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IMPROVEMENT OF SENSITIVITY OF LMH-1 PROPELLANTS

Contract AF04(611)-11381

FINAL TECHNICAL REPORT AFRPL-TR-67-110

E. Gene Goree

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IMPROVEMENT OF SENSITIVITY OF LMH-1 PROPELLANTS

Contract AF04(611)-11381

FINAL TECHNICAL REPORT AFRPL-TR-67-110

E. Gene Goree

[redacted]

FOREWORD

(U) This, the Final Technical Report under Contract AF 04(611)-11381, covers work performed from 3 January 1966 to 2 January 1967. This contract, with the Huntsville Division of Thiokol Chemical Corporation, was initiated under Air Force Rocket Propulsion Laboratory, Research and Technology Division Project 3148. This work was accomplished under the technical direction of R. W. Bargmeyer, 1/Lt., USAF of the Research and Technology Division Air Force Systems Command, United States Air Force, Edwards Air Force Base, California 93523.

(U) Mr. E. Gene Goree of Thiokol's Research and Development Department was the principal investigator on this program. Mr. Goree was assisted in these studies by Dr. W. D. Stephens, who is the principal investigator of all high energy propellant programs at Thiokol's Huntsville Division. Full authority for the management control of this program was the responsibility of Mr. G. F. Mangum of the Project Management Directorate. Mr. Carl J. Whelchel was the Assistant Project Manager. Others who cooperated in the work and in the preparation of this report were Messrs. W. E. Hunter, M. R. Priest, Jr and Mrs. E. J. Grice.

(U) This report has been assigned the Thiokol internal number 16-67 (Control No. C-67-16A).

(C) The overall objective of this program was to define and to improve the general sensitivity characteristics of aluminum hydride propellants.

(U) This report contains no classified information extracted from other classified docuements.

(U) STATEMENT OF APPROVAL

This technical report has been reviewed and is approved.

W.H. EBELKE, Colonel, USAF
Chief, Propellant Division
Air Force Rocket Propulsion Laboratory

[redacted]

UNCLASSIFIED ABSTRACT

Thiokol's program to define the cause of LMH-1 propellant sensitivity and, in turn, to decrease the sensitivity characteristics of these propellants was divided into two phases: Phase I - Sensitivity Definition, and Phase II - Sensitivity Improvement. Factors affecting the sensitivity of both cured and uncured LMH-1 propellant have been investigated and defined. Studies which were conducted with regard to sensitivity definition indicated that both LMH-1 and ammonium perchlorate, separately, are insensitive to both impact and friction. The friction sensitivity of LMH-1 propellants is due to the relative ease of reaction of LMH-1 with oxidizer, and that to desensitize these propellants, contact between the two must be prevented or limited. Various methods of sensitivity improvement were examined. Some of these were surface treatments and coatings, binder solid bond studies, pasting techniques, and interrelationships between propellant variables. The friction sensitivity of the LMH-1 formulation tests varied from 1200 to 6000 rpm. The application of techniques to physically limit the contact of fuel to oxidizer, or to reduce the friction produced by the contact were responsible for these large decreases of sensitivity. These results were far beyond the established goals of the program. Impact sensitivity of propellants was found to be significantly affected by changes in ingredient particle size of solid ingredients.

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NOMENCLATURE LIST

Al	(U)	Aluminum (U)
Al_2O_3	(U)	Aluminum Oxide (U)
AlH_3	(C)	Aluminum Hydride (C)
AP	(U)	Ammonium Perchlorate (U)
B	(U)	Boron (U)
CaF_2	(U)	Calcium Fluoride (U)
E_o	(U)	Impact Measure - level of 10 consecutive negative (no fire) tests (U)
F_o	(U)	Friction measure - rpm level of 10 consecutive negative (no fire) tests (U)
HYPALON	(U)	Synthetic rubber from chlorosulfonated polyethylene (U)
HMX	(U)	Cyclotetramethylene-tetranitramine (U)
HX-874	(U)	Liquid trifunctional imine curing agent (U)
I_{sp}	(U)	Specific Impulse (U)
LMH-1	(U)	Unclassified code name for Aluminum Hydride (C)
MoS_2	(U)	Molybdenum Disulfide (Molykote), product of Alpha Molykote Corp. Stamford, Connecticutt
RDX	(U)	Cyclotrimethylenetrinitramine (U)
rpm	(U)	Revolutions per minute (U)
SiC	(U)	Silicon Carbide (U)
TMETN	(U)	Trimethylolethane trinitrate (U)
TP-90B(R)	(U)	Butyl Carbitol formal (U)
VITON A	(U)	Fluorocarbon
Volan	(U)	(Methacrylate chromic chloride) - Volan's trade name for experimental Werner-type chrome complexes supplied by E. I. du Pont de Nemours & Co., Inc.
WMD	(U)	Weight Mean Diameter (U)
ZL-437	(U)	Polyester propellant binder (U)

SECTION I

INTRODUCTION

(C) The advancement of solid propellant technology is directly related to the reduction in the sensitivity of new high energy propellant ingredients and formulations, thus making it mandatory to use utmost caution in selection of propellant materials and propellant formulations, and to develop safe processes. Thiokol Chemical Corporation has emphasized, since its entry into the industry in 1949, development of safe manufacturing procedures and delivering to its customers the safest and most reliable product obtainable. Thiokol's efforts in working with high energy propellant ingredients, such as nitronium perchlorate, hydrazine diperchlorate, organic difluoramines, boron compounds, and particularly aluminum hydride (LMH-1)[1], have provided Thiokol with an insight to sensitivity problems and in many instances solutions to these problems.

(U) The use of LMH-1 in solid propellant formulations affords one of the most desirable methods available today for obtaining high performance with non-toxic exhaust gases. Thiokol and other propulsion contractors have developed LMH-1 containing propellants which have substantiated the increased ballistic performance.

(U) One of the biggest problems delaying the use of LMH-1 containing propellants in practical propulsion systems is the sensitivity to friction, impact, and electrostatic discharge in both the uncured and cured conditions. The development of a technique or method for reducing the sensitivity of LMH-1 containing propellant is highly desirable, since this would lessen both costs and hazards involved, and allow its use in future propulsion systems.

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1. A nomenclature list may be found at the beginning of this report.

(U) The value of this material and the desire for reduced friction sensitivity is recognized by the Services. The U. S. Air Force contracted with the Huntsville Division of Thiokol to conduct a 12-month applied research program, the over-all objective of which was to determine the cause of the sensitivity of LMH-1 propellant, and to decrease this sensitivity to a level where the propellant is practical. This was to be accomplished without a significant loss in performance (below 280 lb-sec/lb, theoretical specific impulse). Thiokol's established goals to work toward during the program were:

UNCLASSIFIED

	Cured Propellant	Uncured Propellant
E_o, kg-cm	40	30 - 40
F_o, rpm	3000	2500

UNCLASSIFIED

This sensitivity range places it in the region of standard production types of aluminized perchlorate propellants such as TP-H8126 (Nike Zeus Propellant) which has been made in large quantitites. This propellant has a cured sensitivity of E_o = 45.0 kg-cm, and F_o - 3500 rpm; the uncured propellant E_o = 45.0 kg-cm and a F_o of 2500 rpm.

(U) Thiokol's program to define the cause of LMH-1 propellant sensitivity and, in turn, to decrease the sensitivity characteristics of these propellants was divided into two phases.

(U) Phase I - Sensitivity Definition

(U) The specific objective of this phase of work was to define the cause of the sensitivity of both cured and uncured LMH-1 propellant. The approach taken was designed to determine and investigate each of the factors affecting the sensitivity of LMH-1 and to relate them to processing hazards.

(U) Phase I was divided into three tasks as follows:

(U) Task 1 - Physical Factors

(U) The factors of LMH-1 particle size and surface area, oxidizer particle size and surface area, and coatings of LMH-1 and/or oxidizer, were investigated in this task.

(U) Task 2 - Processing Factors

(U) Propellant Microstructure

(U) Propellants using large and small particle LMH-1 were manufactured to choose the optimum solids packing which should eliminate voids and reduce sensitivity. Optimum packing was determined by measuring the bulk density of mixtures of different particle size ammonium perchlorate (AP) and the selected LMH-1. In addition, the wetting of the solids by the polymer, the plasticizer and polymer/plasticizer/curing agent combination were investigated.

(U) Processing

(U) Processing variables were studied in both the cured and uncured state, in typical propellant formulations using two sizes of LMH-1. These variables were (1) type of mixer (different shear); (2) mixing time; (3) mixing speed; (4) type of atmosphere and (5) order of addition of ingredients.

(U) Formulation Variables

(U) Percent Plasticizer

(U) LMH-1 was evaluated with 14, 10, 7, 4 and 0 percent energetic plasticizer (TMETN), and sensitivity versus TMETN content was plotted.

(U) Quantity of LMH-1

(U) The quantity of LMH-1 was varied from 15 to 30 percent in 5 percent increments for the manufacture of these mixes. Data is presented as plots of sensitivity versus LMH-1 concentration.

(U) Task 3 - Chemical Factors

(U) The effect of various hydride surface treatments on propellant sensitivity were determined under this task.

(U) Phase II - Sensitivity Improvement

(U) The specific objective of this phase of work was to find methods for reducing the sensitivity of LMH-1 containing propellant while maintaining the performance level of 280 lb-sec/lb theoretical specific impulse.

(U) This phase was divided into the following three tasks:

(U) Task 1 - Investigation of Surface Treatments and Coatings

(U) The purpose of Task 1 was to determine which coatings and/or surface treatments for LMH-1 and/or ammonium perchlorate would reduce the sensitivity of LMH-1 propellants the most.

(U) Task 2 - Interrelationship Among Propellant Variables

(U) Upon completion of Task 1, Task 2, which was the manufacture of propellant samples for determination of the sensitivity of these propellants, was initiated. This factorial experiment followed the work of Task 1 because that information was used to reduce the number of variables in the factorial experiment.

(U) Task 3 - Effect of LMH-1 and /or Ammonium Perchlorate Particle Size on Propellant Sensitivity

(U) Task 3 was conducted to determine the best particle size of LMH-1 and/or ammonium perchlorate to obtain minimum propellant sensitivity, based on the knowledge gained in Task 2.

(U) This final report discussed the work performed in the above area of research and presents the conclusions drawn as a result of these investigations.

SECTION II

SUMMARY

(U) The overall objective of this applied research program was to determine the cause of the sensitivity of LMH-1 propellant and to decrease this sensitivity to a practical level. This objective was to be accomplished with a processable propellant and without a significant loss of the theoretical specific impulse (280 lb-sec/lb).

(U) At the initiation of this program, propellants made from LMH-1 and ammonium perchlorate with a polyester binder and TMETN had friction sensitivities (F_o) in the range of 1400 to 1800 rpm, and impact sensitivities (E_o) in the range of 6 to 8 kg-cm. Spark sensitivity values were in the region of 0.5 to 1 joule.

(U) At the completion of this program LMH-1 propellants had been made which had E_o values in excess of 15 kg-cm, and F_o values in excess of 4000 rpm. No improvements of electrostatic discharge sensitivity were realized in the course of the program.

(U) The general levels of impact and friction sensitivity are determined by the innerent characteristics of the component ingredients. However, changes may be made within this general level. In defining the problem areas, impact sensitivity was found to be closely associated with ammonium perchlorate in its relationship with the other propellant ingredients. Friction and spark sensitivity were found to be largely attributable to LMH-1 as it relates to other propellant ingredients.

(U) Surface coatings have been found to be important. Coating LMH-1 with a liquid (such as binder) gives improvement in the friction sensitivity properties, but has little effect on impact values. Coating the ammonium perchlorate with binder intensifies the friction sensitivity problem without changes in impact values. The general trend set by these experiments suggests that optimum desensitization would result when solid fuel particles are precoated with liquid fuel components and solid oxidizer particles are precoated with liquid oxidizer ingredients prior to mixing all of the propellant components.

(U) A study of the interrelationships among variables was undertaken as a part of this progrm. Factorial experiments were conducted in an attempt to elucidate relationships among the several parameters. The results of these experiments were quite complex; however, several generalizations can be made.

Reduction in TMETN content gives improvements in impact and friction sensitivity without affecting spark sensitivity. Substitution of RDX for part of the ammonium perchlorate generally improved friction sensitivity, and coatings of LMH-1 generally showed the same effect.

(U) Perhaps the most useful information generated in this study relates to particle size effects with both LMH-1 and ammonium perchlorate in regard to impact sensitivity of uncured propellants. The impact sensitivity of a given formulation in the uncured state is a function of the ratio of the particle size of LMH-1 to the particle size of ammonium perchlorate within a critical range of particle size ratios (2 to 11). Below and above this range of particle size ratios, propellants are much more sensitive to impact. The optimum particle size for LMH-1 was determined to be between 30 and 90 microns.

(U) Experiments with dry blends of LMH-1 and ammonium perchlorate have resulted in a method for predicting impact sensitivities of uncured propellants from data obtained by use of dry blends of the solid components. For any given formulation, this method is capable of quantitatively predicting changes in impact sensitivity due to changes in particle sizes of the solid components.

SECTION III

HYPOTHESIS OF SENSITIVITY

(U) It was anticipated that the sensitivity of LMH-1 propellants could, by various techniques, be improved to a level not far removed from the sensitivity of state-of-the-art composite propellants. Thiokol established the following goals for sensitivity to work toward during the program.

UNCLASSIFIED

	Uncured Propellant	Cured Propellant
Impact (E_o) kg-cm	30 - 40	40
Friction (F_o) rpm	2500	3000

UNCLASSIFIED

These goals approximated the sensitivity values of standard production types of aluminized perchlorate propellants such as TP-H8126 (Nike Zeus propellant), which is measured at 45 kg-cm (E_o) for both the uncured and cured propellants, and 2500 and 3500 rpm (F_o), respectively, for uncured and cured propellant.

(U) Impact sensitivities for the LMH-1 formulation tests of this program ranged from 3 to 18 kg-cm. The highest level of impact sensitivity measured in the investigation for a processable propellant was 12 kg-cm.

(U) The friction sensitivity of the LMH-1 formulation tests varied from 1200 rpm to 6000 rpm. The application of techniques to physically limit the contact of fuel or oxidizer, or to reduce the friction produced by the contact are responsible for these large decreases of sensitivity. This area of the sensitivity investigation has attained results far beyond the established goals.

(U) During the course of this program, efforts were made to decrease the electrostatic discharge (spark) sensitivity of "neat" LMH-1 and of the propellant containing LMH-1. Techniques such as treatments with anti-static agents, coating of the particles with polymers and special processing techniques were not successful in obtaining improvements of spark sensitivity.

(U) HYPOTHESIS OF IMPACT SENSITIVITY

(U) The definition of factors effecting the impact sensitivity of LMH-1 propellants is much more complex than the definition of factors effecting the friction sensitivity. An analysis of the impact test device also considers friction factors of impaction induced to the propellant at the instant of impact. Therefore, in an accurate analysis, friction is not completely separated from impact sensitivity; there are, however, basic differences.

(U) Working Hypothesis

> The two major factors to be considered in impact sensitivity are: (1) the inherent impact sensitivities of the individual materials, which is the most significant in the resulting sensitivity of the propellant, and (2) propellant packing structure (microstructure, or the arrangement of each ingredient in respect to other ingredients).

(U) The inherent sensitivities of the various ingredients is a property which cannot be manipulated by physical changes. However, propellant microstructure adjustments do allow a certain degree of latitude in improvement of impact sensitivity.

(U) It was shown early in this investigation that the particle size of solid ingredients has a significant effect on the impact sensitivity of propellants. This solid particle size effect was also shown in tests of dry mixtures of AP/LMH-1. In the early portion of the program, it was concluded that small ammonium perchlorate, with a given LMH-1 particle size, produced improved impact sensitivities. It was also shown, at that time, that the intermediate particle size of LMH-1 ($\sim$85 micron), with the small particle ammonium perchlorate, was less sensitive to impact than were combinations of the larger or smaller LMH-1 particles.

(U) A limited series of tests were conducted in order to determine the effect of the substitution of aluminum for the LMH-1 in the standard formulation on impact sensitivity. It was concluded from the results of these tests that small ammonium perchlorate particles in this system gave propellants that were less sensitive to impact.

(U) In the latter stages of this investigation, it was discovered that impact sensitivity measurements on dry blends of LMH-1 and ammonium perchlorate could be directly correlated with impact sensitivities of uncured propellant. Furthermore, the correlation is one which lends itself to a simple mathematical treatment, enabling predictions of E_{a} for variations in a propellant formulation due to changes in particle size of the solid ingredients. This topic is discussed in detail under Phase II, Task 3, d. The results of this work indicate that the ratio of particle size of LMH-1 to particle size of ammonium perchlorate is critical, and that not only is this ratio of importance, but also the actual particle diameters are critical. The realization of these relationships awaited the availability of ammonium perchlorate in particle sizes below 2 microns, a development which occurred in the latter stages of the program.

(U) Tests of the impact sensitivities of the individual propellant materials and combinations of materials showed that TMETN is the only "neat" material sensitive to impact (4 kg-cm). It is, therefore, concluded that increases or decreases in TMETN content would directly affect the propellant impact sensitivity.

(U) The impact sensitivity measurements of combinations of two ingredients showed that the dry blend of AP/LMH-1 was most sensitive, while a combination of LMH-1/ZL-437 remained insensitive; other measured combinations were intermediate. A combination of three ingredients, AP/ZL-437/TMETN, gave one of the most sensitive values. A combination of LMH-1/ZL-437/TMETN was considerebly less sensitive to impact than the AP/ZL-437/TMETN combination. It was also shown that the most sensitive dry blends of AP/LMH-1 were two to three times less sensitive to impact than the standard propellant formulation.

(U) These results indicate that addition of the sensitive TMETN is largely responsible for the increase in impact sensitivity. It was also indicated from the material combination tests that the oxidizer (ammonium perchlorate) is more influential on impact sensitivity than the fuel (LMH-1).

(U) These facts and observations then indicate that a relationship of solid particle sizes, packing structure and sensitivity exists.

(U) It was also shown that other factors influence the total impact sensitivity of propellant. Test results of dry lubricants with dry blends of AP/LMH-1 showed an improvement in impact sensitivity. The addition of low concentrations of the lubricants to propellants (low concentrations were necessary to maintain propellant performance) indicated little, if any, improvement in impact sensitivity. The improvement in impact sensitivity of the dry blends with dry lubricants is attributed to the lubricant's reduction of friction.

(U) It was also shown that viscosity decreases were generally associated with an increase in impact sensitivity for uncured and cured propellant. This observation is attributed to the effect of the binder including TMETN. Due to the sensitivity of TMETN, a low propellant viscosity would allow the force of the impact to be applied more directly to the sensitive TMETN, whereas a more viscous formulation would cushion the impact force.

(U) HYPOTHESIS OF FRICTION SENSITIVITY

(U)

Hypothesis

> The friction sensitivity of a given propellant is dependant upon two primary variables; first, the inherent sensitivity of the propellant (as a result of combining the respective ingredients that constitute the formulation) and second, the degree of intimate contact between the oxidizer and the fuel.

(U) The first variable is, in most instances, an uncontrollable variable, unless sensitivity is considered foremost in the formulating of the propellant. The second variable is controllable and techniques may be applied to effectively overcome the sensitivity of the respective ingredients that constitute the formulation.

(U) It was shown that the individual ingredients [ZL-437 (polyester), TMETN, ammonium perchlorate and LMH-1] have a friction sensitivity (F_o) greater than 7000 rpm. However, when ZL-437 is added to ammonium perchlorate, F_o becomes 4600 rpm (becomes more sensitive); when TMETN is added to this mixture, F_o is increased to 5600 rpm, and when LMH-1 is added to complete the propellant, F_o is reduced to ~ 2000 rpm. In addition, dry blends of ammonium perchlorate and LMH-1 have a F_o of 600 rpm.

(U) The largest reductions in F_o (increase in friction sensitivity) occurred when a fuel (ZL-437 or LMH-1) was added to an oxidizer. Since LMH-1 has the highest energy as a fuel, the most severe friction sensitivity noted was with the AP/LMH-1 combination. In support of this theory, it was shown that the addition of ZL-437 to LMH-1 does not reduce the friction sensitivity below 7000 rpm, and to add TMETN to ammonium perchlorate does not significantly change the friction sensitivity (6800 rpm). It was also shown that when coating concentrations of ZL-437 on ammonium perchlorate were increased from 2 to 5 percent in propellant formulations, the friction sensitivity was increased in relation to the increase of coating.

(U) These facts strongly support the oxidizer-fuel contact variable theory of friction sensitivity and suggest that the optimum friction sensitivity characteristics would be obtained in a propellant where the solid oxidizer is coated with liquid oxidizers, and the solid fuel is coated with liquid fuels prior to mixing fuels and oxidizers in a propellant manufacturing operation.

(U) Tecnniques used in this applied research program to reduce friction sensitivity produced measured sensitivities of 6000 rpm. These techniques included the reducing of TMETN, which removed part of the oxidation potential, or the reduction of LMH-1, which removed energetic fuel. Neither of these techniques is practical due to the related effects on propellant performance.

(U) Several other techniques (i.e., coatings, improved particle wetting, use of a dry lubricant) were used without significant decreases in propellant performance. These techniques are applications of the contact variable, and F_o's of over 6000 rpm were measured. The coating of LMH-1 with the binder (a less energetic fuel), utilizing a solvent-nonsolvent method, produced substantial improvements in friction sensitivity. The use of small percentages of wetting agents or pasting of the LMH-1 in the binder was also very effective. These three techniques are ways of providing a separation of the fuel from the oxidizer. The use of lubricating agents (such as RDX or Teflon), a less direct method of fuel and oxidizer separation, but one that reduces friction by lubrication, was also found effective.

SECTION IV

EXPERIMENTAL ACCOMPLISHMENTS

(C) This program was divided into two phases: Phase I - Sensitivity Definition, and Phase II - Sensitivity improvement. The objective of Phase I was to define the causes of the sensitivity of both the cured and uncured aluminum hydride (AlH_3; Code Name, LMH-1) propellant and to relate them to processing hazards. The objective of Phase II was to find methods of reducing the sensitivity of LMH-1 propellant while maintaining the performance level of 280 lb-sec/lb theoretical specific impulse.

(U) 1. Phase I. Sensitivity Definition

(U) The work of Phase I was divided into three tasks which grouped the factors affecting sensitivity. Task 1 considered the physical factors, such as particle size of LMH-1, surface area of ammonium perchlorate and the coatings that can be applied to these two solids. Task 2 dealt with the processing factors in making the propellant. It considered propellant microstructure, processing techniques, propellant density (as governed by particle packing and processing) and finally formulation variables. Task 3 dealt with chemical factors and treated the subjects of thermal stability of LMH-1 and methods of surface treatment of LMH-1.

(U) The standard composition used throughout this program was as follows:

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	Weight, %
LMH-1	25.00
AP	49.50
ZL-437/HX-874	11.50
TMETN	14.00

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Due to the short supply of a single particle size of LMH-1, it was necessary to change LMH-1 particle size for the standard composition throughout the program, thereby necessitating several different standard mixes to be used for comparison purposes.

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(U) The physical characteristics of the materials utilized during this investigation and the experimental evaluations conducted under the sensitivity definition phase of this program are discussed below.

(U) a. Physical Characteristics of Materials

(U) (1) Physical and Chemical Analyses of LMH-1

(U) Several different lots of LMH-1, which were received from the Dow Chemical Company, were utilized in the experimental evaluations conducted under this program. These lots varied in particle size, bulk density, thermal stability and in the type of doping treatment of LMH-1. The initial investigations were conducted with untreated (neat) LMH-1. Several of these untreated lots were selected and submitted to Galbraith Laboratories, Inc., Knoxville, Tennessee for duplicate carbon and hydrogen analyses. The results of these analyses are shown below:

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LMH-1 Lot No.	Carbon	Hydrogen
03254	0.33	9.94
	0.40	10.06
04224A	0.37	9.96
	0.42	10.00
06104	0.52	9.94
	0.49	10.00
01235A	0.12	10.05
	0.10	10.04
02255A	0.07	10.01
	0.08	10.19
02275A	0.30	10.02
	0.23	10.27
03015A	0.10	9.98
	0.12	10.14
03265	0.30	10.05
	0.32	10.16

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The theoretical hydrogen percentage in LMH-1 is 10.078; therefore, these data indicate that each of the selected materials was of a high (99+ percent) purity.

