	144 HRS	240 HRS	336 HRS
24-35-5-5	25	32	5	5	4.43	44.5	51.0	0.59	0.91	1.16	1.96	2.66	3.39
-10				10	4.76	50.5	44.7	0.66	0.89	1.21	1.83	2.67	3.38
-15				15	3.83	52.9	43.3	0.65	0.98	1.31	1.96	2.81	3.37
24-35-2-5	25	34	2	5	6.10	48.4	45.6	0.58	0.91	1.27	2.06	2.95	3.59
-10				10	4.86	50.5	44.7	0.56	0.99	1.21	2.03	2.95	3.65
-15				15	2.91	42.4	54.7	0.60	0.96	1.00	2.08	2.97	3.72
24-65-5-5	21	62	5	5	5.02	55.9	39.1	0.30	0.62	0.85	1.35	2.25	3.04
-10				10	4.99	47.1	47.9	0.27	0.57	0.83	1.26	2.08	2.87
-15				15	4.11	42.1	53.8	0.23	0.48	0.71	1.13	1.88	2.64
24-65-2-5	21	62	2	5	4.98	49.2	45.8	0.25	0.58	0.91	1.33	2.06	2.71
-10				10	4.88	43.8	51.3	0.25	0.55	0.84	1.26	1.91	2.50
-15				15	2.99	47.7	49.3	0.25	0.56	0.83	1.26	1.92	2.50
24-90-5-5	21	90	5	5	5.80	47.8	46.4	0.73	1.13	1.36	2.13	2.89	3.74
-10				10	4.95	46.7	48.4	0.72	1.07	1.37	2.16	2.89	3.66
-15				15	4.36	70.1	25.5	0.71	1.09	1.36	2.16	2.98	3.74
24-90-2-5	21	90	2	5	5.58	41.4	53.0	0.76	1.18	1.53	2.47	3.42	4.31
-10				10	4.66	49.4	45.9	0.76	1.15	1.48	2.39	3.53	4.43
-15				15	4.77	56.5	38.7	0.66	1.01	1.29	2.09	3.54	4.31
41-35-5-5	43	34	5	5	6.51	48.5	45.0	0.52	0.83	1.18	1.88	2.81	3.27
-10				10	4.88	49.5	45.7	0.31	0.61	0.89	1.31	2.15	2.91
-15				15	2.63	57.0	40.4	0.28	0.59	0.86	1.25	2.09	2.89
41-35-2-5	43	34	2	5	5.56	55.3	39.2	0.31	0.62	0.91	1.36	2.19	2.96
-10				10	4.75	47.6	47.6	0.29	0.59	0.86	1.42	2.34	3.17
-15				15	4.23	41.4	54.3	0.29	0.62	0.87	1.47	2.38	3.20
41-65-5-5	39	65	5	5	4.07	45.2	50.7	0.26	0.47	0.72	1.19	1.94	2.30
-10	41			10	6.24	52.0	41.7	0.25	0.46	0.71	1.17	1.88	2.24
-15	40			15	5.09	53.1	41.8	0.26	0.49	0.69	1.20	1.84	2.17
41-65-2-5	40	65	2	5	4.78	42.6	52.7	0.29	0.55	0.78	1.40	2.17	2.54
-10				10	5.87	45.1	49.0	0.30	0.57	0.84	1.49	2.34	2.74
-15				15	3.47	51.7	44.8	0.21	0.40	0.65	1.22	1.96	2,30
41-90-5-5	40	90	5	5	3.89	44.3	51.8	0.30	0.51	0.72	1.19	1.85	2.23
-10	42			10	4.83	44.9	50.3	0.27	0.49	0.70	1.22	1.91	2.23
-15	40			15	4.55	52.4	43.0	0.28	0.50	0.72	1.16	1.93	2.27
41-90-2-5	40	90	2	5	4.43	48.9	46.7	0.29	0.56	0.81	1.31	2.10	2.51
-10	40			10	4.17	46.3	49.5	0.26	0.51	0.77	1.32	2.08	2.47
-15	39			15	5.46	47.0	47.5	0.25	0.48	0.71	1.24	1.96	2.37

0.5 percent, and the innate accuracy of the analytical technique has been given as less than ± 1 percent for any constituent. The observed standard deviations are 5 to 10 times larger, and no trend is observed.