The doping treatment, bulk density, weight mean diameter (WMD), specific surface, and thermal stability for the selected LMH-1 lots are shown on Table I. The bulk density was obtained by tapping a known weight of material into a graduated cylinder to a constant volume, WMD was determined by micromerograph, and specific surface was obtained by nitrogen absorption.

(U) (2) Vacuum Thermal Stability of LMH-1

(U) The thermal stability data as detailed in Table I does not show significant differences of stability between the untreated and doped forms of LMH-1 at the 48-hour test period. A comparison of equivalent particle sizes of the doped forms of LMH-1 does, however, show general improvements as the test period increases. The Mg/DPA-doped LMH-1 appears to be among the most stable at the 200-hour test period, while the Mg-doped LMH-1 is the second most stable at this time.

(U) (3) LMH-1 Sensitivity

(U) Sensitivity tests were conducted on untreated and treated lots of LMH-1 to determine the effect, if any, of doping treatments on sensitivity. The results of these tests are shown below:

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LMH-1 Lot No.	Type LMH-1	Impact (E_o) (kg-cm)	Friction (F_o) (rpm)	Spark (ESD) (joules) (-)	Friction Screw (+) to grit
03265 (138μ)	Untreated	> 250	>7000	0.05	(-) to all grits
06104 (32μ)	Untreated	> 250	>7000	0.10	(-) to all grits
02106	Mg-Doped	> 250	>7000	0.1	(-) to all grits
655-1880-7	Mg/DPA-Doped	> 250	>7000	0.05	(-) to all grits

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These results indicate no difference in LMH-1 material sensitivity as a result of the doping treatments.

TABLE I UNCLASSIFIED

PHYSICAL CHARACTERISTICS OF SELECTED LMH-1 LOTS

LMH-1 Lot No.	Bulk Density (g/cc)	WMD (μ)	Specific Surface (m^2/g)	Thermal Stability % Decomposition At 60°C 48 hrs	100 hrs	200 hrs
03254[a]	0.727	48.0	0.485	0.10	0.19	0.26
04224A[a]	0.655	36.6	0.957	0.07	0.13	0.21
06104[a]	0.637	32.2	0.865	0.05	0.06	0.22
01235A[a]	0.799	84.5	0.194	0.05	0.12	0.43
02255A[a]	0.822	---	---	0.27	0.38	0.86
02275A[a]	0.868	---	0.111	0.07	0.18	0.73
03015A[a]	0.681	---	---	0.12	0.29	0.63
03265[a]	0.904	138.0	0.053	0.06	0.17	0.32
03015A (Screened)[b]	---	69.3	---	(assumed same as above)		
02255A (Screened)[b]	---	110.0	---	(assumed same as above)		
01146 (mg-doped)[c]	0.869	118.0	---	0.106	0.186	0.266
02106 (mg-doped)[c]	0.806	76.0	---	0.086	0.155	0.258
09206 (DPA-doped)[d]	0.784	83.0	0.122	0.065	0.089	0.304
655-1880-6 (mg/DPA-doped)[e]	0.720	---	---	0.082	0.114	---
655-1880-7 (mg/DPA-doped)[e]	0.750	---	---	0.101	0.153	0.232

a. Untreated LMH-1.

b. The original lots were screened (Lot 03015A +230, -170 mesh; Lot 02255A -120, +170 mesh, to obtain a desired particle size of LMH-1.

c. Magnesium treated (or doped) LMH-1.

d. Diphenylacetylene treated (or doped) LMH-1.

e. Both magnesium and diphenylacetylene treated LMH-1.

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(U) (4) Physical Analysis of Ammonium Perchlorate Lots

(U) Several lots of ammonium perchlorate (AP) were selected for use in the desensitization investigation. The WMD and specific surface of these lots were determined by micromerograph and nitrogen absorption, respectively. The results of these determinations are shown below:

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AP Lot No.	WMD (μ)	Specific Surface (m^2/g)
2706	5.7	---
2629	20.0	0.538
1988	60.9	0.269
2699	219.6	~ 0.1
2701	45% > 420.0	< 0.1

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(U) (5) Sensitivity Properties of Other Materials and Combinations of Materials

(U) The sensitivity results of several combinations of materials used in this program, as well as those results for the individual materials, are shown below:

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Material	Ratio	Impact (E_o) (kg-cm)	Friction (F_o) (rpm)	Friction Screw (+) to grit
AP	1	>250	>7000	(-) to all grits
LMH-1	1	>250	>7000	(-) to all grits
ZL-437	1	>250	>7000	(-) to all grits
TMETN	1	4	>7000	(-) to all grits
AP/LMH-1	2/1	32 to 112[a]	600	(+) on CaF_2
AP/ZL-437	6.5/1	240	4600	---
AP/TMETN	6.5/1.22	195	6800	---
LMH-1/ZL-437	6.5/1	>250	>7000	(-) to all grits
LMH-1/TMETN/AP	1/1.32/3	20	---	(+) on Pyrex
LMH-1/ZL-437/TMETN	6.5/1/1.22	52	2000	(+) on Pyrex
AP/ZL-437/TMETN	6.5/1/1.22	10	5600	(-) to all grits
AP/ZL-437/TMETN	6/1/1	36	3600	(-) to all grits

a. Depends on solid particle sizes.

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This information is provided to give an understanding of the part that each material contributes to the total sensitivity of the propellant.

(U) The only individual material that is sensitive to the test devices is TMETN, which has an impact sensitivity (E_0) of 4 kg-cm. The friction sensitivity (F_0) of this material is greater than 7000 rpm.

(U) The most sensitive 2-ingredient blend to both impact and friction tested was the mixture of AP/LMH-1 (2/1). ZL-437 (37 percent oxygen by weight) added to the oxidizer (ammonium perchlorate) shows an increase in friction sensitivity. TMETN in combination with ammonium perchlorate measured a lower impact sensitivity, which would be expected due to the impact sensitivity of the TMETN alone. The sensitivity of the LMH-1/TMETN combination was not tested because it was believed to be exceptionally high.

(U) In considering the 3-ingredient blends, it may be noted that the mixtures of AP/ZL-437/TMETN are the most sensitive to impact and the least sensitive to friction. The blend of LMH-1/ZL-437/TMETN is the least sensitive to impact and the most sensitive to friction. A comparison of the two blends of AP/ZL-437/TMETN are of particular interest. These data show that as the concentration of oxidizer in these blends is reduced, the impact sensitivity is improved and the friction sensitivity is increased (becomes more sensitive).

(U) Experimental evaluations conducted have shown that when all materials are combined in a propellant formulation, the impact and friction sensitivities become generally more sensitive than those of the combinations reported above unless specific techniques are used to improve the propellant sensitivity.

(U) b. Task 1. Investigation of Physical Factors on Propellant Sensitivity

(U) The factors of LMH-1 particle size and surface area, oxidizer particle size and surface area, and coatings for LMH-1 and/or oxidizer, were investigated under this task.

(U) (1) LMH-1 Particle Size and Surface Area

(U) A series of propellant mixes were made and tested for friction sensitivity, impact sensitivity and spark sensitivity in both the cured and uncured state. The standard propellant formulation was used and the only variable was particle size of the LMH-1.

(U) The WMD and specific surface of the LMH-1 particles are directly related in that as the WMD increases, the specific surface decreases(Figure 1). Therefore, for the purpose of this report, WMD will be used to describe these materials. The physical characteristics of the selected LMH-1 lots are given in the preceding section.

(U) The results of these sensitivity tests (Table II) indicate that the particle size of LMH-1 does affect propellant sensitivity. These data show that the effect of LMH-1 particle size on sensitivity varies from uncured to cured propellant, indicating that other factors are involved in the resultant sensitivities.

(U) The uncured propellant is slightly less sensitive to impact with the intermediate size particles and most sensitive at the smallest and largest particles of LMH-1. However, in the cured propellant this is not the case. There is little, if any, difference in the impact sensitivity of cured propellants with varying LMH-1 particle size. The intermediate WMD of LMH-1 particles processed better in the test formulations than the larger or smaller particles, which may be significant. Figure 2 illustrates these results. The sensitivity to friction in the uncured propellant is also different from that of the cured propellant. The uncured propellant is least sensitive when using the smaller LMH-1 particles and the rpm value drops as the WMD increases (becomes more sensitive), probably becoming asymptotic to a minimum rpm. The cured propellant, however, is most sensitive to friction with the smallest LMH-1 particle and slightly less sensitive as the WMD increases (Figure 3). The spark sensitivity was not affected by changes of WMD of LMH-1. The tests resulted in only a slight variance of the spark sensitivity between the cured and uncured propellant (1 to 0.5 joules).

(U) The friction sensitivity of these mixes was determined with the Thiokol Chemical Corporation rotating disc tester and the Esso-type friction screw tester. All propellants, both cured and uncured, were negative with bare tools and CaF_2 grit (Mohs' hardness = 4.0) and positive with Pyrex grit (Mohs' hardness = 5.5). The screw in all cases was tightened with a torque wrench to 300 in-lbs. It was also determined that LMH-1 has a scratch hardness between 4.3 and 6.0 on the Mohs' scale, indicating that LMH-1 itself is hard enought to act as a grit or a source of friction.

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TABLE II

EFFECT OF AlH_3 PARTICLE SIZE AND SURFACE AREA ON SENSITIVITY

Mix No.	AlH_3 Lot No.	(WMD) Particle Size of AlH_3 (μ)	Surface Area of AlH_3 (m^2/g)	Impact (kg-cm)		Friction (rpm)		Spark (Joules)		Friction Screw (Uncured & Cured)		
				U[a]	C[b]	U	C	U	C	Bare Tools (3)[c]	CaF_2 (4)	Pyrex (5.5)
HS-12	06104	32.2	0.865	8	9	2400	1200	1	0.5	-	-	+
HS-13	03254	48.0	0.485	10	9	1600	1000	1	0.5	-	-	+
HS-14	Screened 03015A	69.3	0.407	11	9	1800	1200	1	1	-	-	+
HS-15	01235A	84.5	0.194	11	8	1400	1200	1	0.5	-	-	+
HS-16	Screened 02255A	110	0.120	7	8	1000	1300	1	0.5	-	-	+
HS-17	03265	138.0	0.053	7	8	1200	1500	1	0.5	-	-	+

NOTE: The formulation for the above mixes was the standard using acrylonitrile treated LMH-1 and dried materials in all formulations. A ratio of 3/2 of 420/5.7 micron ammonium perchlorate was selected for use in this series.

a. Uncured results.
b. Cured results
c. Mohs' Hardness.

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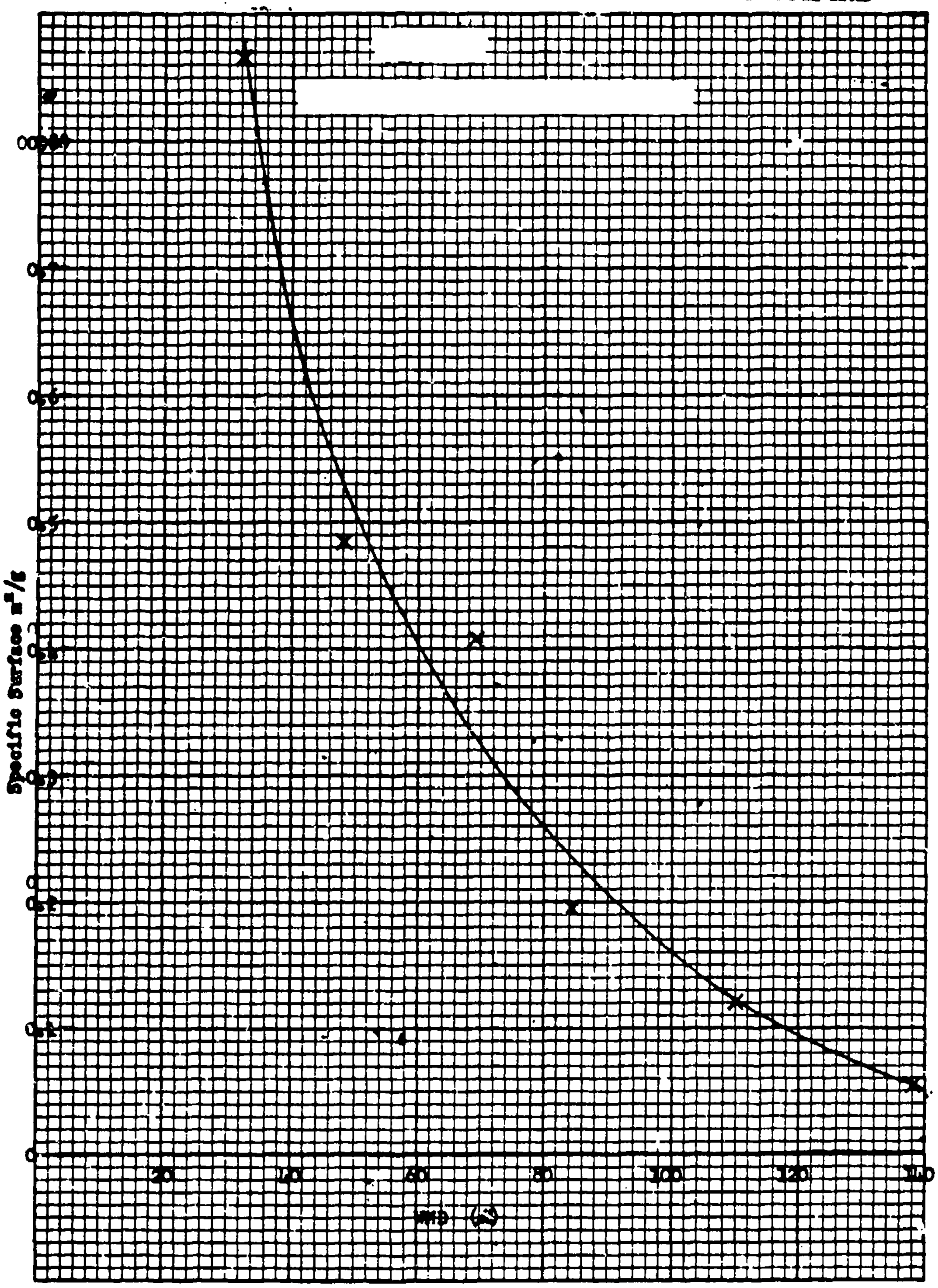

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Figure 1. WMD versus Specific Surface of LMH-1 Lots.

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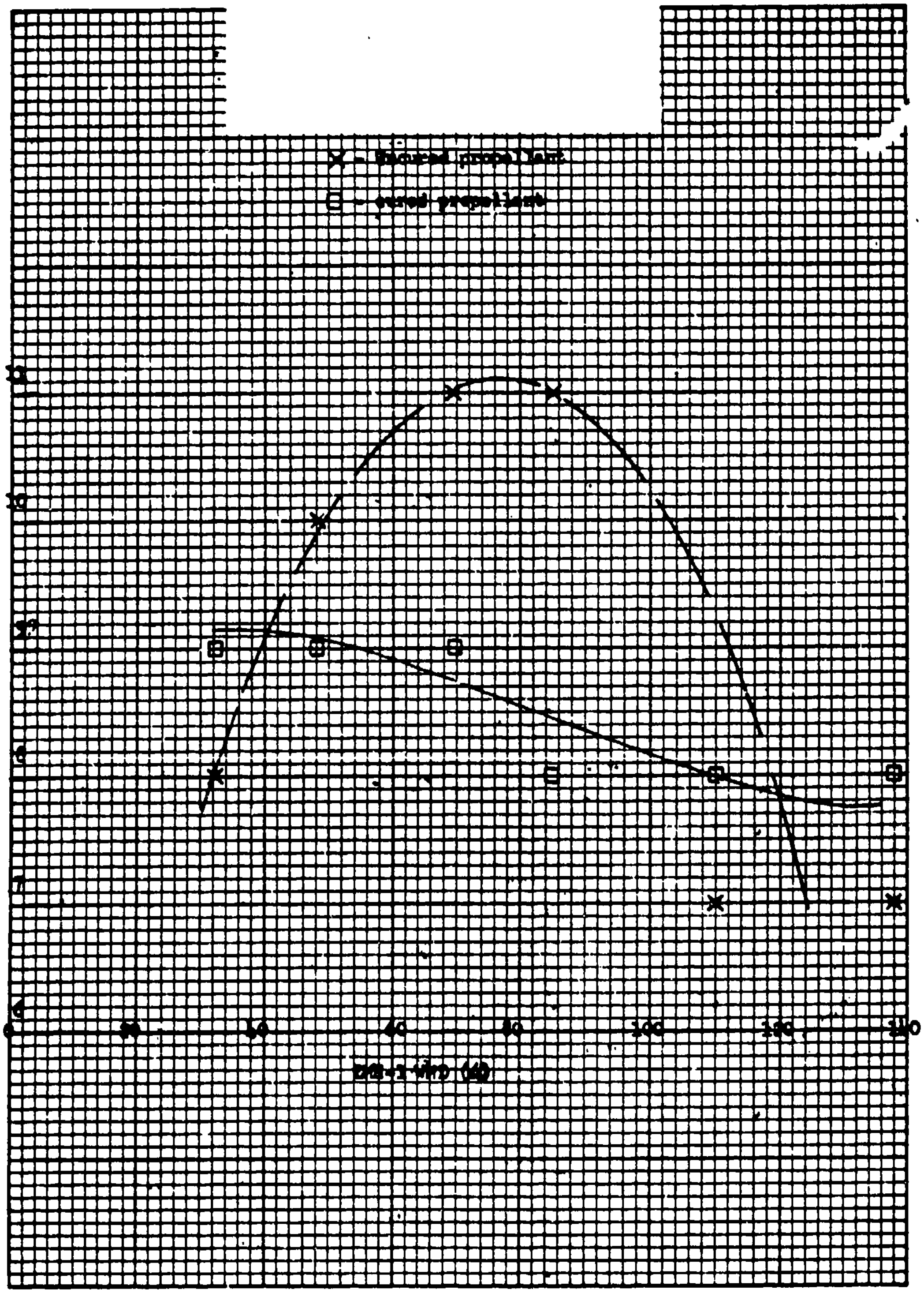

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Figure 2. Impact Sensitivity of LMH-1 Propellants with Constant AP WMD and Ratio

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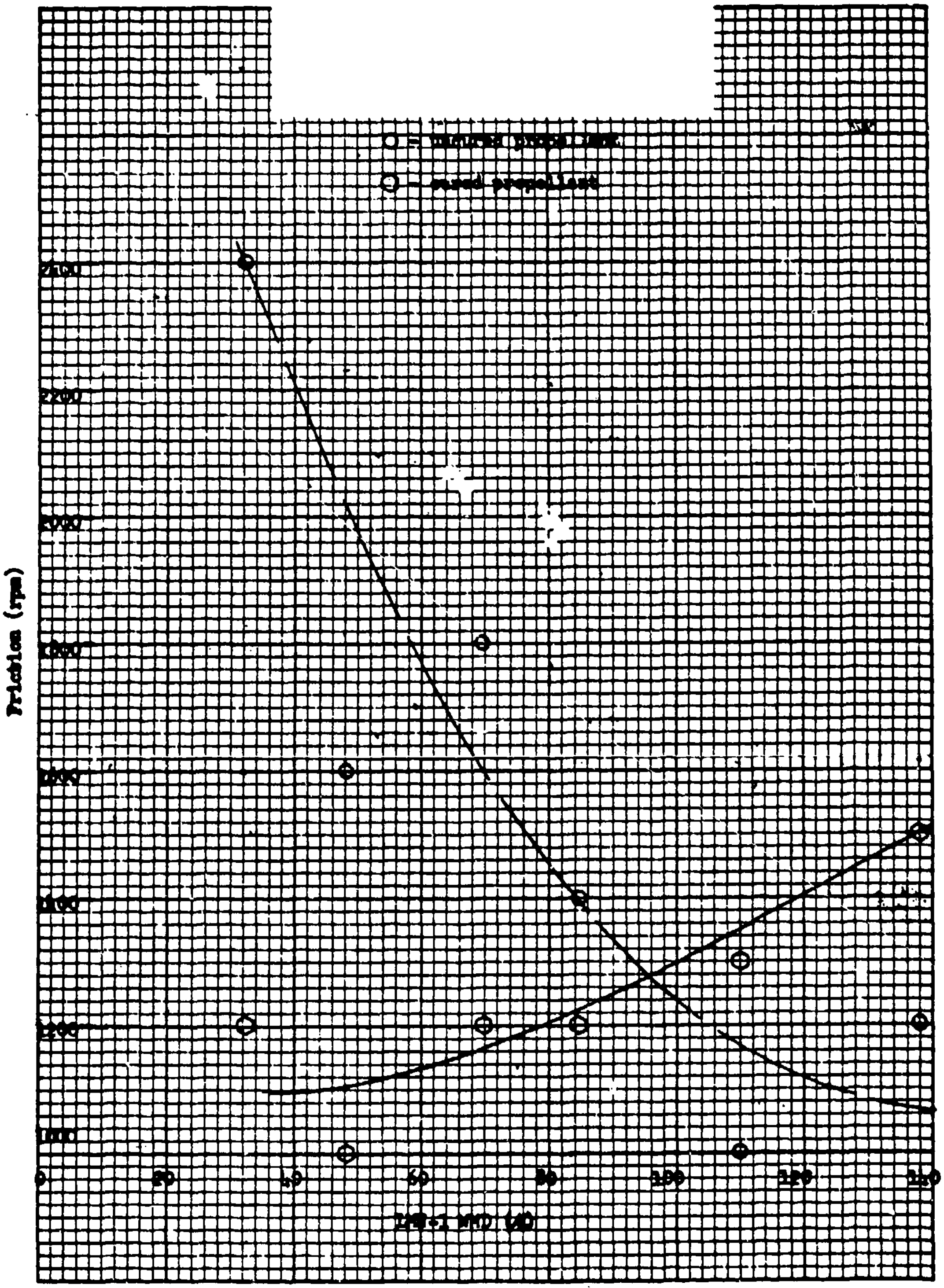

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Figure 3. Friction Sensitivity of LMH-1 Propellants with Constant AP WMD and Ratio.

(U) (2) Oxidizer Particle Size and Surface Area

(U) The purpose of this investigation was to determine the effect of oxidizer particle size and surface area on propellant sensitivity. Two lots of LMH-1 were selected: lot 03254, 48.0 micron WMD, and lot 01235A, 84.5 micron WMD. The particle size and surface area of the lots of ammonium perchlorate chosen for this work are shown below.

AP Lot No.	WMD (μ)	Specific Surface m^2/g
2706	5.7	1.40
2629	20.0	0.538
2699	219.6	~ 0.1 (particles too large to measure)
2701	400.0	~ 0.07 (particles too large to measure)

The weight mean diameter (WMD) and specific surface of the ammonium perchlorate particles are directly related in that as the WMD increases, the specific surface decreases (Figure 4). WMD will be used to describe these materials. The ammonium perchlorate blends investigated were 100 percent 5.7 micron ammonium perchlorate, 2/1 ratio of 220/5.7 micron ammonium perchlorate, 1/2 ratio of 220/5.7 micron ammonium perchlorate, and 3/2 ratio of 400/5.7 micron ammonium perchlorate.

(U) The results of this investigation, which are shown on Table III, indicate that the ammonium perchlorate particle size is a significant variable in the sensitivity of LMH-1 propellants. Mixes HS-18 and 19 (100 percent 5.7 micron oxidizer) gave significant sensitivity decreases and produced an improvement of approximately 20 percent in impact measurement in the cured state of the propellant. Friction sensitivity was also improved (25 to 60 percent); however, there was no change in electrostatic discharge (spark) sensitivity.

(U) Several additional mixes were made in an attempt to substantiate these trends. Mix HS-24 was made in order to determine whether or not the ratio of the particle size of LMH-1/AP alone was the factor determining these changes in sensitivity. The data obtained indicated that this variable was not the only controlling factor; sensitivity to impact and friction did not reach the level of the comparison mix, HS-18. Approximately the same LMH-1/AP particle size ratio was used in mixes HS-18 and HS-24 (48.0/5.7, 138.0/20.0). Mix HS-19A was made for a direct confirmation of the results obtained from mix HS-19.

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TABLE III

INVESTIGATION OF AP PARTICLE SIZE EFFECT ON SENSITIVITY

Mix No.	LMH-1 WMD (μ)	1 AP WMD (μ)	1 AP %	2 AP WMD (μ)	2 AP %	Impact (kg-cm)		Friction (rpm)		Spark (Joules)		Friction Screw (Grit)	
						Uncured	Cured	Uncured	Cured	Uncured	Cured	Cured	Force in-lbs
HS-13	48.0	5.7	19.8	400.0	29.7	10	9	1600	1000	1.0	0.5	Pyrex	---
HS-18	48.0	5.7	49.5	---	---	18	14	1600	2600	0.5	1.0	Pyrex	Back Off
HS-20	48.0	5.7	16.5	219.6	33.0	9	12	2000	1600	0.5	0.5	Pyrex	---
HS-22	48.0	5.7	33.0	219.6	16.5	11	10	1600	1600	1.0	1.0	Pyrex	---
HS-15	84.5	5.7	19.8	400.0	29.7	11	8	1400	1200	1.0	0.5	Pyrex	---
HS-19	84.5	5.7	49.5	---	---	11	15	1600	2000	0.5	1.0	Pyrex	200
HS-21	84.5	5.7	16.5	219.6	33.0	12	8	1600	2000	1.0	1.0	Pyrex	---
HS-23	84.5	5.7	33.0	219.6	16.5	7	9	1600	1400	0.5	1.0	Pyrex	125
HS-19A	84.5	5.7	49.5	---	---	13	17	1200	1800	0.5	0.5	Pyrex	75
HS-24	138.0	20.0	49.5	---	---	7	8	1800	1800	0.5	1.0	Pyrex	250
HS-24A	138.0	5.7	49.5	---	---	12	12	1600	1800	0.5	0.5	Pyrex	100

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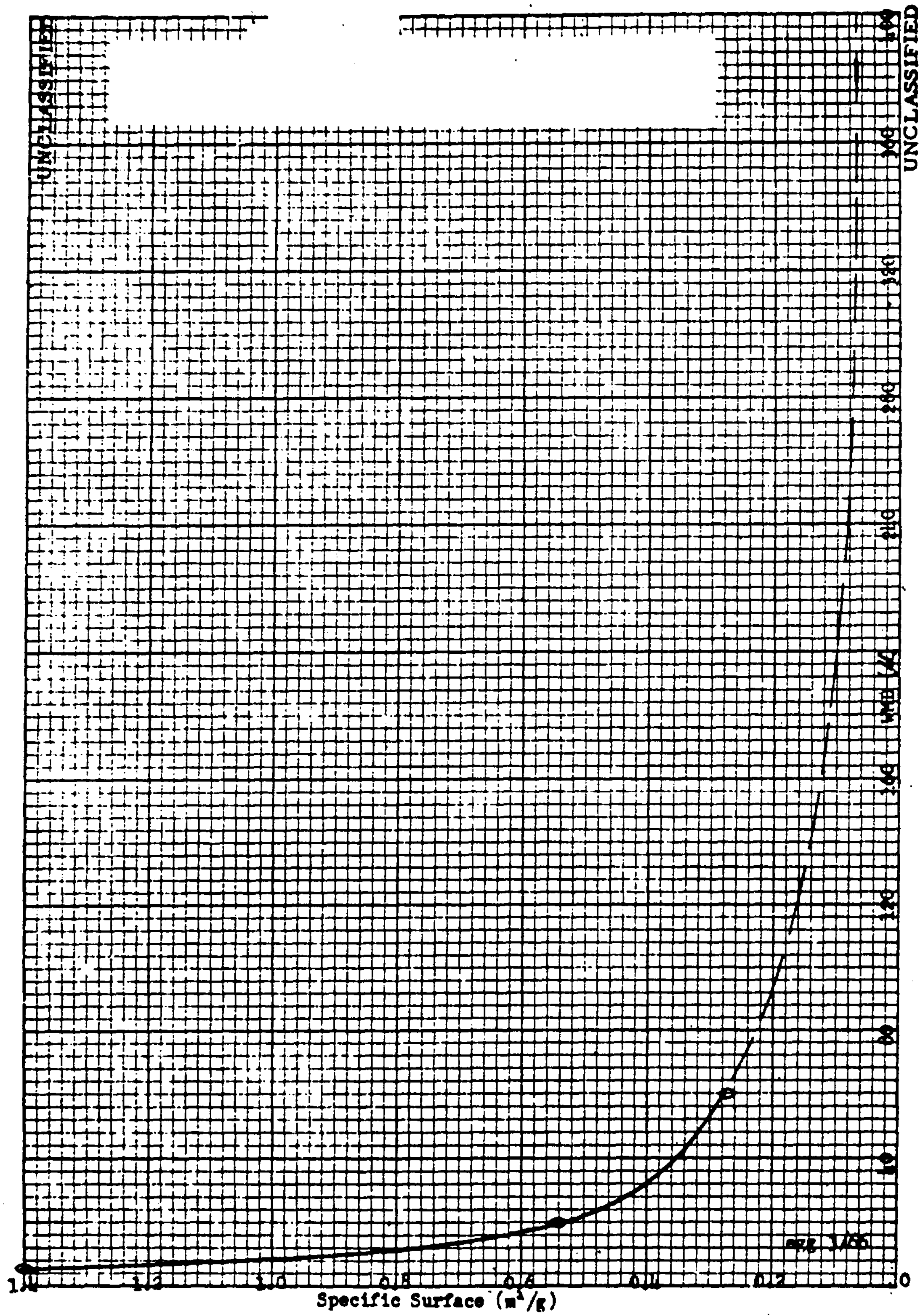


Figure 4. WMD Versus Specific Surface of AP Lots.

The results were in agreement, with impact slightly higher and friction slightly lower. Mix HS-24A was made in order to determine if the small WMD ammonium perchlorate was the controlling factor of sensitivity. This mix did not obtain the sensitivity level of mixes HS-18 or HS-19, but did give a significant improvement in impact sensitivity over its counterpart (HS-24). A detailed discussion of the particle size and particle size ratio of LMH-1 and ammonium perchlorate effect on sensitivity is given in Phase II, Task 3, b and c.

(U) The impact and friction test results of Table III are graphically illustrated on Figures 5 through 8. Figures 5 (cured propellant) and 7 (uncured propellant) show the same trend; as ammonium perchlorate WMD increases the propellant becomes more sensitive to impact with a given LMH-1 particle size. Figure 6 (cured propellant) indicates that as the ammonium perchlorate particle size is increased the propellant becomes more sensitive to friction while Figure 8 (uncured propellant) tends to show little or no effect of ammonium perchlorate particle size on friction sensitivity.

(U) The results of friction testing with the Esso friction screw are reported in Table III. These mixes were tested for both the cured and uncured propellants and all were positive (+) with the Pyrex grit. The cured results are given in the table for simplification. There were small changes from uncured to cured propellant, for those forces required to initiate the sample.

(U) The results of this investigation indicated that ammonium perchlorate particle size is a critical factor for control of sensitivity. However, as shown on Figures 5 through 8, the LMH-1 particle size is complimentary to the ammonium perchlorate particle size for additional control of sensitivity.

(U) (3) Effect of Oxidizer Particle Size on Sensitivity of Aluminum Propellants

(U) A series of three propellant mixes were made, substituting aluminum for LMH-1 in the standard formulation, in order to determine the effect of oxidizer particle size on the sensitivity of mixes containing aluminum. It had been shown in prior investigations that as the ammonium perchlorate particle size increased the propellant became more sensitive to impact.

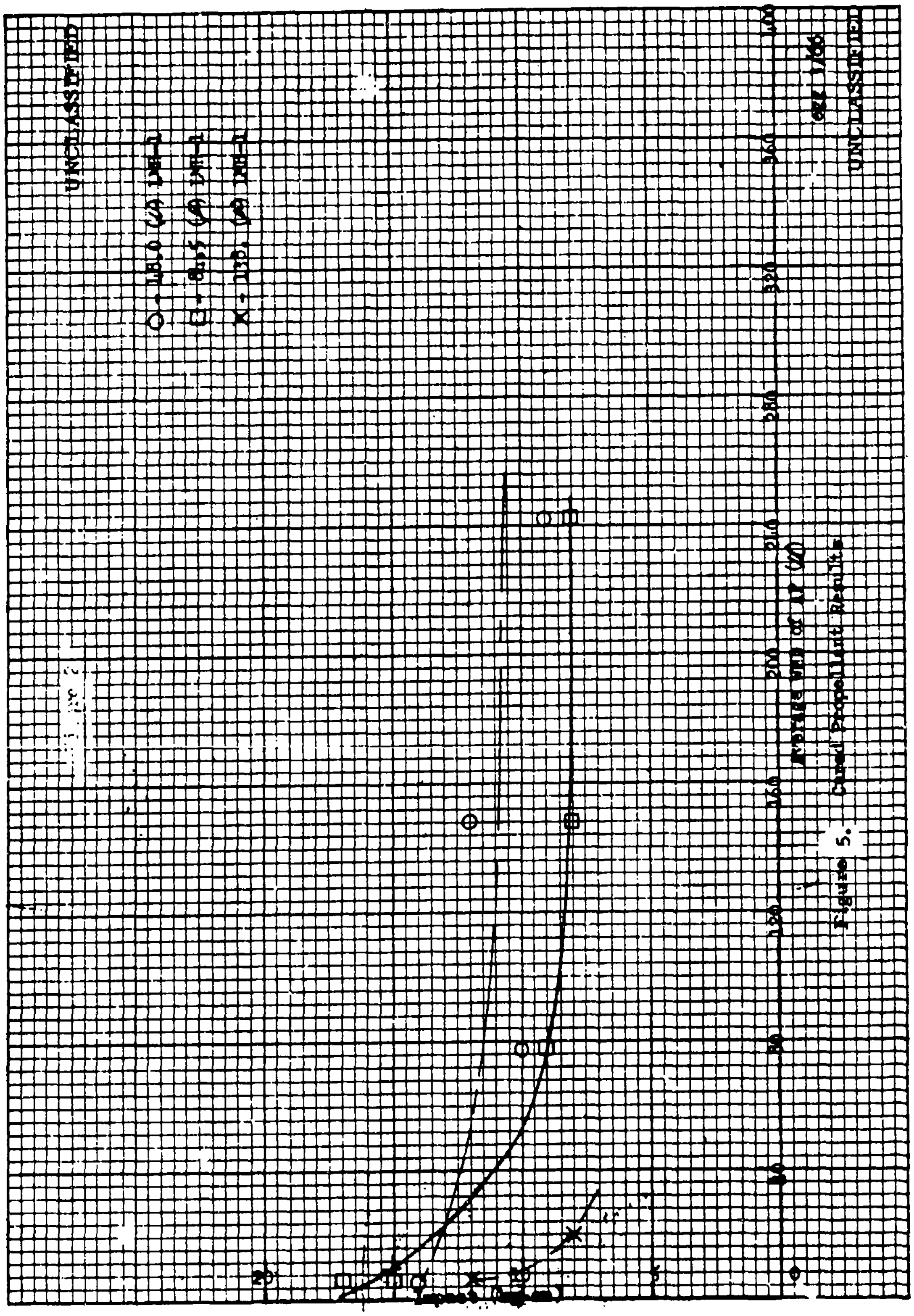
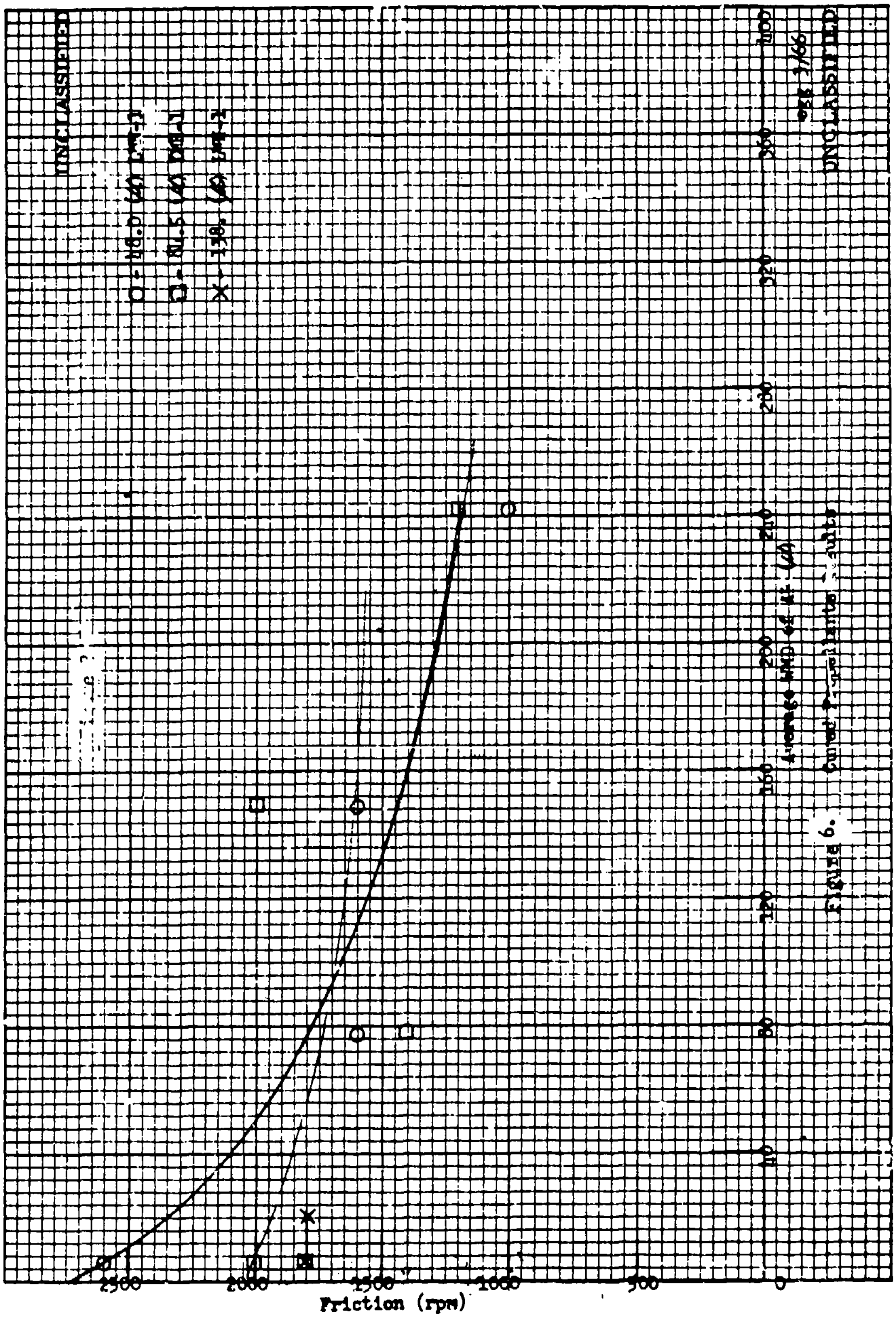


Figure 5. Cased Propellant Results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Friction (rpm)
2500
2000
1500
1000
500
0
40
80
120
160
200
240
280
320
360
400
Average WMD of AP (μ)
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Figure 6.

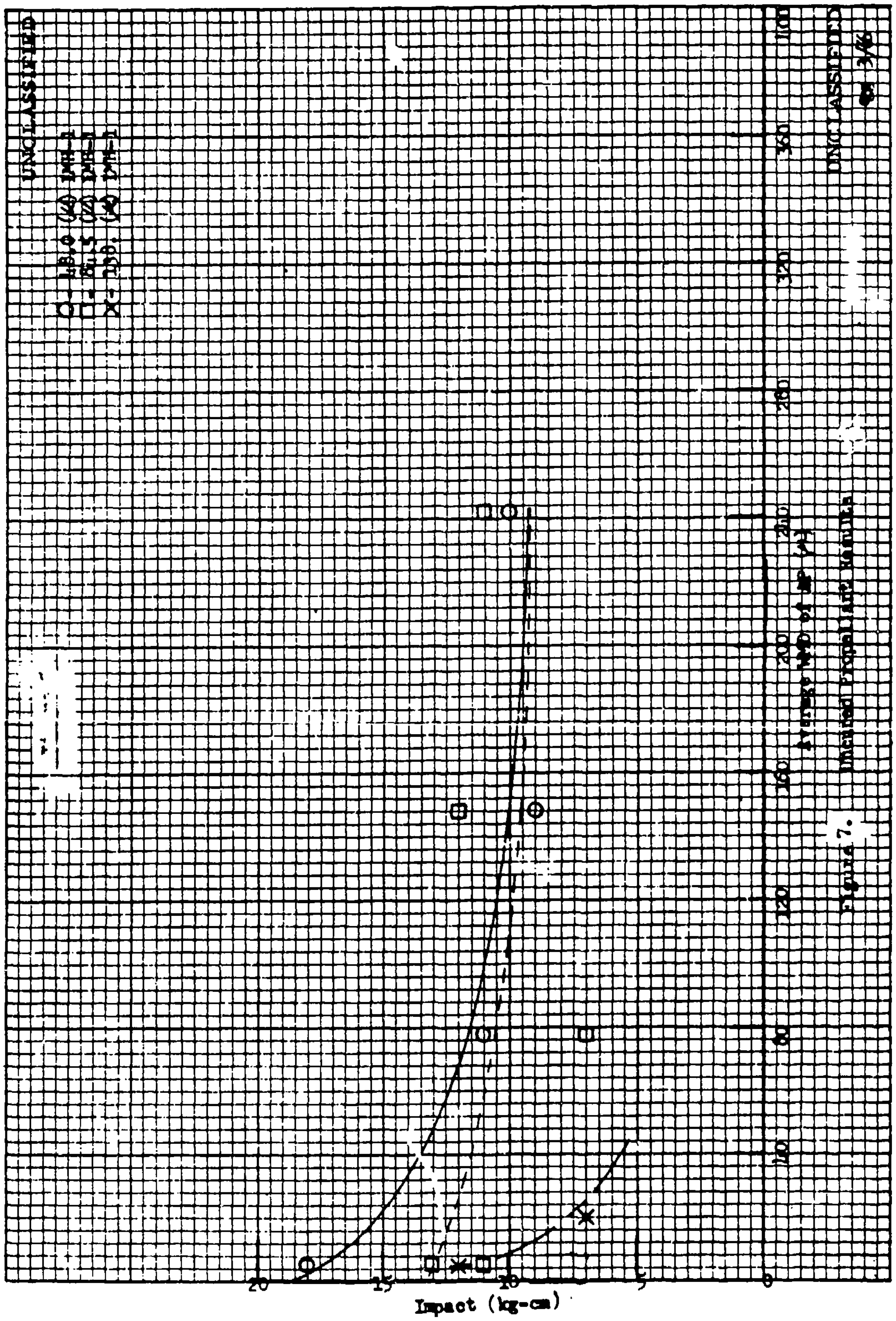

Figure 7. Uncured Propellant Results

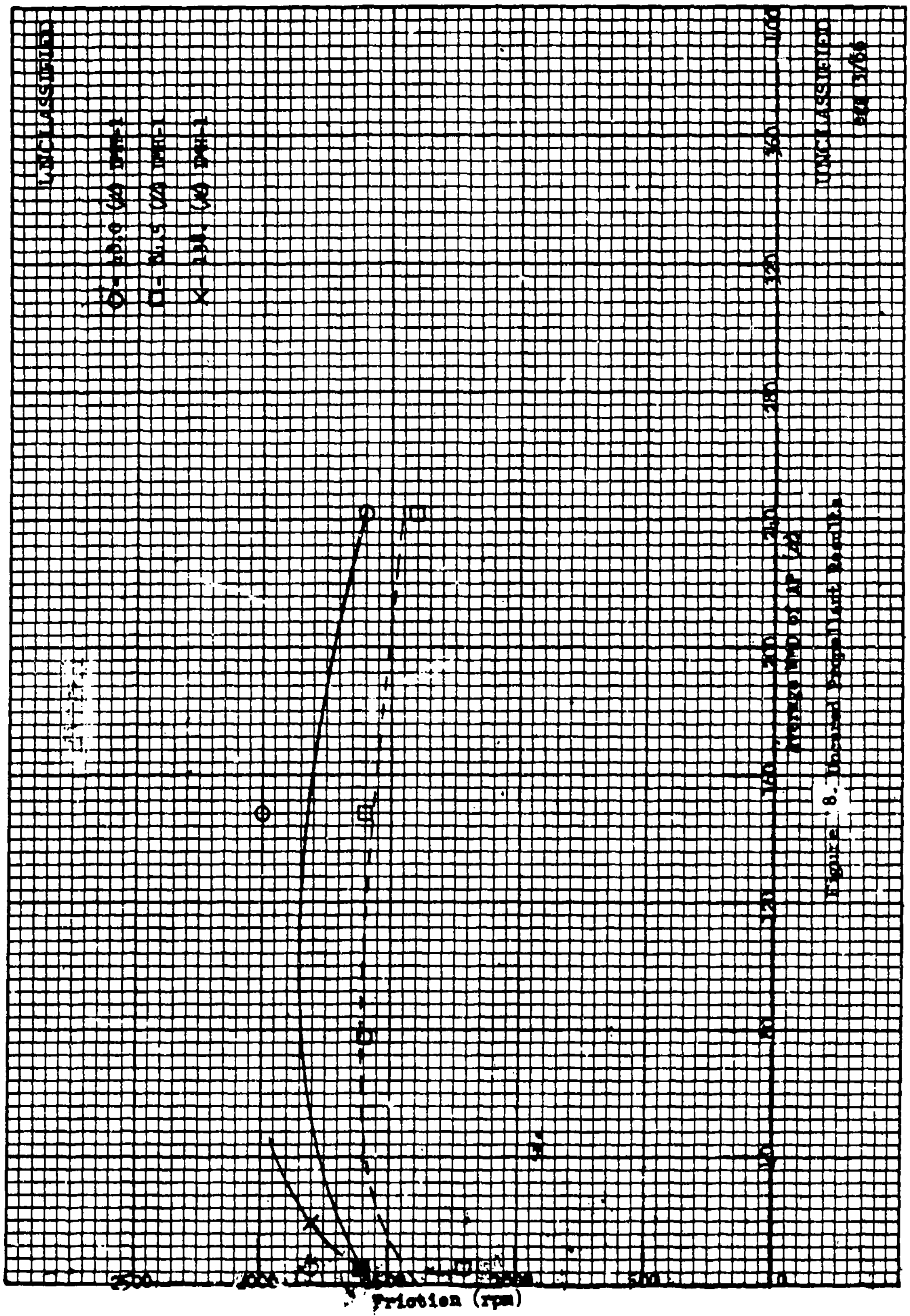

Figure 8. Uncased Propellant Results

(U) It may be seen from the sensitivity test results of Table IV that the uncured propellant becomes more sensitive to impact (37.5 to 30 kg-cm) as the ammonium perchlorate particle size is increased. The cured propellants impact sensitivity also shows that as the ammonium perchlorate particle size increases the propellant becomes more sensitive (49 to 32 kg-cm). These results are in accord with the results shown previously with LMH-1 formulations. The ammonium perchlorate particle size effect has also been indicated in other areas of this sensitivity investigation and is, therefore, considered to be one of the most influencial factors in control of impact sensitivity.

(U) The friction test (rpm) of these propellants, either uncured or cured, does not indicate any pattern of increase or decrease in sensitivity with the increase of oxidizer particle size. The results of the friction screw tests on the uncured propellants indicate no differences in the friction sensitivities; all were negative (-) to the SiC grit.

(U) (4) Tests of Dry Blends of Ammonium Perchlorate and LMH-1

(U) A series of tests using LMH-1 and ammonium perchlorate without binder or other propellant ingredients was introduced into the program to obtain additional data on the effect of solids particle size. The results of these tests are shown in Table V.

(U) These data show that when the LMH-1 WMD was held constant (Tests 2, 3 and 4), sensitivity to impact was least with the smallest ammonium perchlorate and increased as the ammonium perchlorate WMD increased (Figure 9). In Tests 4, 5 and 6, where the ammonium perchlorate WMD is held constant, the least sensitive mixture contained the intermediate WMD of LMH-1 (Figure 10). This relationship of sensitivity to WMD was also noted in the uncured propellant tests (Figure 2). Friction sensitivity tests on the dry blends of LMH-1 resulted in F_o's of 500 ± 100 rpm. The resulting conclusion is that ammonium perchlorate makes LMH-1 very sensitive to friction, but particle size (WMD) of ammonium perchlorate or LMH-1 in the range studied does not control this friction sensitivity. The neat forms of both ammonium perchlorate and LMH-1 are insensitive to the rotating disc friction tests (> 7000 rpm).