- It is likely that samples would, on the average, be more homogeneous for the greater number of blending cycles. However, the results show standard deviations in percent ZnO of ± 4.5 percent both for all five-pulse and all two-pulse sequences; i.e., an insignificant difference. This appears to be due to circumstances other than demonstration of the blending capability of two-pulse sequences.

- For a reasonably well mixed batch, the large 1-gram samples taken for analysis should provide good results, and minor inhomogeneities would yield only an occasional incorrect data point.

To account for these anomalous resuts, it is postulated that the chemical analysis data inconsistencies are due either to insufficient sieving and material breakup prior to charging the mixer, to agglomerative properties of the hexachloroethane, or to improper blending action of the mixer. In either case an inhomogeneous mixture is obtained with consequent probable variations in pyrotechnic characteristics. It is interesting to speculate what consequences might prevail if burning time (quality control) samples were taken from a mix with gram-sized variances in percent aluminum of greater than 100 percent (cf 24-35-2-X, table V). Since no significant increase in sensitivity of mix (paragraph 3.2.1) or temperature rise of mixing process is observed during operation of the Jet Airmixer, longer blending cycles are suggested.

3.2.3 Conditioned Sample Test Data. The Parr bomb calorimetric measurements given in table 7 show rather large standard deviations, primarily due to failure of samples to ignite and/or burn completely. In all cases it was first attempted to ignite the reactant mixture under 1 atmosphere of air pressure to approximate actual burning conditions, but high pressures of oxygen (15 to 20 atmospheres) were necessary for combustion of 60% of the samples. Results obtained under such widely varying conditions cannot be directly compared since the high-pressure experiments are expected to result in formation of the most stable oxidized form of each element, whereas under ambient pressure products of the mixture only are anticipated. The averaged results shown for each sample entry in table 6 are given only for those trials with consistent experimental pressure values and for which evidence of ignition failure or incomplete combustion was absent. The number of replications of usable data is indicated by the "number of results" reported.

Table 6. Comparative Data, Parr Bomb Calorimetry

	Hg (AVG), Cal/gm		
Mix	24 hrs/41°C	All Other	% Difference
1	804 ± 29	837 ± 16	4
2	3400 ± ?	2240 ± 110	-52
3	1050 ± 85	1272 ± 40	17

For a given mixture formulation, there is little or no significant difference in the heats of combustion for samples conditioned under various humidity environments, and nearly all such results are within the standard deviation expected for a single value. The only notable exceptions to this general observation occur in the results for samples oven-dried for 24 hours at 41°C. Comparison of values for this conditioning with data from all other similar samples is shown in table 6. It is noted that the comparison for Mixture 2 is based on a single data point at a different pressure value and is considered to be unreliable.

There does not appear to be any significant trend in the observed percentage differences. It is possible that the differences are due to combustion properties of material remaining after sublimation of hexachloroethane from the oven-conditioned sample, but this should show a greater effect for Mix 1 since the percentage of HC is higher.

The effect of the diluent (ZnO) may be seen in the results shown in table 7. Mixes 1 and 3 both show H_g values significantly lower than that of Mix 3, since the latter contains no zinc oxide. At 1 atmosphere, equation (1) indicated probable formation of zinc chloride rather than ZnO. However, at high pressures of oxygen, fully oxygenated products are anticipated; i.e.,:

$$ZnCl_2 + 3O_2 \text{ (20 atm)} \qquad ZnO + Cl_2O_5 \text{ (etc.)}$$

The net result is that the original zinc oxide does not contribute to the heat of reaction observed and calorie-per-gram quantities are reduced in mixtures containing that constituent.

Caloric (and DTA) measurements on Mix 4 containing only aluminum and zinc oxide were difficult to obtain. Heat from this thermite-type reaction is liberated so rapidly that sample crucibles, thermocouples, and other parts of apparatus were destroyed. Consequently the measurements on this material were seriously curtailed. As expected, the observed value for heat of reaction for Mix 4 is equivalent to that obtained for oven-conditioned (excluded HC) Mix 3; the reason for a low value for oven-dried Mix 1 may be due to the higher pressure used in that experiment.

In general, Differential Thermal Analysis results on a given mixture under various environmental conditions do not exhibit large variations. DTA results from table 8, combined in bands, are compared to values obtained for the Aluminum powder and hexachloroethane constituents in the figure on page 18. (Zinc oxide does not produce isotherms in the temperature range of interest.) The following observations can be made:

- Scatter of data appears to be governed more by sample inhomogeneities and heating rates than to differences in experimental parameters. The heating rate used in the DTA analyses was 25°C per minute, and would appear to be significantly too high.

- Thermograms of oven-dried (41°C) samples appear to be simpler than those of the humidity-conditioned materials, indicating the complexity introduced by the presence of hexachloroethane in the latter. The expelling of HC from a sample during the course of a DTA analysis complicates the spectrum by causing significant base line drift. The presence of water in all samples except those that were oven-conditioned is indicated by the 100°C isotherms.