(U) As shown in Tests 7 and 8 (Table V), spark sensitivity tests of dry blends of ammonium perchlorate and LMH-1 indicate no significant change in spark sensitivity over that of prue LMH-1.

(U) The friction screw was used to determine the sensitivity of the LMH-1/ammonium perchlorate mixture. The mixture was negative to bare tools and positive to CaF_2 and Pyrex.

TABLE IV

EFFECT OF OXIDIZER PARTICLE SIZE ON SENSITIVITY

Mix No.	% Al 60 (Micron)	% 6 Micron AP	% 220 (Micron) AP	% 400 (Micron) AP	Impact E_o (kg-cm) U [(a)]	Impact E_o (kg-cm) C [(b)]	Friction (rpm) U	Friction (rpm) C	Spark (joules) U	Spark (joules) C	Friction Screw (grit) (+) U	Friction Screw (grit) (+) C
HS-Al-2	25.0	49.5	0	0	37.5	49	4600	4400	--	0.5	(-)SiC	--
HS-Al-3	25.0	16.5	33.0	0	30.0	40	3600	4800	--	0.5	(-)SiC	--
HS-Al-1	25.0	19.8	0	29.7	30.0	32	4400	4600	0.5	0.5	(-)SiC	(-)SiC

(a) Uncured Results
(b) Cured Results

TABLE V

SENSITIVITY TEST RESULTS - DRY BLENDS OF AMMONIUM PERCHLORATE AND LMH-1

Test No.	AP (%)	AP WMD(μ)	AP (%)	AP WMD(μ)	LMH-1 (%)	LMH-1 WMD(μ)	Impact (E_o) (kg-cm)	Friction (F_o) (rpm)	Spark (ESD) (Joules) (-)
1	26.75	5.7	39.87	420	33.56	32.2	59	400	.1
2	66.44	5.7	0	0	33.56	32.2	112	500	.1
3	66.44	219.6	0	0	33.56	32.2	42	500	.1
4	66.44	60.0	0	0	33.56	32.2	50	600	.1
5	66.44	60.9	0	0	33.56	138.0	42	600	.05
6	66.44	60.9	0	0	33.56	84.5	99	400	.1
7	0	0	0	0	100.0	138.0	Insensitive	Insensitive	.05
8	0	0	0	0	100.0	32.2	Insensitive	Insensitive	.1

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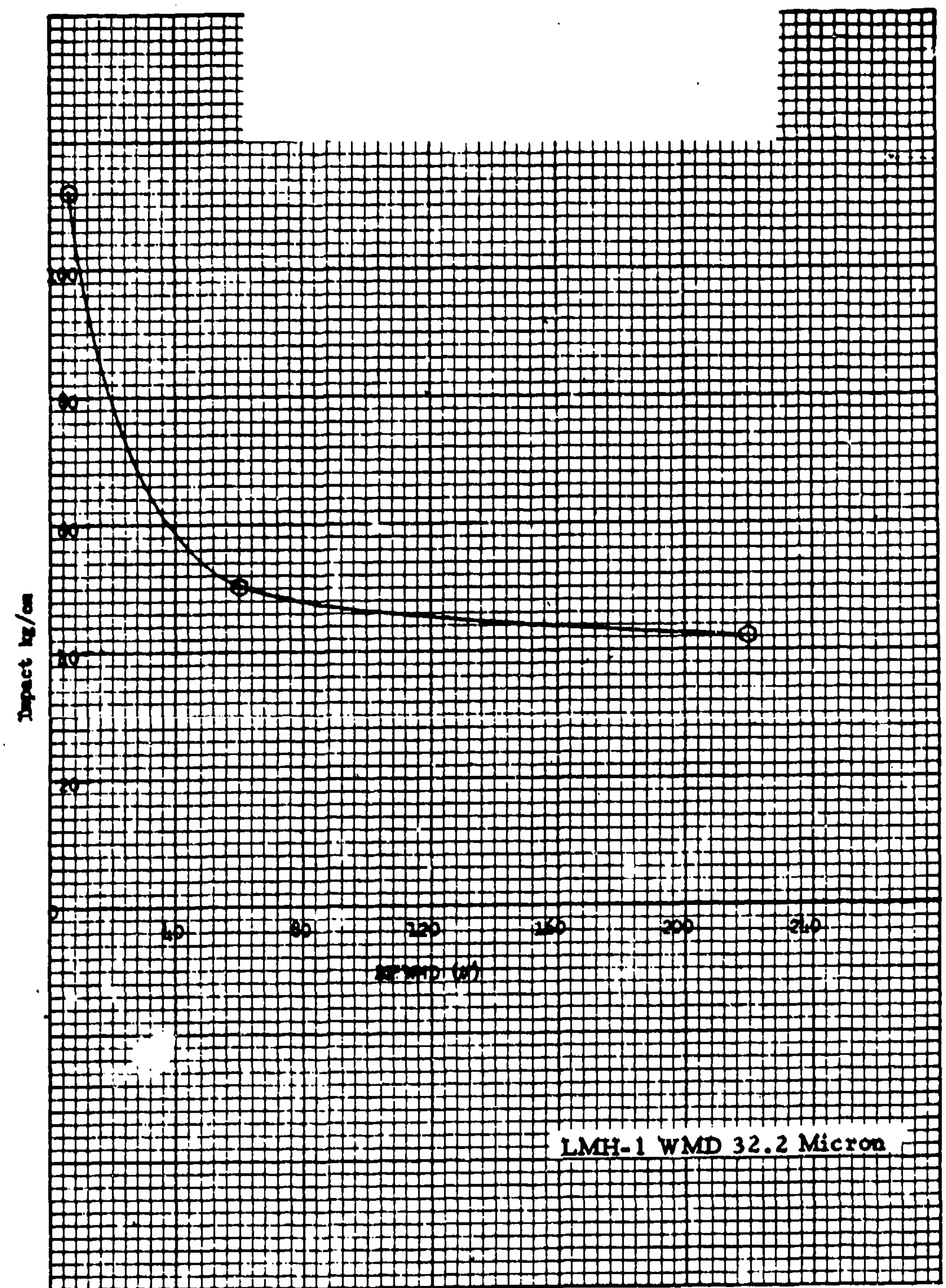

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Figure 9. . Sensitivity of Dry Blend of LMH-1 and AP Where the WMD of the LMH-1 is Constant.

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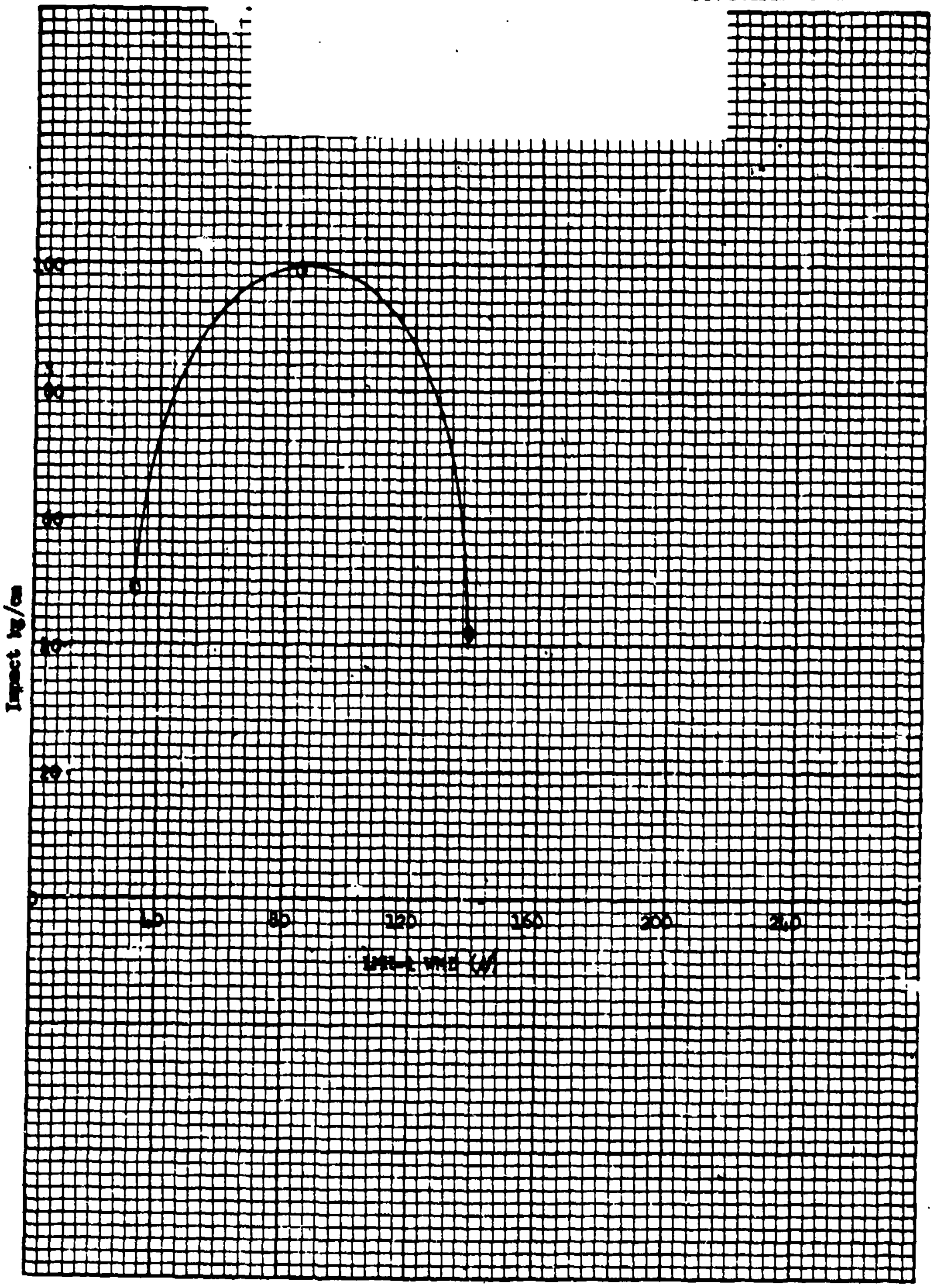

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Figure 10. Impact Sensitivity of Dry Blend of LMH-1 and AP Where the WMD of the AP is Constant.

(U) The results of these dry blend tests are in agreement with the results of the particle size investigation of ammonium perchlorate and LMH-1 using the standard formulation. Note the discussion of additional dry blend results under Phase II, Task 3, b and c.

(U) (5) Dry Lubricants

(U) The dry blend testing was extended to investigate the effect of dry powder lubricants incorporated into the blend at a constant level. Results of this series of tests are shown in Table VI. The standard formulation, 66.44 percent 5.7 micron ammonium perchlorate and 33.56 percent LMH-1 (Test 11), was selected because of its high sensitivity to both friction and impact, thereby enabling improvements to be easily identified. Tests 11A through 11D were processed by premixing the LMH-1 and additive before the addition of the ammonium perchlorate, and Tests 11E through 11G were processed by premixing the ammonium perchlorate and additive before the addition of LMH-1.

(U) It may be seen that the addition of the dry lubricant to the AP/LMH-1 blend improved the impact sensitivity with all additives. The friction sensitivity, as measured on the friction screw, was improved with all additives with the exception of aluminum powder. The spark sensitivity did not indicate any change.

(U) The impact sensitivity was most improved when Molykote and graphite were used as the additive. These two additives resulted in a 62 percent increase of measured impact over the standard mixture and also improved friction from positive on bare tools to negative with CaF_2. (The rotating disc tester could not be used at over 600 to 800 revolutions per minute with these dry powders due to sample loss.) Additional improvements in sensitivity were obtained with Molykote and graphite when the dry lubricant was premixed with the ammonium perchlorate. Talc was less effective in this series. When Molykote was used on ammonium perchlorate, the measured impact was increased 191 percent over that of the standard formulation, and 77 percent over that of the test using Molykote premixed LMH-1. When ammonium perchlorate was premixed with graphite, the measured impact was increased 88 percent over that of the standard blend, and 16 percent over that of the graphite premixed LMH-1. The friction sensitivity was equal to or better (more torque required) than that determined for the LMH-1 additive premixes.

(U) As a result of these findings, thermochemical calculations were made in order to determine the effect of small additions of aluminum powder and graphite on the specific impulse (I_{sp}) of the standard formulation. Results are shown in Table VII. The 5 percent additive level in a propellant formulation is equivalent to the 6.3 percent additive used in dry blend testing. It is apparent that graphite does lower specific impulse considerably.

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TABLE VI

EFFECT OF DRY POWDER ADDITIVES ON SENSITIVITY OF AP/LMH-1 MIXTURES

Test No.	Note	AP WMD (μ)	AP %	LMH-1 WMD (μ)	LMH-1 %	Additive %	Additive	Impact (kg-cm)	Spark (Joules)	Friction Screw Test (Grit): Bare Metal	CaF_2	Pyrex	SiC	Force (in-lbs)
11	Standard	5.7	66.40	138.0	33.56	---	---	34	0.01	(+)				---
11A	LMH-1 Premix	5.7	62.25	138.0	31.45	6.3	Molykote[a]	56	0.01	(-)	(-)	(+)		100
11B	LMH-1 Premix	5.7	62.25	138.0	31.45	6.3	Al Powder (10μ)	49	0.01	(+)				Back-Off
11C	LMH-1 Premix	5.7	62.25	138.0	31.45	6.3	Graphite[b]	55	0.01	(-)	(-)	(+)		100
11D	LMH-1 Premix	5.7	62.25	138.0	31.45	6.3	Talc[c]	48	0.01	(-)	(-)	(+)		150
11E	AP Premix	5.7	62.25	138.0	31.45	6.3	Molykote	99	0.025	(-)	(-)	(+)		250
11F	AP Premix	5.7	62.25	138.0	31.45	6.3	Talc	39	0.025	(-)	(-)	(+)		100
11G	AP Premix	5.7	62.25	138.0	31.45	6.3	Graphite	64	0.01	(-)	(-)	(+)		275

(a) Molykote - A dry lubricant consisting of MoS_2 made by the Alpha Molykote Corporation of Stamford, Connecticut (Type 2).
(b) Graphite - Pencil lead ground and passed through 100 mesh screen.
(c) Talc - Reagent grade talcum powder.

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TABLE VII

EFFECT OF DRY LUBRICANTS ON SENSITIVITY AND SPECIFIC IMPULSE

	1 Standard	2	3	4	5
ZL-437	11.50	11.50	11.50	11.50	11.50
TMETN	14.00	14.00	14.00	14.00	14.00
AlH_3	25.00	23.50	23.50	22.00	22.00
AP	49.50	46.00	46.00	49.50	49.50
Graphite	---	5.00	---	3 00	---
Al	---	---	5.00	---	3.00
ρ (gm/cc)	1.61562	1.63189	1.64155	1.63522	1.64102
I_{sp} (lb-sec/lb)	280.07	267.85	279.83	272.16	278.28

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TABLE VIII

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EFFECT OF DRY LUBRICANTS ON SENSITIVITY AND SPECIFIC IMPULSE

	1 Standard	2	3	4	5	6
ZL-437	11.50	11.50	11.50	11.50	11.50	11.50
TMETN	14.00	14.00	14.00	14.00	14.00	14.00
AlH_3	25.00	22.00	22.00	25.00	22.00	25.00
AP	49.50	49.50	49.50	46.50	49.50	46.50
Graphite	---	3.00	---	---	---	---
Molykote	---	---	3.00	3.00	---	---
Teflon	---	---	---	---	3.00	3.00
ρ (gm/cc)	1.61562	1.63522	1.65422	1.63983	1.63340	1.61937
I_{sp} (lb-sec/lb)	280.07	272.16	273.49	276.78	275.78	276.95

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(U) These data prompted the thermochemical calculations to determine the effect of Molykote and Teflon on specific impulse. Results are shown in Table VIII for comparison. It is evident that Teflon (Test 6), which lowered the theoretical specific impulse only 1.12 lb-sec/lb, is the least damaging to specific impulse at the 3 percent level.

(U) A propellant formulation utilizing Molykote coated 20-micron oxidizer was prepared. Large (138 micron) LMH-1 was used in this formulation for processing purposes. The data of a control mix and the test mix are compared below.

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	Impact (kg-cm)		Friction (rpm)		Spark (Joules)		Friction Screw Grit (+)		Cured Torque (in-lb)
	U[a]	C[b]	U	C	U	C	U	C	
HS-30 (Molykote)	8	11	1800	2200	0.5	0.5	Pyrex	Pyrex	275
HS-24 (Standard)	7	8	1800	1800	0.5	1.0	Pyrex	Pyrex	250

a. Uncured Results
b. Cured Results

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It may be seen from these data that no improvement in impact sensitivity was realized. The cured propellant shows a slight improvement in friction (400 rpm) sensitivity.

(U) It may be concluded from the results of these tests and the effect of Molykote on I_{sp} that the use of this dry lubricant would not be an effective means for sensitivity improvement.

(U) A sample of powdered Teflon (35 micron elongated particles received from E. I. du Pont de Nemours Co., Inc.) was tested for its effectiveness in reducing propellant sensitivity. The data obtained (Table IX) show that uncured samples exhibited a 3 to 6 kg-cm decrease in impact sensitivity, which is a 75 to 150 percent decrease when compared to the standard (4 kg-cm). The cured propellants yielded a maximum of 4 kg-cm decrease in impact sensitivity. It is to be noted that two methods of incorporating the Teflon were used: the preblending of Teflon with ammonium perchlorate before addition (Mix HS-58), and the dispersement of Teflon in the binder (Mix HS-59). Both methods increased viscosity when compared to the standard. This increase is attributed to the elongated Teflon particles.

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TABLE IX

DRY LUBRICANTS - TEFLON

Mix No.	% Teflon	Viscosity (KP) @ 124° -128°F	Density (g/cc)	Penetrometer (cm)	% Pasted AP	% 400 micron AP	Method of Incorporating Teflon	Sensitivity Data: Impact (kg-cm) U(a)	Impact C(b)	Friction (rpm) U	Friction C	Spark (joules) U	Spark C	Friction Screw (grit) 3 Test/grit U	Friction Screw C	Torque for (+) Cured
Standard HS-53	0	17	1.556	9.3	24.22	25.28		4	6	2200	1800	0.5	0.5	Pyrex	Pyrex	150
HS-58	3	64	1.531	5.7	24.22	22.28	Premixed[c] with AP	10	8	2600	3000	0.5	0.5	Pyrex	Pyrex	200
HS-59	3	65	1.582	6.6	24.22	22.28	Dispersed[c] in binder	7	10	2600	3000	0.5	0.5	Pyrex	Pyrex	275

(a) Uncured Results
(b) Cured Results
(c) WMD of Teflon was 35-micron elongated particles

(U) The friction sensitivity of these mixes was improved in both the uncured and cured propellants (400 and 1200 rpm, respectively) when compared to the standard. The method of incorporating Teflon appeared to have no effect on friction sensitivity.

(U) As was expected, Teflon was not effective in reducing spark sensitivity. The results of the friction screw tester show both propellants positive to Pyrex.

(U) (a) Desensitization with Cyclotrimethylenetrinitramine (RDX)

(U) It had been noted in other programs conducted at the Huntsville Division of Thiokol Chemical Corporation that the substitution of RDX for ammonium perchlorate in difluoramino propellants resulted in large reductions in impact and, in particular, friction sensitivity. Several examples are shown below.

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	Impact E_o (kg-cm)	Friction F_o (rpm)	Friction Screw
NFPA-AP-Propellant	17.0	1700	+ Pyrex
NFPA-RDX Propellant	30.0	>7000	- SiC
P-BEP-AP-B Propellant	9.0	2200	+ Bare Tools
P-BEP-RDX-B Propellant	7.0	3200	- SiC

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It may be seen that significant decreases in friction sensitivity are obtained by the substitution of RDX for ammonium perchlorate in some propellants. Also, in most cases, only 3 to 5 lb-sec/lb of specific impulse are lost by using RDX. It was decided that it would be worthwhile to attempt to desensitize the LMH-1/AP/polyester propellant by substituting RDX for part, or all, of the ammonium perchlorate. Theoretical specific impulse calculations are shown on the following page.

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Formulation						
LMH-1	25.0	25.0	25.0	25.0	23.0	20.0
TMETN	14.0	14.0	14.0	14.0	14.0	14.0
ZL-437 Binder	11.5	11.5	11.5	11.5	11.5	11.5
AP	49.5	39.5	24.5			
RDX		10.0	25.0	49.5	51.5	54.5
I_{sp} (lb-sec/lb)	280.1	280.8	277.5	272.0	272.0	271.5
ρ(g/cc)	1.616	1.606	1.592	1.569	1.576	1.586

It may be seen that substitution of 10 percent RDX resulted in a slight increase in specific impulse; however, substitution of 25 and 49.5 percent RDX resulted in 2.6 and 8.1 lb-sec/lb losses. Propellant densities are also lower as a result of the lower density of RDX (1.816 g/cc). Another possible disadvantage is that the use of RDX may cause the propellant to be Class 7.

(U) Propellant mixes were made in which 10 percent 105 micron RDX, 10 percent 16 micron RDX, 25 percent 105 micron RDX, and 49.5 percent 60/40: 400/105 micron RDX were substituted for ammonium perchlorate in the standard formulation. Sensitivity test results are shown in the following table.

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	Uncured			Cured		
	E_o	F_o	Screw	E_o	F_o	Screw
49.5% AP	11	1400	+ Pyrex	8	1200	+ Pyrex
39.5% AP/10% 105 μ RDX	7	2400	+ Pyrex	9	1800	+ Pyrex
39.5% AP/10% 16 μ RDX	6	1800	+ Pyrex	8	1600	+ Pyrex
24.5% AP/25% 105 μ RDX	10	2200	+ Pyrex	--	--	---
49.5% RDX (60/40 - 400 μ/105 μ)	16	4800	- SiC	14	2600	+ Pyrex

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It may be seen that a significant reduction in friction sensitivity was obtained with 10 percent 105 micron RDX, and large reductions in both friction and impact sensitivity were obtained when 100 percent 60/40: 400/105 micron RDX was substituted for ammonium perchlorate. The loss in specific impulse precludes the use of 100 percent RDX as the oxidizer.

(U) A dry blend of 16 micron RDX and 32 micron LMH-1 (2/1) had a friction sensitivity of 2400 rpm as compared to 500 rpm for an AP/LMH-1 dry blend. The RDX/LMH-1 blend was negative with CaF_2 and positive with Pyrex on the friction screw, while the AP/LMH-1 blend was positive with both grits.

(U) A photomicrographic study of the solubility of RDX in ZL-437 at 100°F (propellant cure temperature) indicated that RDX crystals are reduced approximately 6 percent in size in 48 hours. This solubility is also shown to make the crystals smoother because the sharp edges are displaced.

(U) Two mixes of the standard propellant formulation containing 10.0 and 49.5 percent cyclotetramethylene-tetranitramine (HMX) were prepared in order to determine if HMX has the same desensitizing effect as RDX. Sensitivity test results are compared below with previous RDX test results and an ammonium perchlorate oxidized propellant.

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		10% HMX	49.5% HMX	10% RDX	49.5% RDX	49.5% AP
E_o (kg-cm)	Uncured	6	12	7	16	11
	Cured	10	8	9	14	8
F_o (rpm)	Uncured	1800	6500	2400	4800	1400
	Cured	1800	3300	1800	2600	1200
Friction Screw	Uncured	+ Pyrex	-SiC	+ Pyrex	-SiC	+ Pyrex
	Cured	+ Pyrex	-SiC	+ Pyrex	+ Pyrex	+ Pyrex

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It may be seen that the safety characteristics of the corresponding HMX and RDX propellants are similar, and that both represent an improvement especially in friction sensitivity, over the ammonium perchlorate oxidized propellant.

(U) Theoretical ballistic calculations using HMX are shown below.

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	No. 1	No. 2	No 3.
LMH-1	25.0	25.0	25.0
TMETN	14.0	14.0	14.0
ZL-437 Binder	11.5	11.5	11.5
AP	39.5	24.5	---
HMX	10.0	25.0	49.5
I_{sp} (lb-sec/lb)	280.8	277.4	271.8
ρ (lb/in^3)	0.0583	0.0581	0.0578

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These data show that the use of 10 percent HMX resulted in a slight increase in specific impulse (as did the use of 10 percent RDX), while larger quantities of HMX resulted in losses in specific impulse.