Table 7. Calorimetry and Weight Loss Data

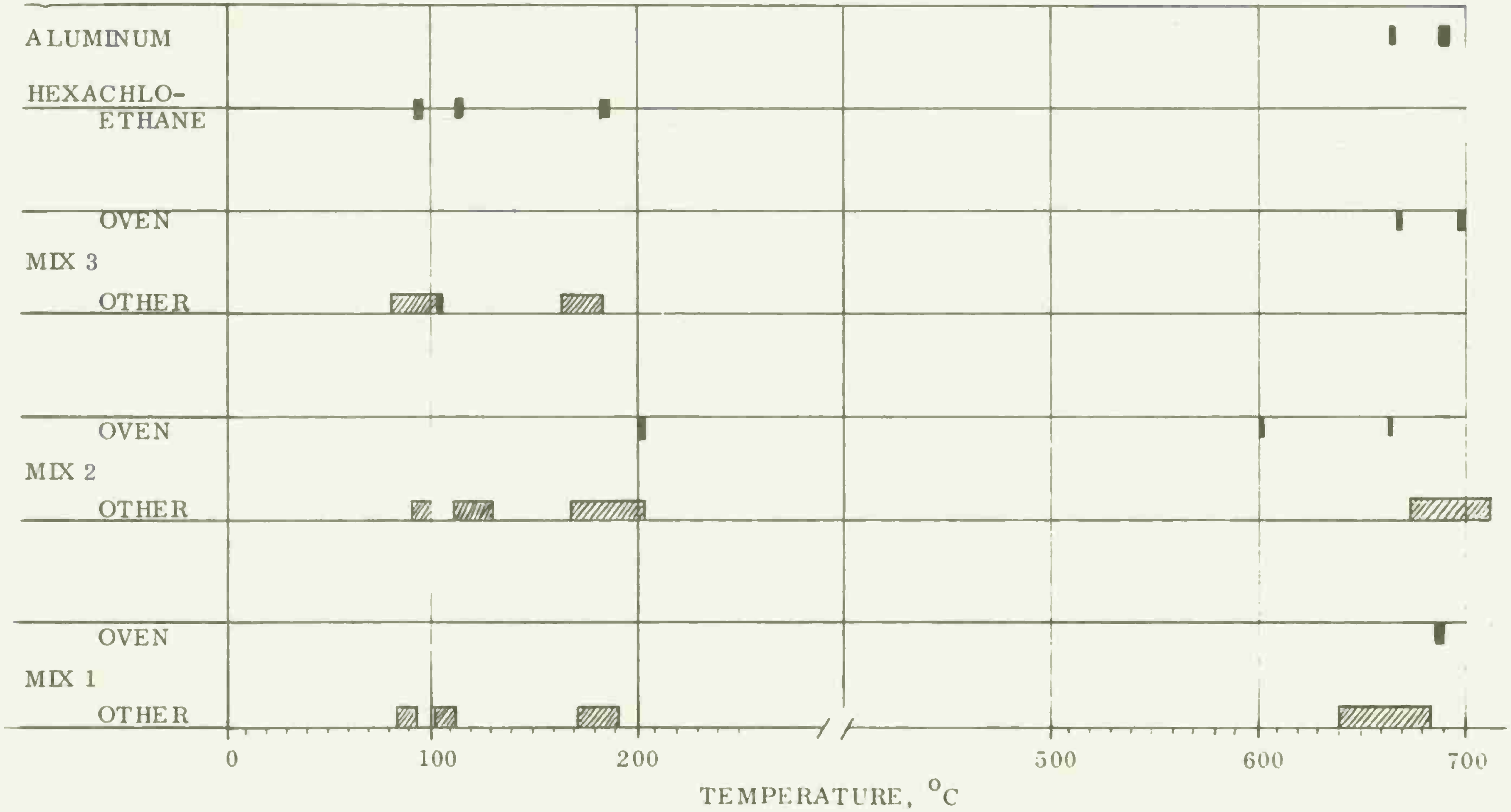
Number of Trials	Number of Results	Conditioning (24 Hr)	Pressure (ATM)	Cal/gm (Average) (± Std Dev)	Acidity**	24 Hour Weight Loss
<u>MIX 1</u>						
4	2	(Immed. after Mix)	20	827±2	0.55	-
3	2	0% RH	20	826.5±0.1	0.47	1.45%
5	2	35% RH	20	831±9	0.90	*0.51%
2	2	65%	20	861±49	0.50	*1.22%
2	2	90% RH	20	840±20	0.50	1.37%
3	2	24 hr at 41°C°C	20	804±29	0.00	49.415%
<u>MIX 2</u>						
7	4	(Immed. after Mix)	15	2,100±180	3.15	-
4	3	0% RH	20	2,377±45	1.65	1.14%
9	2	35% RH	20	2,132±2	3.38	0.93%
3	2	65% RH	15	2,100±240	1.66	0.77%
6	2	90% RH	15	2,510±54	1.85	0.89%
4	1	24 hr at 41°C°C	1	3,402±?	0.20	68.40%
<u>MIX 3</u>						
4	3	(Immed. after Mix)	1	1,294±70	3.07	-
2	2	0% RH	1	1,241±22	4.15	2.01%
3	2	35% RH	1	1,263±50	3.47	1.08%
2	2	65% RH	1	1,264±53	4.23	0.55%
2	2	90% RH	1	1,299±7	3.8	2.48%
3	3	24 hr at 41°C°C	1	1,050±85	* 0.72	49.85%
<u>MIX 4</u>						
3	3	(Immed. after Mix)	1	1,100±16	0.00	-

* Different hexachloroethane lot used.