(U) Further attempts were made to identify the mechanism of the desensitization by RDX. Since RDX melts at 204°C (before it starts to decompose at 210°C), the endothermic melting of the RDX may act as a heat sink for local hot spots, while the melted RDX may also lubricate the system. In order to test the melting theory, two hydrocarbons, with a wide range of melting points, were substituted into the standard formulation: bibenzyl (m.p. = 52.5°C, b.p. = 284°C), and p-terphenyl (m.p. = 213°C, b.p. = 427°C). Uncured sensitivity test results are shown below.

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	Bibenzyl	p-Terphenyl
E_o (kg-cm)	6	9
F_o (rpm)	2300	2400
Friction Screw	- Pyrex + SiC	-SiC

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The desensitization obtained with these compounds compares closely with that obtained with 10 percent RDX on the rotating disc tester. The hydrocarbons gave even greater desensitization on the friction screw.

(U) To further test the melting theory, 10 percent graphite was substituted in the standard mix. Graphite sublimes at 365°C and should not desensitize the propellant if the other compounds desensitize by a melting process. The uncured impact sensitivity was 8 kg-cm, friction sensitivity was 2200 rpm, and the friction screw was negative on SiC. These values agree quite closely with those obtained with the two hydrocarbons.

(U) These data indicate that the desensitization is not obtained by a melting effect. The desensitization is probably obtained by a lubricating effect. RDX, bibenzyl, and p-terphenyl are all soft waxy-type materials, while graphite is a well-known dry lubricant.

(U) (6) Coatings of LMH-1 and Ammonium Perchlorate

(U) (a) Coating of LMH-1

(U) The large particle (138 micron) LMH-1 with low surface area was used in this investigation in order to obtain a more complete coating. Three different coatings were applied at the 3 percent level by a solvent - nonsolvent technique. These were Viton A (Fluorocarbon), Hypalon (synthetic rubber from chlorosulfonated polyethylene), and ZL-437 (polyester propellant binder). The coated hydrides were used in a standard formulation with 20 micron oxidizer. Sensitivity test results are compared below.

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Sensitivity Test Results

Mix No.	3 Percent Coating	Impact (kg-cm) U[a]	Impact (kg-cm) C[b]	Friction (rpm) U	Friction (rpm) C	Spark U	Spark C	Friction Screw Grit (+) U	Friction Screw Grit (+) C	Friction Screw Cured Torque (in-lb)
IS-24	---	7	8	1800	1800	0.5	1.0	Pyrex	Pyrex	250
IS-25	Viton A	9	10	2600	2200	0.5	0.5	Pyrex	Pyrex	150
IS-26	ZL-437	7	11	4000	2400	0.5	0.5	Pyrex	Pyrex	200
IS-27	Hypalon	10	10	2000	2000	0.5	0.5	Pyrex	Pyrex	175

a. Uncured Results
b. Cured Results

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(U) It may be seen that only slight changes in impact sensitivity were noted for any of the coatings, these being improvements of 2 to 3 kg-cm in both the uncured and cured states. Friction sensitivity was improved to a larger extent, especially in the case of the ZL-437 coating (HS-26). A friction sensitivity of 4000 rpm was obtained with uncured HS-26; however, the cured material dropped to 2400 rpm. This propellant, as well as the others shown above, gave positive tests with Pyrex when tested on the friction screw device. A second technique evaluated was the coating of the LMH-1 particle with an inert binder [HX-874 (curing agent) and ZL-437 (polymer)] in the same ratios as used in the standard formulation. This coating was applied by the solvent-nonsolvent procedure with heating after precipitation to cure the polymer on the LMH-1 particle. (This coating would not be soluble in the binder during mixing as would a coating of uncured ZL-437.) The results of this test are compared in Table X with those of a standard mix (uncoated LMH-1) and a mix containing LMH-1 coated with the binder (ZL-437) only.

(U) These data show no significant difference between this mix (HS-63) and the standard in regard to uncured or cured impact sensitivity. The friction sensitivity of the uncured and cured propellants is decreased by 2600 (or over 160 percent) and 600 rpm, respectively, when compared to the standard. The test results of this mix compare favorably with those of the mix containing LMH-1 coated with the binder ZL-437 only (HS-26); both result in equivalent friction sensitivities. HS-63 does exhibit decreased impact sensitivity over HS-26; however, this difference of impact sensitivities is attributed to the larger ammonium perchlorate particle size used in mix HS-26. The results of the friction screw and spark sensitivity tests indicate no decrease or increase of the measured sensitivity.

(U) The technique of coating LMH-1 with an inert binder was used in conjunction with a 49/51 ratio of fine/coarse (6/400 micron) ammonium perchlorate (HS-75) in order to obtain a more processable mix. The results of this test are compared in Table XI with a standard mix (100 percent 6-micron ammonium perchlorate and uncoated LMH-1) and with the previously tested mix (HS-63) of coated LMH-1 and 100 percent 6-micron ammonium perchlorate.

(U) It may be seen that mix HS-75 is much less viscous (48 kp) than mix HS-63 (>300 kp) and is, therefore, a more practical test of the effect of the polymer coated LMH-1. As was expected, both the uncured and cured propellant is significantly more sensitive to impact due to the increase in ammonium perchlorate particle size. The uncured friction sensitivities of mixes HS-63 and HS-75, which are equivalent, show considerable improvements over the standard mix. Cured HS-63 (2600 rpm) is more sensitive to friction than the uncured propellant (4200 rpm) and is 600 rpm less sensitive than the standard.

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TABLE X

SENSITIVITY TEST RESULTS OF LMH-1 COATED SOLIDS

Mix No.	Viscosity (kp) at 124 - 128°F	Density (g/cc)	Penetrometer (cm)	% 85 Micron LMH-1	% 6 Micron AP	% LMH-1 Coated ZL-437 & HX-874[c]	Sensitivity Test Results: Impact (kg-cm) U[a]	Impact (kg-cm) C[b]	Friction (rpm) U	Friction (rpm) C	Spark (joules) U	Spark (joules) C	Friction Screw (grit) (3 test/grit) U	Friction Screw C	Torque for (+) Test on Cured (in-lb)
Standard HS-19	--	--	6.6	25.0	49.5	0	11	15	1600	2000	0.5	1.0	Pyrex	Pyrex	200
HS-63	>300	1.555	2.9	25.0	49.5	25	12	16	4200	2600	1.0	1.0	SiC	Pyrex	150
HS-26[c]	--	--	--	25.0	--	--	7	11	4000	2600	0.5	0.5	Pyrex	Pyrex	Back-Off

(a) Uncured Results
(b) Cured Results
(c) See Table IX

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TABLE XI

COATED LMH-1 WITH CURED POLYMER

Mix No.	Viscosity (kp) at 124 - 128°F	Density (g/cc)	Penetrometer (cm)	% 85 micron LMH-1	% 6 micron AP	% 400 micron AP	% LMH-1 Coated with ZL-437 and HX-874	Sensitivity Test Results: Impact (kg-cm) U(a)	Impact (kg-cm) C(b)	Friction (rpm) U	Friction (rpm) C	Spark (joules) U	Spark (joules) C	Friction Screw (grit) (3 Test/grit) U	Friction Screw (grit) (3 Test/grit) C	Torque for (+) Test on Cured (in-lb)
Standard HS-19	--	--	6.6	25	49.5	0	0	11	15	1600	2000	0.5	1.0	Pyrex	Pyrex	200
HS-63	> 300	1.55	2.9	25	49.5	0	25.0	12	16	4200	2600	1.0	1.0	SiC	Pyrex	150
HS-75	48	1.55	3.0	25	24.25	25.25	25.0	9	7	4000	4600	0.5	0.5	Pyrex	Pyrex	100

(a) Uncured Results
(b) Cured Results

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This is indicative of the high viscosity (approaching "dryness") of this mix. It will be shown that as the viscosity is decreased the difference in friction sensitivity between uncured and cured propellants is diminished, probably due to better bonding between the binder and solids. Mix HS-75, which has a lower viscosity, exhibits a cured friction sensitivity of 4600 rpm. This sensitivity is 600 rpm less sensitive than the uncured propellant, and is significantly improved (2000 rpm) over the cured friction sensitivity of HS-63. The spark sensitivity of these propellants are in the normal range (negative at 0.5 to 1.0 joules). The results of the friction screw tester are listed for consideration.

(U) (b) Coatings of Ammonium Perchlorate

(U) Several sizes of ammonium perchlorate (20, 60, 220, 400 micron) were coated with 3 percent coatings of Viton A, Hypalon and ZL-437. The mixes used the coated 20 micron oxidizer and the 138 micron LMH-1. Sensitivity tests are shown in Table XII. All three coatings gave slight improvements (2 to 3 kg-cm) in impact sensitivity. Friction sensitivity was improved only in the case of the cured propellant with Viton A coated oxidizer. Since better coatings should be obtained as particle size increases and surface area decreases, propellants were made using the coated large particle oxidizer. The results of these tests are combined with particle wetting techniques and tests are reported under the Task 2 effort.

(U) c. Task 2. Investigation of Processing Factors

(U) The factors of propellant microstructure, processing and formulation variables were investigated under this task.

(U) (1) Propellant Microstructure

(U) In this portion of the investigation, the effects of optimum solids packing on propellant sensitivity were studied. In addition, the wetting of the solids by the polymer, the plasticizer and polymer/plasticizer/curing agent combinations are reported. Several approaches were taken to improve wetting and reduce sensitivity by eliminating voids. These approaches involved the use of wetting agents, wetting by pasting of solids, solids packing studies and propellant density. These areas of study are discussed individually below.

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TABLE XII

COATED AMMONIUM PERCHLORATE

Mix No.	3 Percent Coating	Sensitivity Test Results									
		Impact (kg-cm)		Friction (rpm)		Spark (joules)		Friction Screw			
								Grit (+)		Cured Torque (in-lb)
		U[a]	C[b]	U	C	U	C	U	C	
HS-24	---	7	8	1800	1800	0.5	1.0	Pyrex	Pyrex	250
HS-29	Viton A	9	10	1600	2400	0.5	0.5	Pyrex	Pyrex	300
HS-31	Hypalon	9	11	---	2000	0.5	0.5	Pyrex	Pyrex	200
HS-34	ZL-437	10	8	1800	1600	0.5	0.5	Pyrex	SiC	200

(a) Uncured Results
(b) Cured Results

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(U) (a) Wetting Agents

(U) The approach used to study wetting characteristics is measurement of the contact angle of propellant liquids on the propellant solids (ammonium perchlorate and LMH-1). The device used for measurement of contact angles was a monocular microscope with a circular revolving stage graduated in degrees. In a solid-liquid-gas system the contact angle (θ) is conventionally measured as the angle between the planar surface of the solid, and a tangent to the gas-liquid interface at the juncture of the three phases, as illustrated below:

A contact angle of zero indicates complete wetting while a contact argle of 180° would indicate no wetting between the solid and the liquid. Large (0.5 by 0.5 inch) crystals of ammonium perchlorate, which had been grown previously, and 0.25 inch diameter pellets of LMH-1 were used to measure contact angles. The LMH-1 pellets were made on a Stokes automatic single punch press.

The table below gives the solid to be wetted, the wetting liquid, and the contact angle measured.

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Solid	Liquid	Contact Angle
AP	ZL-437	24° 32'
AP	TMETN	13° 50'
AP	Standard Binder Formulation[a]	15° 02'
LMH-1	ZL-437	38° 09'
LMH-1	TMETN	11° 14'
LMH-1	Standard Binder	17° 02'

a. 54.9% TMETN, 39.65% ZL-437, 5.45% HX-874.

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(U) It may be seen that TMETN wets both the oxidizer and LMH-1 quite well, ZL-437 does not wet LMH-1 as well as desired and the standard binder formulation (as used in propellant) wets both AP and LMH-1 in a range intermediate between the separate ingredients. In order to lower this contact angle, a number of wetting agents of various chemical types (nonionic, anionic, cationic, amphoteric) and of both hydrophilic and lipophilic types were added to the standard binder as 0.1 percent based on the propellant weight. This amount is based on previous work performed at Thiokol's Huntsville Division, where percentages of wetting agents from 0.02 to 0.2 percent were investigated. The wetting agents, chemical composition and contact angles with AP and LMH-1 are shown in Table XIII.

(U) This list is representative of the various types of surfactants available. It may be seen from the table that only Armeen SZ, Ethomeen C/12, and MAPO reduced the contact angle (improved wetting) in the case of the oxidizer. Almost all wetting agents gave some improvement for LMH-1; however, Armeen SZ, Armeen Z, and MAPO appeared to be the best.

(U) Propellant mixes were prepared to determine the effect of wetting agents on propellant processing and sensitivity. The three wetting agents that appeared most effective from those shown in Table XIII were selected for propellant tests; these were MAPO, Armeen SZ and G-2684. The results of these tests are compared in Table XIV with control formulations. It may be seen from these data that there is no difference in sensitivity, viscosity, density and degree of cure (as measured by a penetometer) for the propellant containing 0.1 percent MAPO (HS-43). The ammonium perchlorate and LMH-1 particle sizes were changed in the evaluation mixes of the wetting agents Armeen SZ and G-2684, therefore, another control formulation (HS-53) is given for comparison of these propellants.

(U) Armeen SZ, an anionic type chemical, which is an aliphatic metal salt of N-coco beta amino butyric acid, was used in test mix HS-85. This mix resulted in no significant improvement in propellant viscosity. The sensitivity results were not improved for impact, but an improvement in friction sensitivity is indicated beyond that of the standard mix. The uncured and cured friction is 45 percent (1000 rpm) and 100 percent (1800 rpm), respectively, less sensitive than the standard.

(U) Wetting agent G-2684, sorbitan monooleate polyoxyethylene ester, was used in mixes HS-86 (0.1 percent) and HS-87 (0.5 percent). Both mixes failed to cure; however, evaluation of the data obtained indicates that no real improvement was made in propellant viscosity when compared to the standard and no improvement in impact sensitivity was observed. It appears that the uncured friction sensitivity was improved more than 100 percent.

(U) Since the propellants containing G-2684 failed to cure, the only significance of these uncured results is to show the effect of the potential use of some wetting agent. Tests to obtain proper cures of formulations with G-2684 were necessary. Properly cured mixes containing G-2684 were obtained using small percentages of a cure catalyst (FeAA). Additional tests of G-2684 propellants are discussed under Phase II.

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TABLE XIII

MEASURED CONTACT ANGLES OF BINDER MATERIALS

Wetting Agent[1]	Chemical Composition	AP Contact Angle	AlH_3 Contact Angle
None	---	15° 02'	17° 02'
Lecithin	$C_{42}H_{84}O_9PN$ (a phospholipid)	15° 39'	13° 19'
Tween 80[(b)]	Polyoxyethylene 20 sorbitan monoleate (nonionic HLB = 15)	23° 31'	15° 23'
Span 80[(b)]	Sorbitan monoleate (nonionic, HLB = 4.3)	22° 16'	15° 15'
Sterox SK[(c)]	Polyoxyethylene thioether (nonionic)	23° 25'	14° 21'
Aerosol 18[(d)]	N-octyl disodium sulfosuccinate (anionic)	22° 30'	22° 03'
Armeen SZ[(e)]	Alkali metal salt of N-coco beta amino butyric acid (anionic)	11° 12'	9° 54'
Ethomeen C/12[(e)]	Polyoxyethylene coco amine (cationic)	14° 42'	13° 06'
G2684[(b)]	Sorbitan monooleate poly-oxyethylene ester (HLB = 7.8)	15° 27'	13° 12'
Isothan DL-1[(f)]	Dialkyl dimethyl ammonium Bromide (cationic)	20° 00'	16° 57'
Armeen Z[(e)]	N-coco beta amino butyric acid (amphoteric)	16° 49'	11° 00'
MAPO[(g)]	Methyl-aziridinyl phosphine oxide	11° 48'	11° 15'

1. 0.1 percent based on propellant weight in standard binder.

a. 0.1 percent based on propellant weight in standard binder.
b. Trademark of Atlas Powder Company, Wilmington, Delaware.
c. Trademark of Monsanto Chemical Company, St. Louis, Missouri.
d. Trademark of American Cyanamid Company, New York, New York.
e. Trademark of Armour Chemical Division, Armour & Company, Chicago, Illinois.
f. Trademark of Onyx Oil, Chemical Company, Jersey City, New Jersey.
g. Product of Interchemical Corporation, New York, New York.

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TABLE XIV

EFFECT OF WETTING AGENTS

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Mix No.	Viscosity KP 124 - 130°F	Density g/cc	Wetting Agent	Percent of wetting agent	LMH-1 Particle Size	AP Average Particle Size	Sensitivity Test Results: Impact (kg-cm)		Friction (rpm)		Spark (joules)		Friction Screw (+) Grit 3 test/grit		Torque for (+) Test Cured
							U[a]	C[b]	U	C	U	C	U	C	in-lb
Standard HS-43	9	1.561	--	--	138	142	6	7	2400	2600	0.5	0.5	Pyrex	Pyrex	Back-off
HS-44	9	1.556	MAPO	0.1	138	142	6	6	2400	2600	0.5	0.5	Pyrex	Pyrex	150
Standard HS-53	17	1.556	--	--	85	231	4	6	2200	1800	0.5	0.5	Pyrex	Pyrex	150
HS-85	16	1.492	Armeen S Z	0.1	85	231	5	6	3200	3600	0.5	0.5	Pyrex	Pyrex	200
HS-86	14.4	--	G-2684	0.1	85	231	6		5000		0.5		Pyrex		
HS-87	15	--	G-2684	0.5	85	231	7		5000		0.5		Pyrex		

a. Uncured Results

b. Cured Results

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(U) (b) Improved Wetting by Pasting of Solids

(U) A method for improving the wetting of the solids, and one that is closely related to coating, is that of dispersing the solid (LMH-1 or ammonium perchlorate) in a liquid (ZL-437) by a pasting process. Ammonium perchlorate and LMH-1 were pasted into ZL-437 in this investigation. After pasting, the mixture appeared much smoother and possessed a much lower viscosity.

(U) Fifty-eight-and-eight-tenths percent LMH-1 was pasted with the ZL-437. The resulting mixture was quite fluid. Additional LMH-1 was added (bringing the total to 70 percent) prior to further processing of the mixture. Attempts were made to dissolve the ZL-437 in methylene chloride, and filter or centrifuge the pasted LMH-1; however, the solid was so finely divided that it could not be completely separated. Carbon and hydrogen analyses on LMH-1 before and after pasting are shown below.

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	Carbon (%)	Hydrogen (%)
Before pasting	0.11	10.05
After pasting	0.36	9.80

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The very slight increase in carbon and corresponding decrease in hydrogen are probably due to incomplete polymer removal. It can be concluded, however, that little or no decomposition of LMH-1 occurred during pasting.

(U) Propellant mixes made using the pasted oxidizer and LMH-1 (separately) are compared below with the standard mix (HS-19), which contains 85 micron LMH-1 and 6 micron ammonium perchlorate. Mix HS-28 contained 23.75 percent pasted oxidizer (limited by amount of ZL-437 to be used), and 25.75 percent 6 micron oxidizer. Mix HS-32 contained 22.6 percent pasted LMH-1 and 2.4 percent 85 micron LMH-1. This mix was viscous and the cured propellant was very dry and weak. A mix using coated LMH-1 and pasted ammonium perchlorate is also shown (HS-35).

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Sensitivity Test Results

	LMH-1 (Coated)	LMH-1 (Pasted)	AP (Pasted)	Impact (kg-cm)		Friction (rpm)		Spark (Joules)		Friction Screw		
										Grit (+)		Cured Torque (in-lb)
				U[a]	C[b]	U	C	U	C	U	C	
HS-19	-	-	-	11	15	1600	2000	0.5	1.0	Pyrex	Pyrex	200
HS-28	-	-	yes	16	12	2800	2200	0.5	0.5	Pyrex	Pyrex	175
HS-32	-	yes	-	17	18	5000	1800	1.0	0.1	(-)SiC	Pyrex	100
HS-35	yes	-	yes	6	14	5000	5200	0.5	0.5	(-)SiC	(-)SiC	---

a - Uncured Results
b - Cured Results

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(U) Mix HS-28 (pasted ammonium perchlorate) gave significant improvements in uncured propellant sensitivity. Cured propellant sensitivity was only slightly changed from the standard. HS-32 (pasted LMH-1) also gave a large improvement in uncured propellant sensitivity. The friction sensitivity of 5000 rpm was one of the highest measured for LMH-1 propellants. Impact sensitivity was also improved in the cured state. The uncured propellant was negative with SiC on the friction screw and the cured propellant was positive with Pyrex. A large difference between cured and uncured propellant was also noted in spark tests. The uncured was negative at 1.0 joule, whereas the cured was negative at 0.1 joule (+ at 0.5).

(U) The large differences in sensitivity between uncured and cured propellants have been noted before and are especially apparent here. A possible explanation of this observation is as follows. Often the uncured propellant ingredients are completely wet by the binder (good processing, pasting, etc.) and the mix is thus desensitized. When the propellant is cured, solids become de-wet and are easily popped out from the binder by gentle rubbing. The de-wet particles then cause the cured propellant to be more sensitive than the uncured. Hence, methods to improve the adhesion of binder to solids should improve cured propellant sensitivity just as wetting improves uncured propellant sensitivity.

(U) In the case of the mixes with pasted oxidizer and pasted LMH-1, the uncured propellant is desensitized by obtaining extremely good wetting, while the cured propellants are only slightly different from the standard. The lack of adhesion between cured binder and LMH-1 is especially clear in HS-32 where the cured propellant is much more sensitive to spark than normal. This would be expected if the very fine pasted LMH-1 is directly exposed. Work conducted previously under other programs had shown that LMH-1 that has been pasted (fresh surfaces exposed) is much more sensitive to spark than untreated LMH-1.

(U) HS-35 is a combination of pasted ammonium perchlorate and coated LMH-1 (85 micron, 3 percent ZL-437). It may be seen that this mix has a friction sensitivity of 5000 and 5200 rpm in the uncured and cured states, respectively. Both cured and uncured are negative with SiC on the friction screw. The uncured propellant was more sensitive to impact; however, the cured was essentially unchanged. It is to be noted that the cured propellant was quite soft and actually undercured. In the semi-cured propellant the solid particles did not easily pop out.

(U) The use of pasted ammonium perchlorate was continued in conjunction with coated ammonium perchlorate and/or coated LMH-1 in the standard propellant formulation. The particle size (WMD) of the ammonium perchlorate coated and used in these tests was 220 micron. This 220 micron ammonium perchlorate was combined with pasted ammonium perchlorate in order to obtain the desired propellant viscosity. The results of these tests are shown in Table XV. The data of mixes HS-28, 32 and 35 are repeated for comparative purposes.

(U) Of interest from these data is a comparison of mixes HS-35 and 50. The only difference in these mixes is the particle size of the untreated ammonium perchlorate. In the uncured propellant, mix HS-50 is almost twice as sensitive to friction as mix HS-35 (2800 rpm to 5000 rpm). The friction sensitivity of the cured propellants was of the same order as the uncured propellant; mix HS-50 was twice as sensitive to friction as mix HS-35 (2600 rpm to 5200 rpm). It is to be noted that the cured mix HS-35 was quite soft and actually undercured, while mix HS-50 was a normally cured propellant. This difference in friction sensitivity was also indicated on the friction screw where mix HS-35 was negative with SiC; while mix HS-50 was positive with Pyrex. These mixes did, however, show improved friction sensitivity when compared to the standard (6 micron ammonium perchlorate).

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TABLE XV

RESULTS OF PASTING OF SOLIDS

Mix No.	23.6% Pasted LMH-1 (d,e)	LMH-1 Coated (d)	Particle Size of Coated(e) AP (micron)	Particle Size of Untreated AP (micron)	23.75% Pasted AP(e)	Sensitivity Test Results: Impact (kg-cm) U (a)	Impact (kg-cm) C (b)	Friction (rpm) U	Friction (rpm) C	Spark (joules) U	Spark (joules) C	Friction Screw: Grit (+) U	Grit (+) C	Cured Torque (in-lb)
Standard														
HS-19	--	--	--	6	--	11	15	1600	2000	0.5	1.0	Pyrex	Pyrex	200
HS-28	No	No	--	6	Yes	16	12	2800	2200	0.5	0.5	Pyrex	Pyrex	175
HS-32	Yes	No	--	6	No	17	18	5000	1800	1.0	0.1	(-)SiC	Pyrex	100
HS-33(c)	No	Yes	6	--	Yes	5	--	1800	--	0.1	--	Pyrex	--	--
HS-35	No	Yes	--	6	Yes	6	14	5000	5200	0.5	0.5	(-)SiC	(-)SiC	--
HS-45(c)	No	Yes	220	--	Yes	6	--	2800	--	0.5	--	Pyrex	--	--
HS-46(c)	No	No	220	--	Yes	6	--	1400	-	0.5	--	Pyrex	--	--
HS-50	No	Yes	--	220	Yes	6	11	2800	[illegible]	0.5	0.5	Pyrex	Pyrex	150

(a) Uncured Results
(b) Cured Results
(c) These mixes did not cure
(d) All LHM-1 was 85 micron particle size.
(e) The liquid used for coating and pasting was ZL-437.