** Ml standard alkali (0.0725N) to titrate calorimeter residue.

Table 8. Summary Date, DTA (°C)

Mix	Conditioning	Endotherms				
		1	2	3	4	5
1	0% RH	667.61	86.49	103.99	176.43	682.05
	35% RH	684.83	90.33	110.08	191.33	693.83
	65% RH	682.50	89.00	106.25	182.75	714.50
	90% RH	660.50	95.50	--	172.88	671.25
	105°F 0% RH	--	--	--	--	687.03
	Immed. after Mix	640.08	92.31	112.81	191.18	683.93
2	0% RH	697.22	99.30	124.30	205.60	712.22
	35% RH	653.56	96.31	--	168.56	673.06
	65% RH	647.00	92.50	110.00	178.75	680.25
	90% RH	683.50	92.50	115.50	196.13	700.00
	105°F RH	603.67	--	—-	201.67	664.17
	Immed. after Mix	672.78	92.78	132.28	178.53	692.28
3	0% RH	648.75	99.50	---	164.38	666.25
	35% RH	671.47	104.78	---	171.72	681.72
	65% RH	678.00	81.00	104.25	184.25	692.75
	90% RH	663.67	--	103.67	171.67	680.92
	105°F 0% RH	669.80	--	--	--	698.55
	Immed. after Mix	689.96	91.45	—	183.20	727.25
Aluminum 0%		665.89	--	-	--	690.54
Hexachloroethane		--	92.57	112.64	182.59	--
Zinc Oxide	Based on Handbook of Chemistry: decomposes at >1800°C					



Summary of DTA Results
Temperature of Endotherms

- Isothermal behavior was observed in the region of 530°C-600°C only for oven-dried Mixes 2 and 3 and for 90 percent RH samples of Mix 3. This result may be attributed to improperly obtained thermograms or to peculiar sample behavior. The possibility that the isotherms are due to presence of $Al/H_2O/C_2Cl_6$ reaction products (eqs. 1A, 1B) cannot be proven from the existing data. Possible reaction products and known isotherms are:

$AlCl_3 \cdot 6H_2O$	100°C (Decomposition)
$AlCl_3$	178°C (Sublimation)
$Al(OH)_3$	300°C (Decompositon)
C_2HCl_5	162°C (Boiling point)
$ZnCl_2$	283°C (Melting point) 732°C (Boiling point)

None of these temperatures correspond to the anomaly observed.

3.2.4 General Discussion. The results obtained in this experiment showing marked differences from those obtained previously may be a function of the purity differences in laboratory samples prepared from chemically pure components and technical grade commercial materials used in the manufacturing process. It is possible that technical grade materials would produce less sensitive mixes than that prepared from pure components, as observed, but this phenomenon would not be expected. The absence of gross moisture absorption by the mixes prepared from chemically pure components may not relate to the same effect in plant material. It is feasible that impurities in the hexachloroethane or the other components could contribute significantly to absorption of moisture. These effects cannot be completely determined by the results of this experiment.

The choice of HC white smoke mix and the Jet Airmix blender as subjects for this study of environmental effects and reaction processes was prompted by the current interest in the products. However, it devolved that this selection was ill-advised. The reactions of the hexachloroethane-based pyrotechnics are apparently quite complex and deduction of reaction mechanisms are difficult. Furthermore, the sensitivity of the normal mix to input energy tests is such that slight variations dependent on environmental or other parameters cannot be readily detected. Other objections relate to the quality of technical grade materials and the difficulty in achieving satisfactorily homogeneous blending of semi-solid, glutinous hexachloroethane.

The use of the Jet Airmixer for these studies was also unfortunate. Sample exposure times to environmental conditions is so brief and mixing energy so low that little effect on the mixes is expected. It is interesting to speculate what results may have been obtained had a mechanical mixer been used with blending times of several minutes rather than a few seconds.

The large quantity of data available from the DTA and Parr bomb calorimetry measurements in this study have not been extensively studied. Interpretation of results will require a more exhaustive effort and careful analysis of all contributing factors.