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(U) Mixes HS-45 and 46 were made in order to determine why mix HS-33 did not cure. Mix HS-45 contained both pasted and coated ammonium perchlorate and coated LMH-1, while mix HS-46 contained both pasted and coated ammonium perchlorate and uncoated LMH-1. Both mixes failed to cure. These data indicate that whenever the oxidizer has been completely coated, either by pasting or solvent-nonsolvent coating, the propellant cure is inhibited. Several methods of eliminating this problem are possible. These include using excess curing agent, and cure catalysts.

(U) It had been experimentally determined that pasting of LMH-1 reduced the particle size to such an extent that proper propellant processing was not obtained. A second batch of LMH-1 was pasted in ZL-437. This mixture contained 67.5 percent LMH-1. Propellant tests using this material are shown in Table XVI.

(U) Two particle sizes (6 and 400 micron) of ammonium perchlorate were used in this series of tests; therefore, two standard mixes and their sensitivities are shown (mixes HS-19 and 38) for comparison.

(U) Mixes HS-32 (made with the initial batch of pasted LMH-1) and HS-60 (made with the second batch of pasted LMH-1) may be compared directly to the standard mix HS-19. These two mixes, when compared to the standard, show a significant improvement in uncured and cured impact sensitivity. In the uncured propellant there is a 6 to 7 kg-cm improvement (55 percent). In the cured propellant, the improvement is 3 kg-cm over the 15 kg-cm of the standard. The uncured friction sensitivity is greatly improved, giving 2600 to 3400 rpm more than the standard. The cured friction sensitivity of mix HS-32 is not improved, while the cured mix HS-60 is 800 rpm greater than that of the standard. This decrease in improvement of friction sensitivity of the cured propellant, as compared to the uncured propellant, is explained by the fact that these mixes cured to a dry, hard material, and the solids were easily separated from the binder. These separated solids are extremely friction sensitive, as are dry blends of ammonium perchlorate and LMH-1. Since these two mixes are identical formulations, but with different pasted LMH-1, it is of interest to compare the two. In mix HS-32, 1.95 percent more of the LMH-1 was pasted for a longer period of time. A viscosity determination was not possible on either mix (both listed as "dry"); however, the penetrometer measurement indicated the cured propellant of mix HS-32 to be much harder than mix HS-60. There is practically no difference in the impact sensitivity of the two mixes, but there is a considerable difference in the friction sensitivity. The uncured friction sensitivity of mix HS-60 is 800 rpm less than that of mix HS-32, and the cured friction sensitivity of mix HS-60 is 1000 rpm greater than that of mix HS-32. It was evident from both sensitivity tests and visual observation that mix HS-60 was a much better mix than mix HS-32, even though it was still dry. Spark sensitivity was in the normal range (0.5 to 1.0 joule).

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TABLE XVI

PASTED AND COATED SOLIDS

Mix No.	Viscosity (kp) at 124 - 128°F	Density (g/cc)	Penetrometer (cm)	% Pasted LMH-1	% 85 Micron LMH-1	% 6 Micron AP	% 400 Micron AP	% 400 Micron Coated AP	Impact (kg-cm) U[b]	Impact (kg-cm) C[c]	Friction (rpm) U	Friction (rpm) C	Spark (joules) U	Spark (joules) C	Friction Screw (grit) (3 test/grit) U	Friction Screw (grit) (3 test/grit) C	Torque for (+) Cured (in-lb)
Standard HS-19	--	--	6.6	0	25.00	49.50	0	0	11	15	1600	2000	0.5	1.0	Pyrex	Pyrex	200
HS-32[a]	Dry	--	1.5	23.60	1.40	49.50	0	0	17	18	5000	1800	1.0	0.1	(-)SiC	Pyrex	100
HS-60	Dry	1.489	2.5	21.65	3.35	49.50	0	0	18	18	4200	2800	1.0	0.5	Pyrex	Pyrex	200
Standard HS-38	18	1.577	13.5	0	25.00	24.75	24.75	0	6	6	1400	2200	0.5	0.5	Pyrex	Pyrex	Back-Off
HS-61	26	1.431	6.5	21.65	3.35	24.26	25.24	0	8	8	4400	3000	0.5	0.5	Pyrex	Pyrex	250
HS-62	91	1.422	5.2	21.65	3.35	24.26	0	25.24	5	10	4400	3000	0.5	0.5	Pyrex	Pyrex	Back-Off

(a) This mix also shown on Table XV.
(b) Uncured Results
(c) Cured Results

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(U) Mixes HS-61 and 62, which were made in order to evaluate pasted LMH-1 in more processable propellants, may be compared directly to the standard mix HS-38. These mixes were made with a bimodal blend of 6 and 400 micron ammonium perchlorate. (The only difference between mixes HS-61 and 60 is the particle size of ammonium perchlorate.) Mix HS-62 was made identical to mix HS-61, except that the large (400 micron) ammonium perchlorate was coated by the solvent-nonsolvent technique with ZL-437.

(U) The impact sensitivities of these two mixes are generally slightly improved over that of the standard. The uncured propellant ranged from slightly more sensitive (HS-62) to 2 kg-cm less sensitive (HS-61) than the standard. The cured propellant was from 2 to 4 kg-cm less sensitive to impact. The differences in the impact sensitivities of mixes HS-60 and 61 may be attributed to the difference in the ammonium perchlorate particle size and the relation to viscosity. The friction sensitivities of mixes HS-61 and 62 are identical. In the uncured propellant an improvement of 3000 rpm, or over 200 percent, was obtained. In the cured propellant, a 800 rpm improvement was obtained when compared to the standard. The spark sensitivity was normal (0.5 joules) and the friction screw test gave positive results to Pyrex on all samples.

(U) It may be seen that the viscosities of these mixes were significantly higher than that of the standard [Mix HS-61 still processed easily, mix HS-62 (coated ammonium perchlorate) was the most viscous]. It is also noted that the densities of mixes HS-61 (88.57 percent of theoretical) and HS-62 (88.02 percent of theoretical) are significantly changed from the standard (97.61 percent of theoretical).

(U) Microscopic examination of the cured propellants revealed distinct gassing voids. Apparently, the reactivity of LMH-1 had been substantially increased by pasting. Unless this problem is eliminated by special processing techniques (vacuum pumping, etc.), pasted LMH-1 cannot be used.

(c) Solids Packing Studies

(U) The effects of optimum solids packing and consequently a minimum of voids, on propellant sensitivity were studied in this area. The investigation of solids packing was initiated with dry blends of LMH-1 and ammonium perchlorate, with the ratio of the dry ingredients being equal to that of the ratio of ammonium perchlorate and LMH-1 in the stanard formulation. The bulk density of each ingredient and various mixtures of these ingredients (ammonium perchlorate and LMH-1) were measured. The results of these measurements are shown in Table XVII.

TABLE XVII

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BULK DENSITIES OF AP LMH-1 MIXTURES

One Gram Mixtures

Test No.	Mixture Ratio of AP by WMD (μ) (%) 5.7	20	20.9	219.6	400	LMH-1 (μ) WMD	AP Average WMD (μ)	Theo. Crystal Density (g/cc)	Measured Bulk Density (g/cc)	Percent of Crystal Density
A	---	---	---	---	---	32.2	---	1.45	0.637	43.93
B	---	---	---	---	---	84.2	---	1.45	0.799	55.10
C	---	---	---	---	---	138.0	---	1.45	0.904	62.34
D	100	---	---	---	---	---	5.70	1.95	0.655	33.59
E	---	100	---	---	---	---	20.00	1.95	0.955	48.97
F	---	---	100	---	---	---	60.90	1.95	1.124	57.64
G	---	---	---	100	---	---	219.60	1.95	1.264	64.82
H	---	---	---	---	100	---	400.00	1.95	1.225	62.82
1-1	100	---	---	---	---	32.2	5.70	1.749	0.666	38.07
1-2	---	100	---	---	---	32.2	20.00	1.749	0.708	40.48
1-3	---	---	100	---	---	32.2	60.90	1.749	0.788	45.07
1-4	---	---	---	100	---	32.2	219.60	1.749	0.861	49.23
1-5	40	---	---	---	60	32.2	240.20	1.749	0.840	48.03
1-6	30	---	70	---	---	32.2	44.34	1.749	0.760	43.45
1-7	20	---	---	---	80	32.2	321.10	1.749	0.949	54.26
1-8	30	---	---	---	70	32.2	281.70	1.749	0.894	51.11
1-9	10	---	---	---	90	32.2	360.60	1.749	0.938	53.63
1-10	25	---	---	75	---	32.2	166.10	1.749	0.874	49.97
2-1	100	---	---	---	---	84.5	5.70	1.749	0.616	35.23
2-1A[a]	100	---	---	---	---	84.5	5.70	1.749	0.611	34.93
2-2	---	100	---	---	---	84.5	20.00	1.749	0.648	37.05
2-3	---	---	100	---	---	84.5	60.90	1.749	0.901	51.52
2-4	---	---	---	100	---	84.5	219.60	1.749	0.981	56.09
2-5	---	---	---	---	100	84.5	400.00	1.749	0.907	51.86
2-6	67	---	---	33	---	84.5	7.70	1.749	0.842	48.14
2-7	33	---	---	---	---	84.5	14.80	1.749	0.870	49.74
2-8	40	---	---	---	60	84.5	24.23	1.749	0.903	51.63
2-9	90	---	---	---	10	84.5	45.13	1.749	0.690	39.45

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TABLE XVII (Cont'd)

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Test No.	Mixture Ratio of AP by WMD (μ) 5.7	20	20.9 (%)	219.6	400	LMH-1 (μ) WMD	AP Average WMD (μ)	Theo. Crystal Density (g/cc)	Measured Bulk Density (g/cc)	Percent of Crystal Density
2-10	---	20	---	80	---	84.5	179.70	1.749	0.973	55.63
2-11	---	---	60	---	40	84.5	196.50	1.749	0.970	55.46
2-12	10	---	---	90	---	84.5	198.20	1.749	0.971	55.50
2-13	---	---	---	67	33	84.5	279.70	1.749	0.962	55.00
2-14	23	---	---	---	77	84.5	309.31	1.749	0.924	52.83
2-15	15	---	---	---	85	84.5	348.60	1.749	0.990	56.60
2-16	10	---	---	---	90	84.5	360.60	1.749	1.01	57.75
2-17	---	10	---	---	90	84.5	362.00	1.749	0.986	56.38
2-18	5	---	---	---	95	84.5	380.30	1.749	0.960	54.89
2-19	---	---	30	---	70	84.5	298.30	1.749	0.934	53.40
2-20	77	---	---	---	23	84.5	96.40	1.749	0.672	38.42
2-21	84	---	---	---	16	84.5	68.80	1.749	0.670	38.31
2-22	50	---	---	---	50	84.5	202.80	1.749	0.805	46.03
3-1	100	---	---	---	---	138.0	5.70	1.749	0.665	38.02
3-2	---	100	---	---	---	138.0	20.00	1.749	0.845	48.31
3-3	---	---	100	---	---	138.0	60.90	1.749	0.906	51.80
3-4	---	---	---	100	---	138.0	219.60	1.749	0.975	55.75
3-5	86	---	14	---	---	138.0	13.43	1.749	0.72	41.17
3-6	40	---	---	---	60	138.0	24.23	1.749	0.903	51.63
3-7	---	20	---	80	---	138.0	179.70	1.749	0.969	55.40
3-8	---	---	20	80	---	138.0	187.90	1.749	1.03	58.89
3-9	---	10	---	90	---	138.0	198.20	1.749	0.931	53.23
3-10	---	---	20	---	80	138.0	332.20	1.749	0.981	56.09
3-11	---	20	---	---	80	138.0	324.00	1.749	0.947	54.15
3-12	10	---	---	---	90	138.0	360.60	1.749	0.958	54.77
3-13	67	---	---	33	---	138.0	77.00	1.749	0.842	48.14

(a) Test No. 2-1A with carefully dried ammonium perchlorate and measured in a dry box.

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(U) The theoretical crystal density of the ammonium perchlorate/LMH-1 mixture was calculated and found to be 1.749 grams/cubic centimeter. The percentage of this crystal density, as determined by the bulk density measurements, is shown in Table XVII. Figures 11, 12 and 13 give the results in graphic form as percent voids.

(U) Test 2-1A was performed utilizing dried ammonium perchlorate. The dried ammonium perchlorate and other equipment necessary for measurement of the bulk density was placed in a closed nitrogen purged dry box for determination of bulk density in a controlled atmosphere. The other bulk densities reported were conducted at ambient conditions. The purpose of Test 2-1A was to determine the effect, if any, of moisture on the measurement of bulk density. The values of the two measurements (Tests 2-1 and 2-1A) have only a 0.005 gram/cubic centimeter (less than 1 percent) difference. It was therefore concluded that the tests may be run in the atmosphere.

(U) Generally, it is concluded that the best packing of these solids occurs at the 30/70 to 10/90 ratio of fine to coarse ammonium perchlorate.

(U) The optimum packing for each of the three particle sizes of LMH-1 used in this investigation required either different fine/coarse ratios and/or different particle sizes of the fine and/or coarse ammonium perchlorate. The 32.2 micron LMH-1 gave the best packing with a 20/80 ratio of 6/400 micron WMD ammonium perchlorate; the 85 micron LMH-1 was best with a 10/90 ratio of 6/400, the 138 micron LMH-1 was best at a ratio of 20/80 of 61/220 micron ammonium perchlorate (Figures 11, 12 and 13). It is of interest to note that as the weight mean diameter of the LMH-1 increased the best packing resulted with higher concentrations of larger particles of ammonium perchlorate in bimodal blends, and the best packing of all investigations was obtained with large LMH-1 and the two intermediate sized ammonium perchlorate particles.

(U) Theoretically, accoring to Dallavalle[1], the best packing of spheres of a single diameter is with 26.95 percent voids and the worst packing with these limits is with 47.64 percent voids. When two or more sizes of spheres are used, this theoretical packing can be improved. However, the materials used in the present investigation is not spherical and was not expected to obtain these values.

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1. Dallavalle, J. M., Micromeritics - The Technology of Fine Particles, Chapter 6, Pitman Publishing Corp. New York and London, 1948.

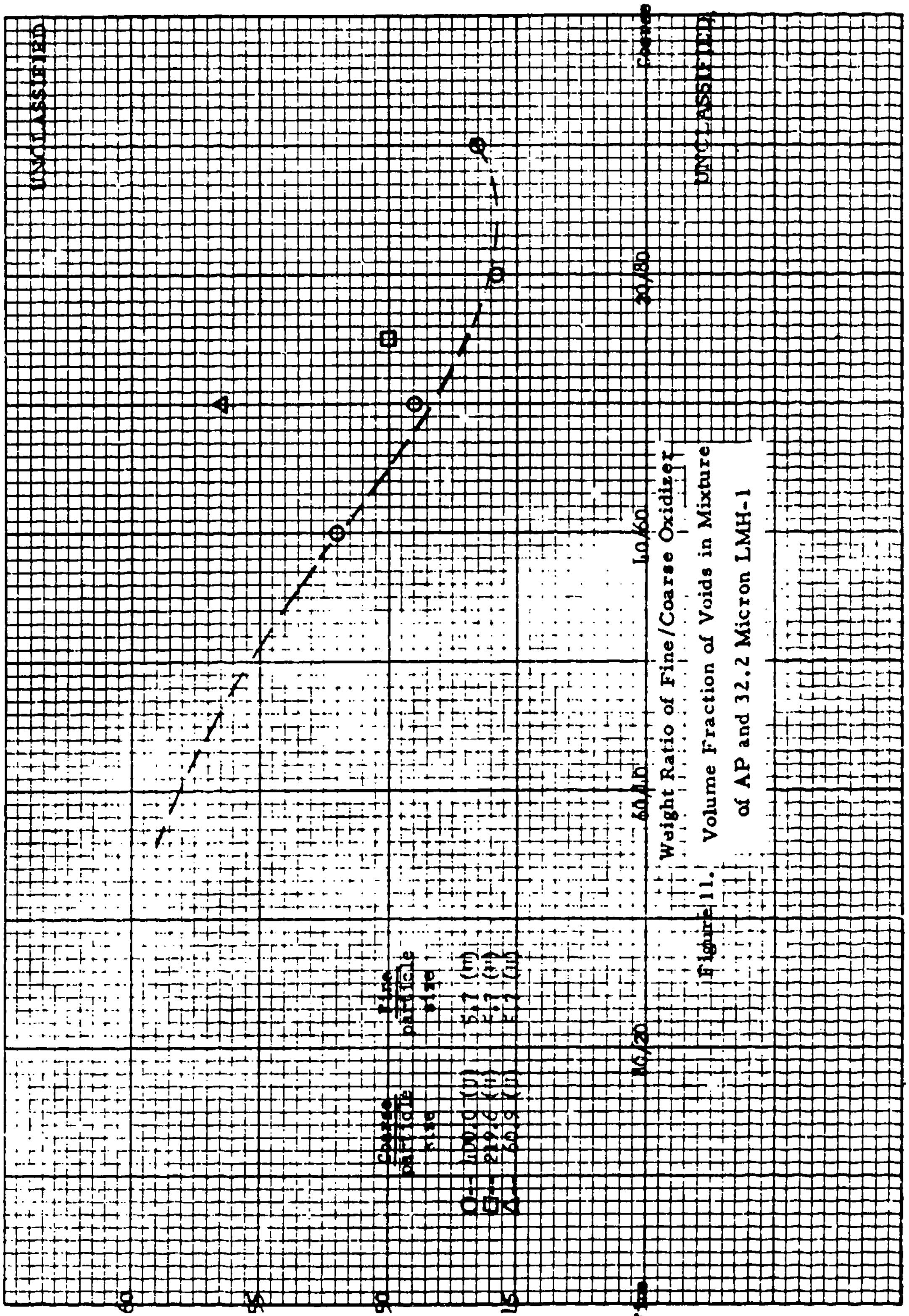

Figure 11. Volume Fraction of Voids in Mixture of AP and 32.2 Micron LMH-1

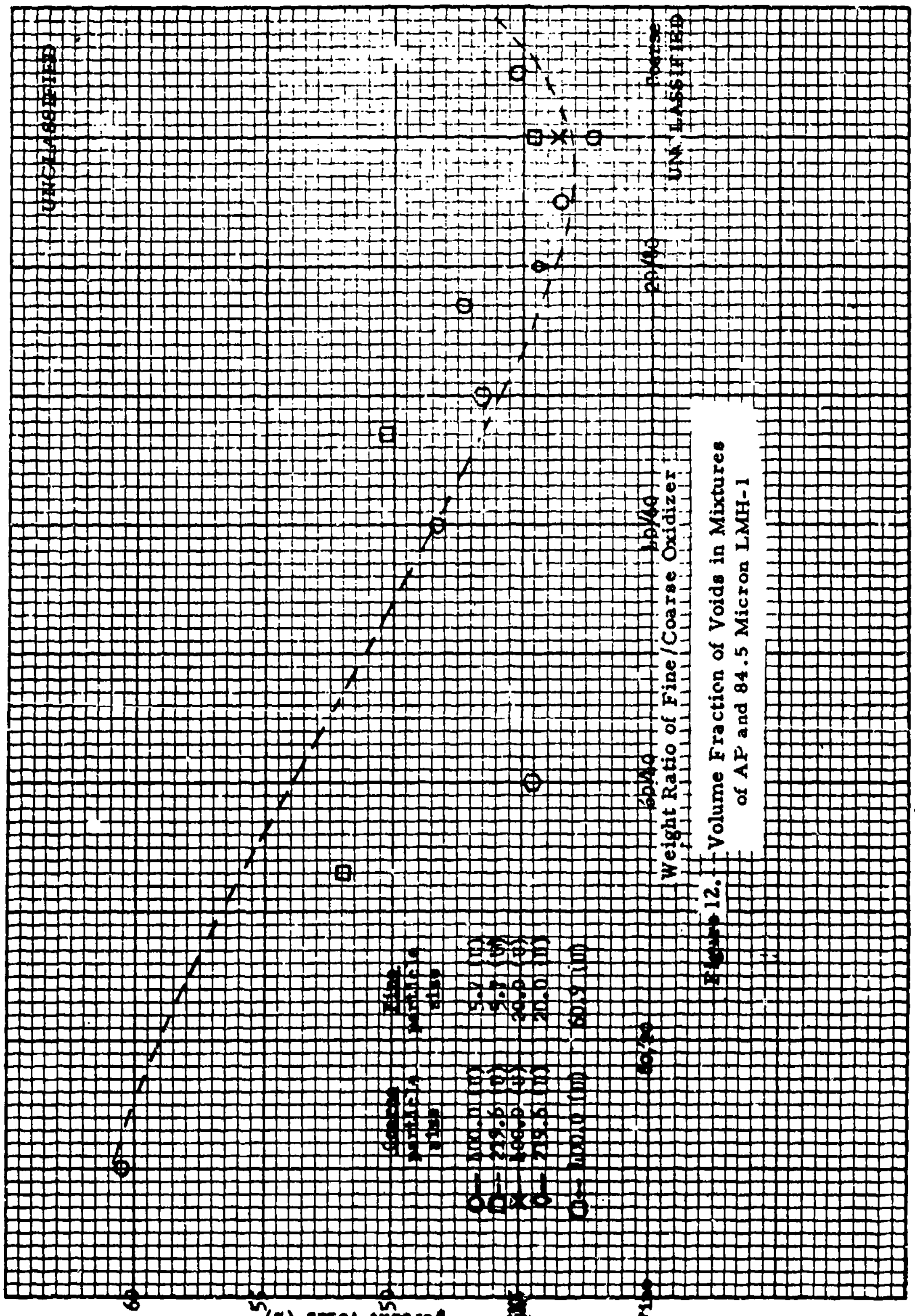

Figure 12. Volume Fraction of Voids in Mixtures of AP and 84.5 Micron LMH-1

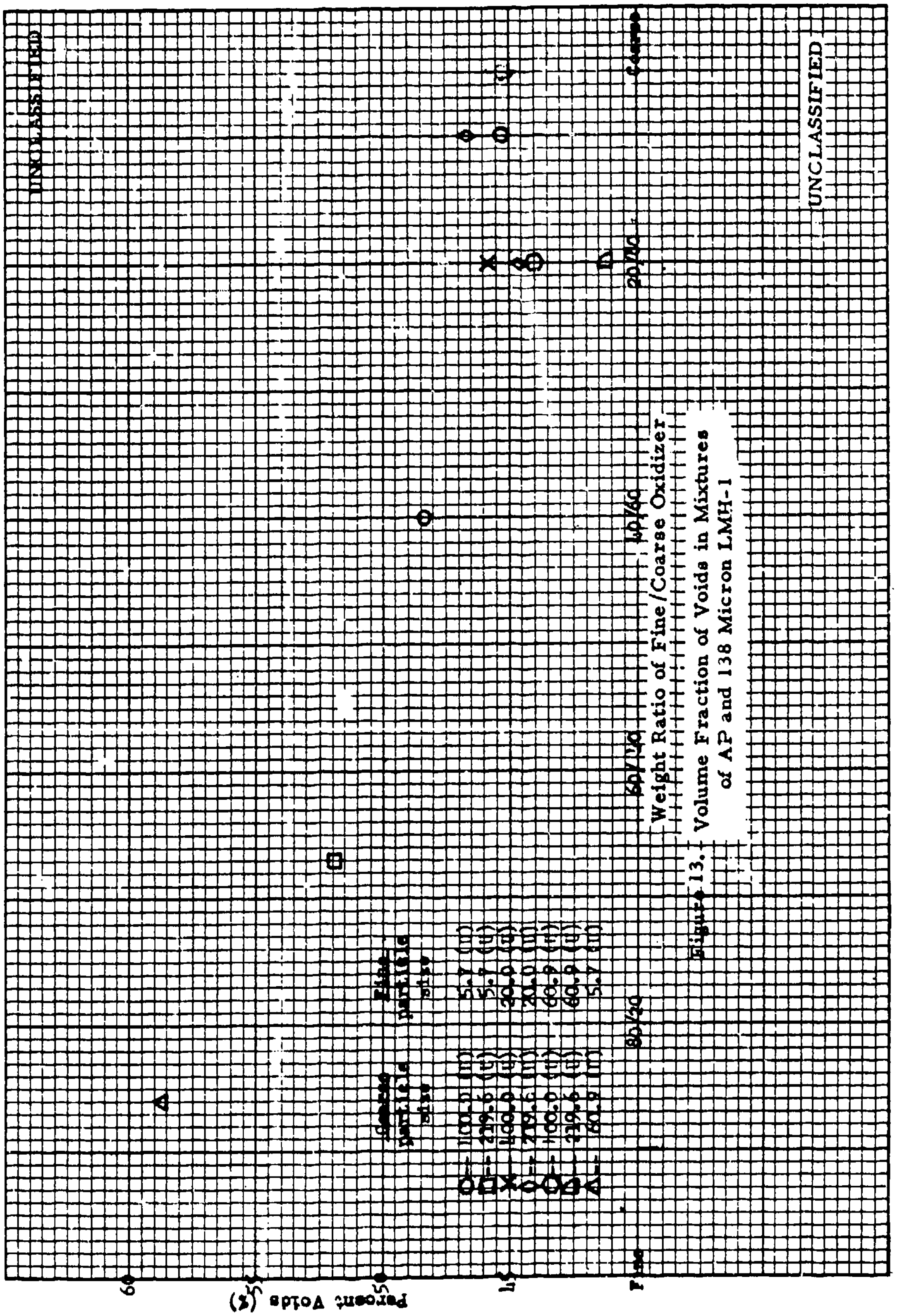

Figure 13. Volume Fraction of Voids in Mixtures of AP and 138 Micron LMH-1

(U) In the case of 85 micron LMH-1, the best solids packing (42.25 percent voids) was measured with a 90/10 ratio of 400 micron/6 micron oxidizer. However, when this mixture was used in the standard propellant formulation (HS-36 of Table XVIII) a dry, grainy material resulted. It was also found that a propellant (HS-38) made with a 50/50 ratio of 400 micron/6 micron gave a processable material with a viscosity of 18 kilopoise. The corresponding mixture of dry solids gave a percentage of voids of 54 percent. Other propellants using 138 micron LMH-1 and 48/52 ratios of 6/400 micron oxidizer gave viscosities of 6 to 9 kilopoise. These dry mixtures also gave high percentages of voids ($\sim$ 50 percent).

(U) Apparently the dry solids packing studies cannot be correlated to propellant processing. This is probably due to the shape (cubic) of the LMH-1 particles. Packing theory is based on the use of spheres[2], and may be used when the solids that go into propellants are spherical or nearly spherical.

(U) The propellants which have been discussed are shown in Table XVIII with their sensitivity data. It may be seen from these data that the dry unprocessable propellant, which has the highest percent of large untreated ammonium perchlorate, was the least sensitive to impact and most sensitive to friction. The two formulations containing pasted ammonium perchlorate (mixes HS-43 and 42) show a reduction of viscosity and improved friction sensitivity for the uncured and cured propellant. The impact tests of the pasted ammonium perchlorate formulation was slightly more sensitive than the unprocessable mix HS-36.

(U) These observations of viscosity effect led to the decision to observe more closely, for the remainder of the program, the propellant viscosity and the resulting sensitivities. Mix HS-36 [90 percent large (400 micron) ammonium perchlorate] was the least impact sensitive whereas mixes HS-38 and 42 (higher concentrations of small ammonium perchlorate) resulted in greater impact sensitivity. These facts are not in agreement with the results of the Task 1 ammonium perchlorate particle size investigation. It may also be noted that the cured propellants with low viscosity are less sensitive to friction than the uncured propellants. Apparently, good wetting of the solids makes them less likely to unbond or pop-out of the cured propellant.

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2. Ibid.

TABLE XVIII

EFFECT OF VISCOSITY ON PROPELLANT SENSITIVITY

Mix No.	Viscosity at 124° F (kp)	Density (g/cc)	LMH-1 Particle Size (μ)	AP Content (%)				Sensitivity Test Results: Impact (kg-cm)		Friction (rpm)		Spark (joules)		Friction Screw	
				6μ	Pasted	220μ	400μ	U(a)	C(b)	U	C	U	C	(+) Cured	Torque (in-lb)
HS-36	Dry	1.422	85	4.95	--	--	44.55	9	9	1200	1200	0.5	0.5	Pyrex	50
HS-38	18	1.577	85	24.75	--	--	24.75	6	6	1400	2200	0.5	0.5	Pyrex	Back-Off
HS-43	9	1.561	138	--	23.76	25.74	--	6	7	2400	2600	0.5	0.5	Pyrex	Back-Off
HS-42	6	1.500	138	--	23.76	--	25.74	6	8	2200	2800	0.5	0.5	Pyrex	150

(a) Uncured results.
(b) Cured results.

(U) (d) Propellant Density

(U) The effect of propellant density on LMH-1 propellant sensitivity was investigated during this portion of the program. The standard formulation was used with standard materials and material treatments which have been investigated. The procedure changes, introduced to give various densities, are shown in Table XIX with the sensitivities of the respective mixes. It may be seen from these data that the densities of these propellants varied from 1.536 g/cc to 1.569 g/cc, or from 95.0 percent to 97.1 percent of the theoretical density. This variance in theoretical density is not wide enough for an accurate determination of the effect of density on sensitivity but is a reasonable approximation of the extremes that would be encountered in normal propellant mixing. It is doubtful, therefore, that this study of the individual effect of density would produce conclusive data due to the extreme process changes required to produce a sufficient range of densities. These process changes would thermselves be variables in the propellant sensitivity. It is believed that propellant density does influence propellant sensitivity inasmuch as density relates to the physical structure of the propellant. Section II of this report contains additional observations on this point.

(U) (2) Variables of Mixing

(U) The effect of several processing variables on sensitivity were studied. The propellant materials and formulation were held constant in all mixes of this series. The variables that were studied are: (a) type of mixer (different shear), (b) mixing speed, (c) type of atmosphere, and (d) order of addition of ingredients. The results of these tests are given in Table XX.

(U) (a) Type of Mixer

(U) Two mixers, an ARC 2 CV double vertical cone mixer with intermeshing blades and a Barbender Plastograph horizontal sigma blade mixer were selected for this investigation. The ARC 2 CV mixer was used for processing all other mixes of this program. The Barbender Plastograph mixer was selected because the design and size permitted processing of small quantities of propellant; thus, depletion of the specific particle sizes of LMH-1 would not be so rapid. The blades of the plastograph mixer rotate at 60 rpm, whereas the ARC 2 CV mixer has a blade speed range of 20 to 200 rpm. A control setting of 2 ($\approx$45 rpm) was used with the ARC mixer. The shear of these mixers has not been established; however, by consideration of the respective designs, it is apparent that the Barbender Plastograph has a higher shear than the ARC 2 CV mixer.

TABLE XIX

EFFECT OF DENSITY

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Mix No.	Density g/cc	% of Theoretical Density	Viscosity 122°F - 128°F	Penetrometer-cm	Procedure	Sensitivity Results: Impact (kg-cm) U[a]	Impact (kg-cm) C[b]	Friction (rpm) U	Friction (rpm) C	Spark (joules) U	Spark (joules) C	Friction Screw U	Friction Screw C	Friction Screw Torque cured sample (in-lb)
HS-70	1.542	95.44	24	14.5	c	4	8	3000	4400	1.0	0.5	Pyrex	Pyrex	150
HS-73	1.556	96.31	18	18	d	5	8	3200	5600	0.5	0.5	Pyrex	Pyrex	150
HS-71	1.536	95.07	17	7.7	e	4	8	3000	3800	0.5	0.5	Pyrex	Pyrex	100
HS-72	1.569	97.11	17	20.4	e & f	4	6	3000	4600	0.5	0.5	Pyrex	Pyrex	150
HS-74	1.560	96.56	22	8.4	d & g	3	7	3600	3200	0.5	0.5	Pyrex	Pyrex	300

(a) Uncured results
(b) Cured results

Procedure Code

(c) No vacuum used, 45 minute mix time
(d) 15 minute vacuum after 30 minutes of blending
(e) 30 minute vacuum after 30 minute of blending
(f) Mix was vacuum cast
(g) Acrylonitrile treated LMH-1

UNCLASSIFIED

TABLE XX

EFFECT OF PROCESSING TECHNIQUES ON SENSITIVITY

UNCLASSIFIED

Mix No.	122 - 128°F Viscosity	Penetrometer - cm	Density g/cc	Comments	Impact (kg-cm)		Friction (rpm)		Spark (joules)		Friction Screw (grit +)		Torque Required for (+) Test on cured (in-lb)
					U[a]	C[b]	U	C	U	C	U	C	
HS-76	17	6.4	1.53	Processed in A. R. C vertical mixer	8	7	3800	5200	.5	.5	Pyrex	Pyrex	150
HS-77	56[c]	8.5	1.46	Processed in Plasto-graph mixer	5	6	3600	3600	.5	.5	Pyrex	Pyrex	125
HS-78	--	6.0	1.51	Repeat of HS-77	5	6	3800	4000	.5	.5	Pyrex	Pyrex	75
HS-79	21	6.0	1.55	Repeat of HS-76	5	5	3800	4600	.5	.5	Pyrex	Pyrex	125
HS-80	21	6.5	1.53	LMH-1 added prior to AP in mixer	5	7	3200	3600	.5	.5	Pyrex	Pyrex	100
HS-81	26	12.0	1.53	ZL-437, LMH-1 added then TMETN, HX-874 and AP	4	6	4000	4600	1	.5	Pyrex	Pyrex	100
HS-82	80[d]	4.7	1.44	Standard process except mixer speed doubled	5	7	4200	4200	1	.5	Pyrex	Pyrex	150
HS-83	29	10.0	1.45	Standard process with N_2 purge; No vacuum	4	6	4600	5000	.5	.5	Pyrex	Pyrex	250

(a) Uncured Results
(b) Cured Results
(c) Viscosity measured at 117°F
(d) Propellant was partially cured at time of viscosity

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(U) Two mixes were made in each type mixer. Mixes HS-76 and 79 were processed in the ARC 2 CV mixer and mixes HS-77 and 78 were processed in the plastograph mixer. It may be noted that the sensitivity test results indicate that the impact sensitivity is apparently not affected by mixer types. The impact sensitivity of the ARC mixes were 5 to 8 kg-cm and the plastograph mixes were 5 and 6 kg-cm (cured and uncured, respectively). Therefore, the ranges of impact sensitivity overlap for the two mixer types. Friction sensitivity tests gave uncured results of 3600 to 3800 rpm; however, the cured friction sensitivity results of the ARC made mixes are 600 to 1200 rpm less sensitive than those mixes made in the plastograph mixer. The improvement in the cured friction sensitivity of those mixes processed in the ARC mixer is attributed to the lesser shear of that mixer. The more shear, the more the solid particles are broken, creating fresh reactive surfaces. The spark sensitivity of these four mixes indicate no differences. The results of the friction screw tester are given as additional information.

(U) (b) Mixing Speed

(U) In consideration of this variable, mix HS-82 is compared to mixes HS-76 and 79 (standards). Mix HS-82 resulted in an impact sensitivity of 5 to 7 kg-cm (uncured and cured, respectively), which is within the range of impact sensitivities of mixes HS-76 and 79. The friction sensitivity of uncured HS-82 is 400 rpm less than the standards; however, this is not considered significant. The cured friction sensitivity of this mix is within the range of the friction sensitivity of the cured standards. Apparently the mixing speed in the range studied does not significantly affect the propellant sensitivity.

(U) It is of interest to note that this mix, with its increased mixing speed, resulted in a short potlife. This is probably due to a slight increase in induced heat from the higher mixing speed.

(U) (c) Type of Atmosphere

(U) Mix HS-83 was made to determine the effect on propellant sensitivity of maintaining a nitrogen purge during mixing. This mix, when compared to the standard mixes (which have vacuum mixing during the latter one-third of mixing time) resulted in a slightly higher viscosity. The impact sensitivity, both uncured and cured, is not significantly different from that of the standards. The friction sensitivity of the uncured propellant is 800 rpm (or 21 percent) less than the standards, although there is apparently no improvement in the cured friction sensitivity.

(U) (d) Order of Addition of Ingredients

(U) Two mixes, shown below, were made in which the order of addition of the ingredients were altered from that of the standard.

(UNCLASSIFIED)

Order of Addition	Standards HS-76 and HS-79	HS-80	HS-81
1	ZL-437	ZL-437	ZL-437
2	TMETN	TMETN	LMH-1
3	HX-874	HX-874	TMETN
4	AP	LMH-1	HX-874
5	LMH-1	AP	AP

(UNCLASSIFIED)

(U) A comparison of mix HS-81 with tne standards (Table XX) shows that no significant changes resulted from this order of addition.

(U) The impact sensitivity of HS-80 is not significantly different from the standards. Friction sensitivity is slightly greater (600 rpm) than the standards (3800 rpm) and cured friction sensitivity is increased (1000 to 1400 rpm).

(U) (3) Formulation Variables

(U) This series of tests was conducted to determine the effects of TMETN and LMH-1 concentrations upon propellant sensitivity.

(U) (a) TMETN Reduction

(U) A limited search for plasticizers to replace or partially replace TMETN was conducted. Plasticizers such as dioctyl adipate (DOA), dioctyl phthalate (DOP), benzyl butyl phthalate (SA-160) and butyl carbitol formal (TP-90B)[3] were investigated as replacements for TMETN. DOA and DOP were determined to be insoluble in ZL-437 and the use of SA-160 resulted in a large loss of theoretical specific impulse. TP-90B was determined to be an effective plasticizer for the binder (ZL-437) and, in addition, did not alter the desired specific impulse of 280 lb-sec/lb to any appreciable extent. The thermochemical calculations conducted with TP-90B are shown in Table XXI.

(U) Several mixes of the standard formulation, with reductions of the TMETN content, were prepared for evaluation. The results of these tests are given in Table XXII. All mixes shown, with the exception of the standard (HS-53) have increased ammonium perchlorate and/or TP-90B concentrations to replace the TMETN. The calculated specific impulse on all test formulations was virtually unchanged from that of the standard.

3. "Reg. U. S. Patent Office"

TABLE XXI

THERMOCHEMICAL CALCULATIONS OF REDUCED TMETN

	HS-53 1 Standard	HS-55 2	HS-56 3	HS-57 4	HS-54 5
LMH-1	25.00	25.00	25.00	25.00	25.00
AP	49.50	54.50	55.50	58.50	53.50
ZL-437	11.50	11.50	11.50	11.50	11.50
TMETN	14.00	7.00	4.00	5.00	10.00
TP-90B		1.00	4.00	5.00	0.0
Density (g/cc)	1.61562	1.63279	1.60497	1.60881	1.63330
I_{sp} (lb-sec/lb)	280.07	280.25	280.47	280.55	279.91

TABLE XXII

REDUCTION OF TMETN

Mix No.	% TMETN	% TP-90B	Viscosity (kp) at 124 - 128°F	Density (g/cc)	Penetrometer (cm)	%Pasted AP(c)	% 6 Micron AP	% 500 Micron AP	I_{sp}	Impact (kg-cm) U(a)	Impact (kg-cm) C(b)	Friction (rpm) U	Friction (rpm) C	Spark (joules) U	Spark (joules) C	Friction Screw (grit) (3 test/grit) U	Friction Screw (grit) (3 test/grit) C	Torque for (+) Cured
Standard HS-53	14	--	17.00	1.556	9.3	24.22	--	25.28	280.1	4	6	2200	1800	0.5	0.5	Pyrex	Pyrex	150
HS-54	10	--	75.00	1.570	4.2	24.22	2.00	27.28	279.9	6	13	2600	2600	0.5	0.5	Pyrex	Pyrex	300
HS-55	7	2	64.00	1.561	6.6	24.22	2.50	27.78	280.2	13	12	3000	3600	0.5	0.5	SiC	Pyrex	200
HS-56	4	4	66.00	1.581	6.8	24.22	2.96	28.32	280.5	13	13	3600	3000	0.5	0.5	(-)All Grits	(-)All Grits	--
HS-57	0	5	72.80	1.557	4.4	24.22	4.45	29.83	280.6	13	16	2400	2600	0.5	1.0	(-)All Grits	Pyrex	100
HS-84	0	9	19.20	1.503	15.0	24.46	2.61	27.43	280.2	12	8	6200	5000	0.5	0.5	Pyrex	Pyrex	275

(a) Uncured Results
(b) Cured Results
(c) Pasted AP was initially 6 micron.

All mixes had a 49/51 ratio of fine/coarse oxidizer.

(U) The impact sensitivity of the uncured propellants resulted in a 2 to 9 kg-cm improvement over the standard (4 kg-cm), while the cured propellants were from 6 to 10 kg-cm less sensitive (6 kg-cm cured). This indicated that the cured propellants are less sensitive to impact than the uncured propellants. It may be seen that when the TMETN content was reduced to 7 percent (mix HS-55), no further improvements, of significance, are realized on impact sensitivity by these tests.

(U) The friction sensitivity also showed improvements of up to 60 percent for uncured propellants, with a range of 2400 to 3600 rpm, as compared to 2200 rpm of the uncured standard. The cured propellants indicated an improvement of up to 100 percent in friction sensitivity, with a range of 2600 to 3600 rpm, compared to 1800 rpm of the cured standard.

(U) Mix HS-57 was made with zero percent TMETN and 5 percent TP-90B. It may be seen that the viscosity was extremely high. The dryness of this mix is a possible reason for its high friction sensivity. Due to this deviation from the trend of sensitivity of the other tests of this series, an additional mix (HS-84) containing a higher plasticizer content (9 percent) and zero percent TMETN was processed and tested. This mix was considerably less viscous than mix HS-57 and the formulation meets the specific impulse requirements of 280.0 lb-sec/lb, or greater. The friction sensitivity of HS-84 is considerably improved in comparison to HS-57 and the other propellants in this series.

(U) The cured impact sensitivity of HS-84 is only one-half (8 kg-cm) that of HS-57 (16 kg-cm); however, this mix is 2 kg-cm less sensitive than the cured standard propellant. The impact sensitivity of the reduced TMETN formulations also shows considerable improvement as the quantity of the energetic plasticizer is reduced. In addition, as the quantity of plasticizer is lowered the viscosity of the systems are generally increased. The degree of sensitivity at each level of TMETN is shown on Figure 14. The values of HS-84 were used for the zero percent TMETN test shown. The uncured propellant sensitivity curve shows friction sensitivity as a function of the TMETN concentration. Although the most improved formulation to friction (HS-84) also has a reduced viscosity, it is believed that the reduction of TMETN is most significant in the friction sensitivity reduction. This is indicated by the fact that HS-84 is no less viscous than the standard formulation. It is also notable that TP-90B is a better plasticizer than TMETN. By comparison, mix HS-54 ,10 percent TMETN and 53.50 percent ammonium perchlorate (LMH-1 content constant at 25 percent) was more viscous than mix HS-84 (9 percent TP-90B and 54.50 percent ammonium perchlorate).

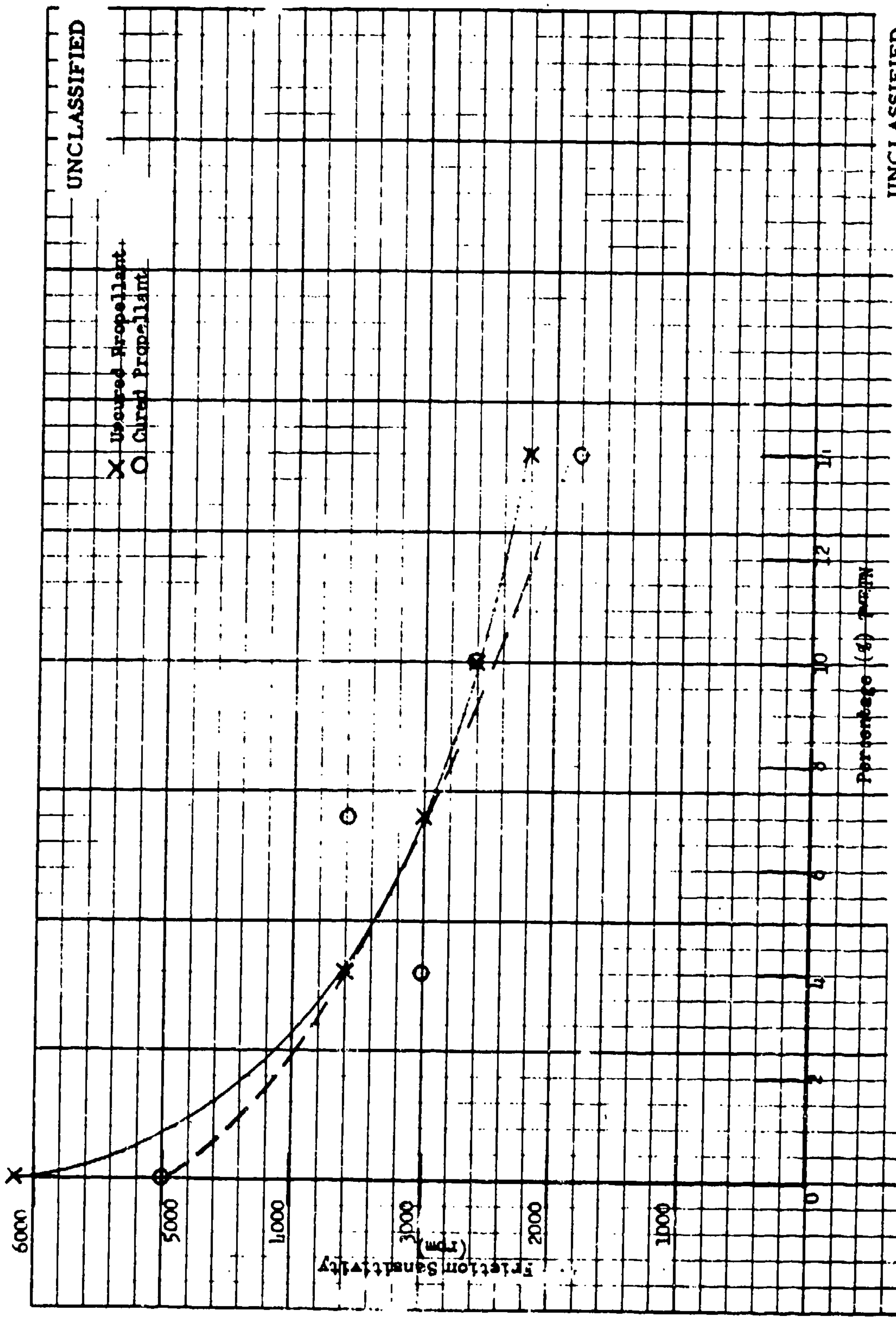

Figure 14. Effect of TMETN Concentration on Propellant Sensitivity to Friction.

(U) The spark (electrostatic discharge) sensitivity is from 0.5 to 1.0 joules, which is in the normal range. The results of the friction screw tester are also shown in Table XXII.

(U) The substitution of TP-90B for TMETN results in a diminished supply of available oxygen in the system inasmuch as 54.29 percent of the TMETN by weight is oxygen and only 31.80 percent of the TP-90B is oxygen. This TMETN reduction would then change the oxygen to fuel (O/F) ratio. The effect of the O/F ratio on the impulse efficiency for high energy propellant systems has been demonstrated by several organizations. The Huntsville Division of Thiokol Chemical Corporation[4] has demonstrated this effect on LMH-1/AP/polyester (ZL-437) systems. The O/F ratio is defined here, and generally, as the number of moles of oxygen available, divided by the amount needed to convert all aluminum and carbon to aluminum oxide (Al_2O_3) and carbon monoxide (CO). Several O/F calculations were computed on formulations with reduced TMETN content. These results are shown in Table XXIII. It may be seen in examples 5 through 8 that the quantity of TP-90B, or any selected "inert" plasticizer substituted for the TMETN, is critical in regard to the O/F ratio and the resultant system efficiency. This factor has to be considered in desensitization approaches in order to maintain the proper efficiency of the 280 lb-sec/lb theoretical specific impulse requirement.