The following observations and discussion are relevant to this study:

- In the presence of mercury salts, aluminum undergoes reaction to produce elemental mercury:

  $$3Hg^{+2} + 2Al \longrightarrow 2Al^{+3} + 3Hg$$

  The resulting amalgram of aluminum metal in mercury destroys the protective oxide coating of the aluminum and rapid oxidation occurs. A large quantity of heat is liberated in a short time.

  $$2Al(Hg) + 3O_2 \longrightarrow Al_2O_3 \ (\Delta H = -399 \text{ KCal/Mole})$$

  The reaction of the aluminum with highly chlorinated hydrocarbons would be similarly affected and the "hot spot" from this could enhance other reactions with low reaction rates at lower temperatures. Mercurial impurities might account for the anomalous accidental ignitions of HC smoke that have been reported. It is noted that mercuric compounds are common impurities in zinc oxide.

- The well-known and very reactive Grignard reagents are formed by reaction of a metal with halides of hydrocarbons; e.g.,:

  $$R\text{-}Br + Mg \longrightarrow R\,MgBr$$

  It is feasible that Grignard-type reactions may occur between aluminum and hexachloroethane:

  $$Cl_5C_2\text{-}Cl + Al \longrightarrow Cl_5C_2\text{-}AlCl_2, \text{ etc.}$$

  It is noted that such reagents attack water readily and are explosive when dry. This phenomenon is a possible mechanism by which the relation between sensitivity and water content can be explained.

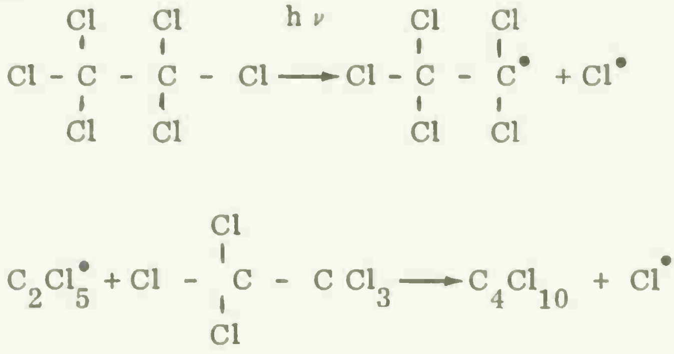
- Delocalization of electronic charge in highly chlorinated hydrocarbons is expected. For example, a considerable amount of double-bond character in the C-Cl bonds are indicated by NMR and Nuclear Quadrupole Resonance Spectroscopy. These observations support hypotheses for the stability of free radicals and ions formed from the chlorocarbons:

  $$C_2Cl_6 \xrightarrow{h\nu} C_2Cl_5^{\bullet} + Cl^{\bullet}$$

  or

  $$C_2Cl_6 \longrightarrow C_2Cl_5^{+} + Cl^{-}$$

Since free radical reactions usually obey apparent high order kinetics, fast reaction involving the reactive aluminum metal and such radicals or ions may be possible. The high enthalpy of formation of most aluminum salts act to favor this type of reaction. Possible reactions involving free radical catalysis are shown below:



$$\mathrm{Cl-\overset{Cl}{\underset{Cl}{C}}-\overset{Cl}{\underset{Cl}{C}}-Cl \xrightarrow{h\nu} Cl-\overset{Cl}{\underset{Cl}{C}}-\overset{Cl}{\underset{Cl}{C^{\bullet}}} + Cl^{\bullet}}$$

$$\mathrm{C_2Cl_5^{\bullet} + Cl-\overset{Cl}{\underset{Cl}{C}}-C\,Cl_3 \longrightarrow C_4Cl_{10} + Cl^{\bullet}}$$

$$\mathrm{3Cl^{\bullet} + Al \longrightarrow AlCl_3 + heat}$$

.

.

.

Etc.

Similar electrophilic and nucleophilic mechanisms would be possible if ionization schemes are important.

4.0 FINDINGS AND CONCLUSIONS

4.1 Summary Findings.

a. Impact sensitivity data obtained from HC smoke mix differ radically from previous results and from interpretation of the Class 2 designation for the bulk material.

b. Sublimation of hexachloroethane from HC smoke mixes is significant under any of the conditions studied, even under conditions of semiconfinement. Complete loss occurred when openly stored for 24 hours at 41°C.

c. Gross inhomogeneities were found for HC smoke formulations prepared in the bench model Jet Airmixer.

d. Evidence was obtained that absorption of moisture occurs under the conditions studied; however, quantitative evaluation of moisture content was inconclusive.

e. No contributions to input sensitivity or output energy were found from blending or storage in humid environments or from variances in mixing times.

f. Reaction mechanisms were indeterminant, and changes thereto with concentration of hexachloroethane were not proven with certainty.

g. DTA and Parr bomb calorimetry did not provide readily interpretable, useful results.

4.2 Conclusions (Refer to Paragraph 3.2.4).

a. The present Class 2 hazard classification for bulk HC smoke mix does not correlate with the overall results of this experiment; an error exists in one or the other.

b. There is little influence of moist atmosphere or moderately high temperatures on the sensitivity of HC smoke mix; results were consistently inconsistent with prior work.

c. Mixing rates and times, or blending procedure, used for the Jet Airmixer, may not produce an adequately homogeneous HC smoke mix.

d. Sublimation of hexachloroethane from HC smoke mix occurs at normal ambient temperatures. Mix sensitivity as a function of lost HC is inconclusive.

e. Reaction process/mechanism determinations were inconclusive.

5.0 RECOMMENDATIONS

The following recommendations are made:

- A study should be made to determine suitability of end items prepared from material blended in pneumatic mixers.
- The classification of bulk HC smoke mix should be reexamined.
- The sensitivity of HC smoke mixes to all normal modes of initiation should be investigated, including dependency on hexachloroethane concentration.
- Quantities of HC white smoke mix should not be stored in open or semiconfined containers for more than a few hours.
- The entire scenario of HC smoke mix life cycles should be investigated to determine the influence of hexachloroethane sublimation.
- Techniques should be developed for detection of chloride ion in raw materials and in the mixing process.

REFERENCES

1. Pyrotechnic Mix Formulary and End Item Information, Weapons Development and Engineering Laboratories, Chemical Process Laboratory, Edgewood Arsenal, Maryland, 1970; drawing number B-143-1-1.

2. GE-MTSD-R-035, Pyrotechnic Hazards Classification and Evaluation Program, Phase I, Contract NAS8-23524, May 1970.

3. EA-FR-4D21, Identification and Evaluation of Hazards Associated with Blending of HC White Smoke Mix by Jet Airmix Process, Edgewood Arsenal, Maryland, 1974.

4. Engineering Design Handbook, Military Pyrotechnic Series Part 1, Theory and Application, AMC P 706-185, -186, -187, and -189, revision 1967.

5. Dangerous Properties of Industrial Materials, N. Irving Sax, Second Edition, 1963.

6. Department of the Army Technical Bulletin 700-2, 19 May 1974, Chapters 3 and 5.

7. EATR, Application of Explosive Test Technology to Determine Pyrotechnic Hazard Classification, 1974, in preparation.

GENERAL BIBLIOGRAPHY

1. Edgewood Arsenal, Electrostatic Hazard Evaluation of Pneumatic Dispersive Mixing Operation, Final Report EA-FR-1HOX, 1973.

2. US Army Munitions Command, Military Chemistry and Chemical Agents, Technical Manual TM3-215, 1963.

3. National Bureau of Standards, Precision Measurement and Calibration-Heat, NBS Special Publication 300, Vol, 6, 1970.

4. Edgewood Arsenal, Pyrotechnic Hazards Classification and Evaluation Program, Phase III, Segments 1-4, Investigation of Sensitivity Test Methods and Procedures for Pyrotechnic Hazards Evaluation and Classification, Final Report GE-MTSD-R-059, 1971.

5. AMC 385-100 Safety Manual, April 1970 revised 4 January 1974, Electrostatic Hazard Evaluation of Pneumatic Dispersive Mixing Operation, EA-FR-1HOX, 30 June 1973.

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