(U) (b) Reduction of LMH-1

(U) Mixes were made and tested with LMH-1 concentrations ranging from 15 to 30 percent in 5 percent increments. In each mix, ammonium perchlorate was adjusted to the LMH-1 percentage in order that solids content of the mix was constant at 74.5 percent by weight. The results of these tests are given in Table XXIV. Figures 15, 16, and 17 show the effect of LMH-1 concentration on viscosity, impact sensitivity, and friction sensitivity. In addition, small mixes with 74.5 percent LMH-1 and no ammonium perchlorate, and 74.5 percent ammonium perchlorate and no LMH-1 were tested. In these tests it was shown that as the concentration of LMH-1 decreases, the viscosity decreases (Figure 15). This is not unexpected since more spherical particles with a smaller volume (higher density) are replacing the cubic LMH-1.

4. Quarterly Technical Summary Report No. 5, High Energy Propellant Evaluation (U), Contract DA-36-034-AMC-0074(Z), 1 April - 30 June 1964, Huntsville Division, Thiokol Chemical Corporation, August 1964 (Report No. 28-64) (Confidential)

TABLE XXIII

OXYGEN TO FUEL RATIO FOR REDUCED TMETN FORMULATIONS

Formulation	1 Standard	2	3	4	5	6	7	8	9
	(Weight, %)								
AP	49.5	55.5	54.5	58.5	54.5	49.5	49.5	52.5	53.5
ZL-437	11.5	11.5	11.5	11.5	11.5	11.5	11.5	11.5	11.5
LMH-1	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
TMETN	14.0	7.0	7.0	0	0	7.0	9.0	6.0	7.0
TP-90B	--	1.0	2.0	5.0	9.0	7.0	5.0	6.0	3.0
I_{sp}	280.07	280.03	280.25	280.58	280.07	280.09	280.33	-	--
Density	1.6156	1.6328	1.6190	1.6008	1.5843	1.5956	1.5707	--	--
O/F	1.1554	1.2122	1.1785	1.1648	1.0430	1.0308	1.0697	1.0032	1.1463

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TABLE XXIV

EFFECT OF DECREASE OF LMH-1 ON SENSITIVITY

Mix No.[a]	Viscosity (kp) at 124 - 128°F	Penetrometer (cm)	% 85 Micron LMH-1	% 6 Micron AP	% 400 Micron AP	Sensitivity Test Results: Impact (kg-cm) U[b]	Impact (kg-cm) C[c]	Friction (rpm) U	Friction (rpm) C	Spark (joules) U	Spark (joules) C	Friction Screw (+) Grit U	Friction Screw (+) Grit C	Torque Cured (in-lb)
HS-64	42	6.4	30.0	21.81	22.69	7	8	3400	2200	0.5	0.5	Pyrex	Pyrex	250
Standard HS-67	19	6.9	25.0	24.26	25.24	4	7	3000	2400	0.5	0.5	Pyrex	Pyrex	100
HS-65	14	7.9	20.0	26.70	27.80	4	7	4600	2400	0.5	0.5	Pyrex	Pyrex	200
HS-66	12	7.9	15.0	29.15	30.35	3	6	6000	6000	0.5	0.1	SiC	Pyrex	200
HS-A[d]	--	--	74.5	0	0	52	--	2000	--	0.5	--	Pyrex	--	--
HS-B[d]	--	--	0	36.50	38.00	10	--	5600	--	0.1	--	(-) All Grits	--	--

(a) Solids percentage held constant.
(b) Uncured Results
(c) Cured Results
(d) Small mixes tested, uncured propellant only.

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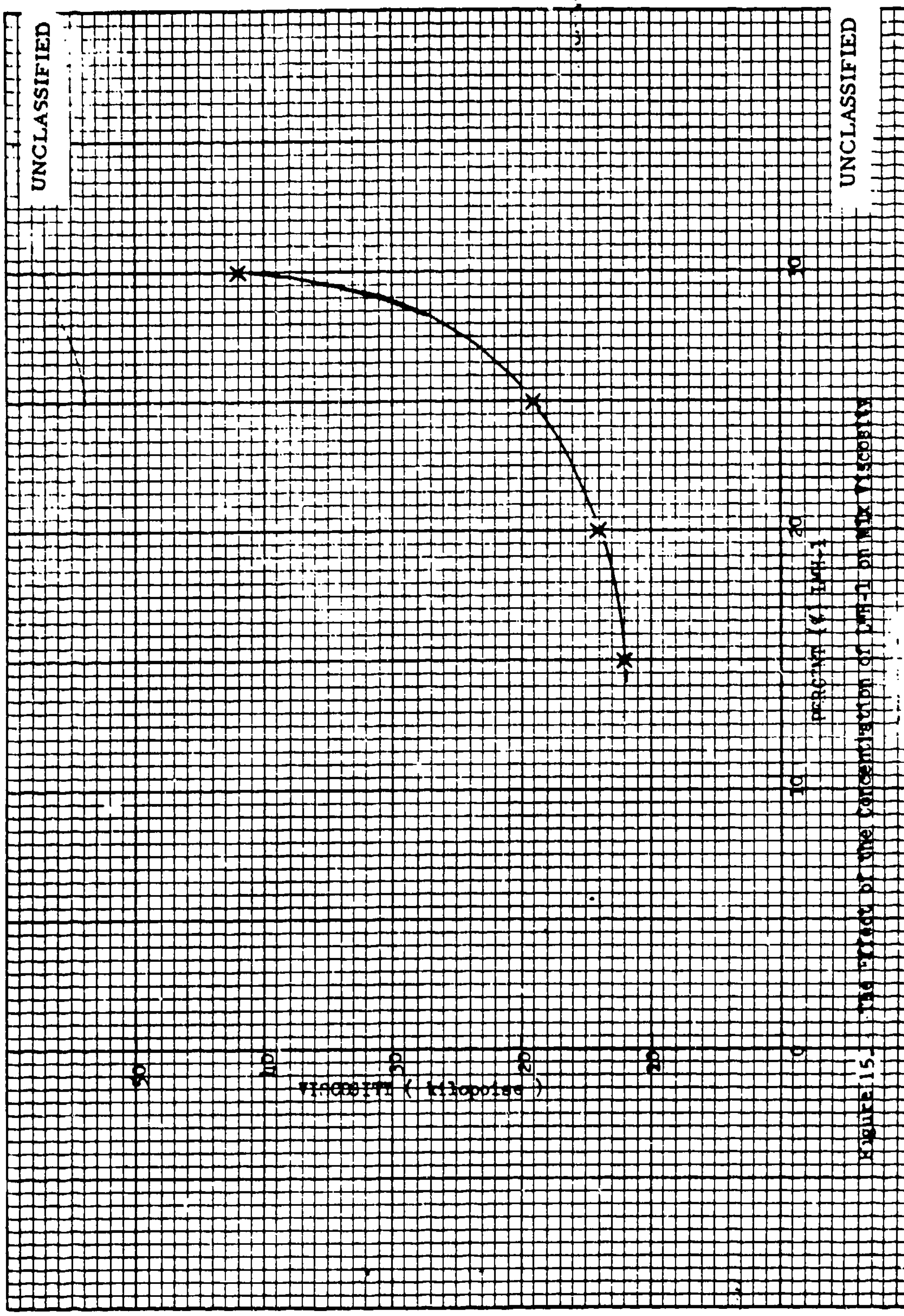

Figure 15. The Effect of the Concentration of LWH-1 on Mix Viscosity

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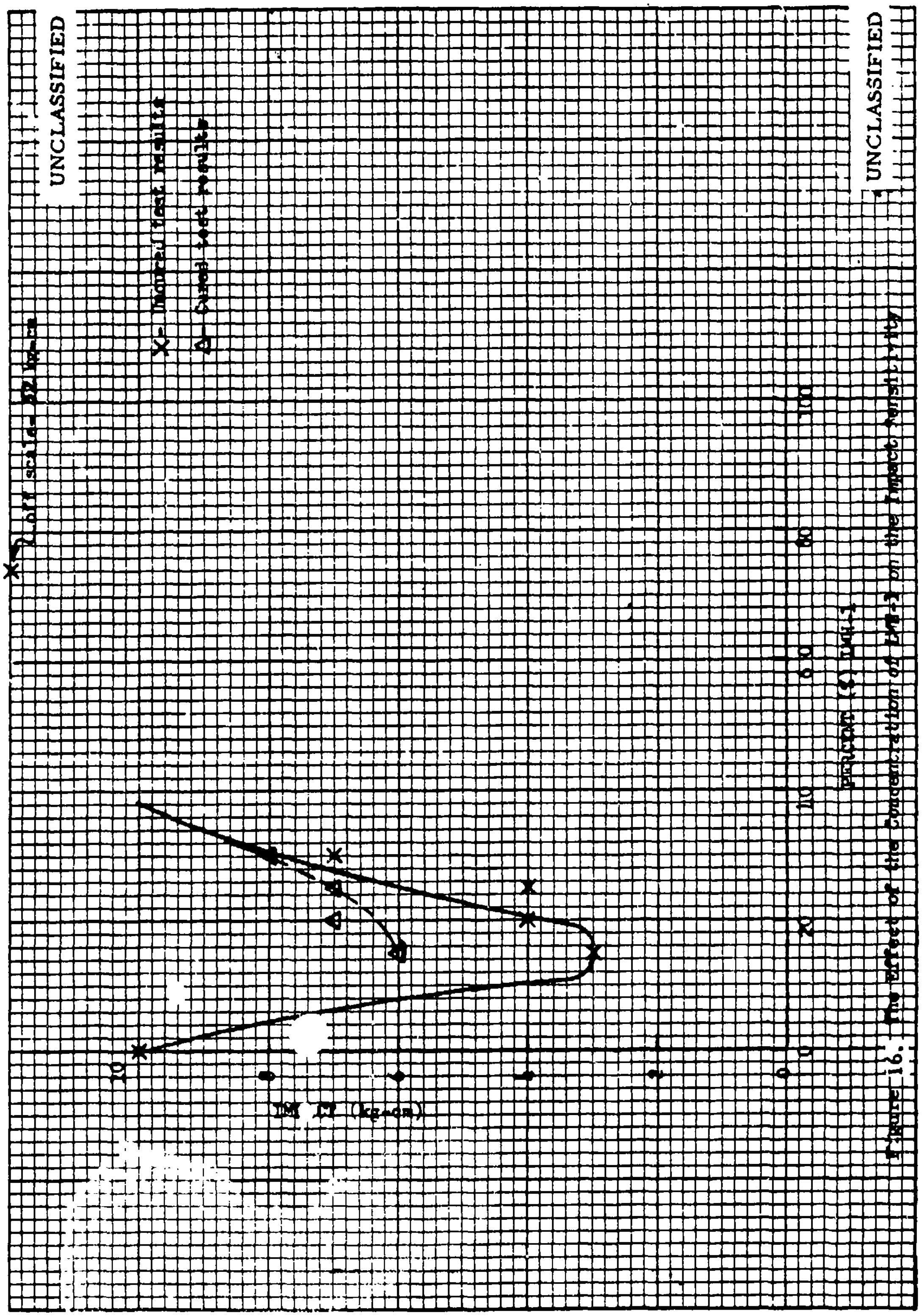

Figure 16. The Effect of the Concentration of LMH-1 on the Impact Sensitivity

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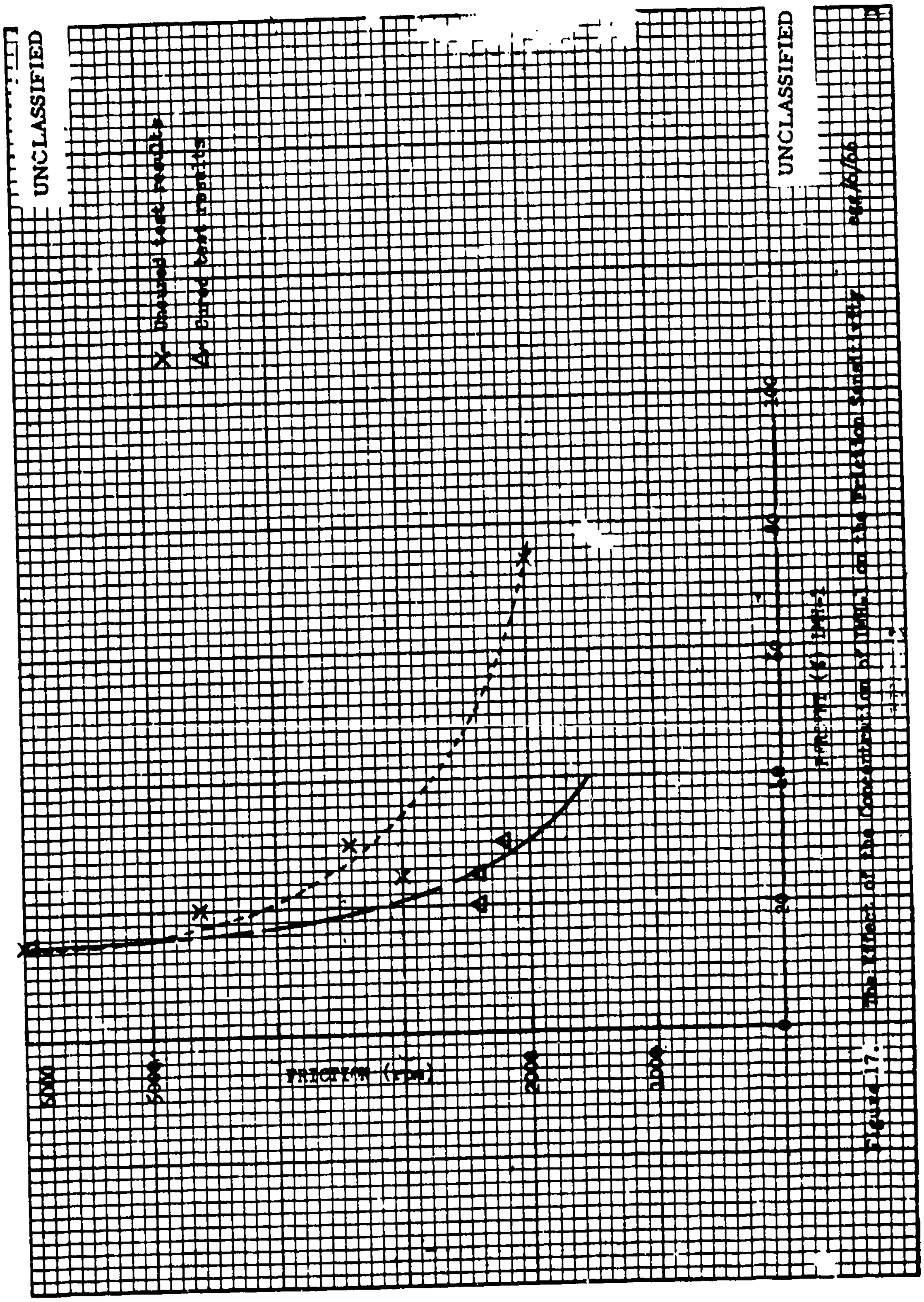

Figure 17. The Effect of the Concentration of [illegible] on the Friction Sensitivity

(U) It may be seen from Table XXIV and Figure 16 that when concentrations of LMH-1 are between 15 and 74.5 percent, the sensitivity to impact decreases as the concentration is increased. Both the uncured and cured results follow this trend, although the cured propellant is slightly less sensitive than the uncured. Mix HS-64, which has the highest concentration of LMH-1, is the least sensitive to impact in both uncured and cured (7 and 8 kg-cm, respectively). Mix HS-66, which has the lowest concentration of LMH-1, is the most sensitive to impact (3 and 6 kg-cm, cured and uncured) of the four mixes. The other mixes are intermediate in impact sensitivities.

(U) In direct opposition to the impact sensitivity, the friction sensitivity (Figure 17) is increased as the concentration of LMH-1 is increased. Again, both uncured and cured follow this trend, with the cured being more sensitive to friction than the uncured at higher concentrations of LMH-1. The cured propellant is more sensitive at the 20, 25 and 30 percent LMH-1 levels than the uncured propellant. The most sensitive is mix HS-64, at 2200 rpm (30 percent LMH-1); the least sensitive is mix HS-66 (15 percent LMH-1), at 6000 rpm.

(U) The tests using the friction screw were all positive with Pyrex, with the exception of the uncured sample of mix HS-66, which was positive with SiC grit.

(U) Two small mixes, HS-A (74.5 percent LMH-1 and no ammonium perchlorate) and HS-B [74.5 percent (49/51 ratio fine/coarse) ammonium perchlorate and no LMH-1] shown in Table XXIV, were made in order to determine the effect of these solids with the binder. The results of these small mixes (uncured) indicate that the ammonium perchlorate in the binder is sensitive to impact, but relatively insensitive to friction. However, the LMH-1 in the binder is sensitive to friction, but relatively insensitive to impact. The testing of the extreme opposites verifies the conclusion that as the concentration of LMH-1 is decreased, the propellant becomes more sensitive to impact but less sensitive to friction within the limits of 15 to 74.5 percent LMH-1.

(U) The spark sensitivity of these mixes were normal (0.5 to 1.0 joule), except in the case of cured mixes HS-66 (0.1 joule) and HS-B (0.1 joule).

(U) (1) Effect of LMH-1 Reduction on Specific Impulse

(U) Reduction of the LMH-1 concentration will significantly reduce the specific impulse values as shown in Table XXV.

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TABLE XXV

I_{sp} CALCULATIONS OF REDUCED LMH-1 MIXES

	Standard	HS-65
LMH-1	25.00	20.00
AP	49.50	54.50
ZL-437	11.50	11.50
TMETN	14.00	14.00
Density (g/cc)	1.6156	1.6390
I_{sp} (lb-sec/lb)	280.07	274.43

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(U) d. Task 3.- Investigation of Chemical Factors on Propellant Sensitivity

(U) The effect of various LMH-1 surface treatments on propellant sensitivity was determined in this task.

(U) (1) Surface Treatments

(U) The two particle sizes of LMH-1 selected for this test series was 32.2 micron (Lot 06104) and 138 micron (Lot 03265). These materials were subjected to surface treatments by acrylonitrile, ether extraction, acetonitrile and pyridine. These surface treatments, with the exception of the ether extraction, were carried out by soaking LMH-1 in the liquid for a 24-hour period. The material was then filtered and dried under vacuum. The ether extraction consisted of refluxing the ether through a Soxhlet Extractor containing the LMH-1 for 72 hours. In addition, the large (138 micron) material was exposed to moist air (60 to 70 percent relative humidity) for 24 hours.

(U) Attempts were made to find a common ratio of ammonium perchlorate particle size that would process with both sizes of LMH-1. In order to expedite the program, the common ratio of ammonium perchlorate for the two sizes was discarded and individual ratios were selected. A ratio of 3/2 of 420/5.7 micron ammonium perchlorate was selected to be used with the small (32.2 micron) particle size mixes, and a ratio of 2/1 of 220/5.7 micron ammonium perchlorate was selected for the large (138 micron) particle size mixes. All propellant ingredients were rigorously dried before using.

(U) The sensitivity tests results of the formulations containing surface treated LMH-1 are compared in Table XXVI with control formulations processed for both of the selected particle sizes, using untreated LMH-1. The control formulations (HS-3 and 8) produced impact sensitivities in the range of 9 to 12 kg-cm for both the uncured and cured propellant tests whereas the test formulations range between 8 to 12 kg-cm, indicating small but insignificant changes in sensitivity.

(U) The friction sensitivity of the control formulations were 1400 to 1600 rpm for the large LMH-1 particle tests and 1400 to 2000 rpm for the small particle LMH-1 formulations; no significant differences are noted with the test formulations when compared to the respective controls. The major change observed was that of the increase of spark sensitivity for the pyridine treated LMH-1 (HS-6 and 11). This increased spark sensitivity may be due to a complex formation between the pyridine and LMH-1 by hydrogen bonding.

(U) It may be concluded from the results of this series of tests that surface treatments of this nature do not result in a reduction of the propellant sensitivity when compared to control propellants HS-3 and 8.

TABLE XXVI

PROPELLANT SENSITIVITY OF (UNCLASSIFIED)

SURFACE TREATED LMH-1 FORMULATIONS

Mix No.	Hydride Surface Treatment	AlH_3 Particle Size (μ)	Impact (kg-cm) E_0 Uncured	Impact (kg-cm) E_0 Cured	Friction (rpm) F_0 Uncured	Friction (rpm) F_0 Cured	Spark (joules) Uncured	Spark (joules) Cured
HS-2	Acrylonitrile	138	10	9	1400	1600	1	1
HS-3	Untreated	138	11	11	1400	1600	2	2
HS-4	Ether Extraction	138	10	10	1600	1800	2	2
HS-5	Acetonitrile	138	9	9	1600	1600	1	2
HS-6	Pyridine	138	8	No Cure	1500	No Cure	0.025	No Cure
HS-7	Humidity	138	8	8	1500	1400	1	1
HS-8	Untreated	32.2	9	12	2000	1400	2	1
HS-9	Acetonitrile	32.2	10	11	2400	1500	1	1
HS-10	Ether Extraction	32.2	11	10	2200	1600	1	0.5
HS-11	Pyridine	32.2	10	12	1600	1800	0.1	0.5
HS-12	Acrylonitrile	32.2	8	9	2400	---	1	0.5

(UNCLASSIFIED)

(U) (2) Anti-Static Agents

(U) Two anti-static agents, STATIKILL[5] and NEUTRO-STAT[6], were tested as coatings to improve the electrostatic discharge (spark) sensitivity of LMH-1 and LMH-1 propellants. Lot 01140, 118 micron magnesium-doped LMH-1, was treated with STATIKILL and NEUTRO-STAT. These treatments were applied by placing the LMH-1 particles in a thin layer and spraying with the anti-static agent. The particles were then dried and the spraying operation repeated. The particles were stirred after spraying to enhance complete coverage. These treated particles were then subjected to the spark test. The results of these tests are shown in Table XXVII. It may be seen that the use of these anti-static agents with this technique did not produce any improvement in the spark sensitivity.

(U) A propellant test of STATIKILL was also conducted. The LMH-1 particles (Lot 02106, 76 micron, magnesium doped) were covered with the STATIKILL solvent solution for 20 hours, vacuum filtered and dried at ambient temperature. The treated LMH-1 was then processed in mix HS-107 and tested. The results of the tests performed utilizing this mix are compared in Table XXVIII with mix 94, which is identical with the exception of the STATIKILL treated LMH-1. These data show that no significant differences in propellant sensitivity occurred in the uncured propellants. The spark sensitivity of both uncured mixes is 0.5 joules, indicating that there is no improvement in the spark sensitivity of LMH-1 propellants due to the use of anti-static coatings.

(U) (3) Bond Strengths

(U) It has been shown that certain cured propellants containing LMH-1 are more sensitive, especially to friction, than the uncured material. It is believed that this is due to oxidizer and/or LMH-1 de-wetting and becoming unbonded from the binder. Tests have shown that simple dry mixtures of oxidizer and binder are extremely sensitive to friction (F_o = 500 to 800 rpm). A possible method of improving the sensitivity of cured propellant would be to improve the adhesion between the binder and the solid particles.

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5. Manufactured by Statikill, Inc. Cleveland, Ohio

6. Manufactured by Simco Company, Landsdale, Pennsylvania.

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TABLE XXVII

RESULTS OF ANTISTATIC AGENTS TESTS

Treatment of LMH-1	Results at 2.0 joules	1.0 joules	0.5 joule	0.1 joule	0.01 joule
No treatment	positive (+)	positive (+)	positive (+)	positive (+)	negative (-)
STATIKILL	positive (+)	positive (+)	positive (+)	positive (+)	negative (-)
NEUTRO-STAT	positive (+)	Positive (+)	positive (+)	positive (+)	negative (-)

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TABLE XXVIII

TREATMENT OF LMH-1 WITH STATKILL (ANTISTATIC) AGENT

Mix No.	Viscosity (kp) at 124 - 130°F	LMH-1 Treatment	Sensitivity Test Results: Impact (kg-cm) Uncured	Friction (rpm) Uncured	Spark (Joules) Uncured	Friction Screw (+) grit Uncured
HS-94	14	None	8	2400	0.5	Pyrex
HS-107	15	STATIKILL	6	2800	0.5	Pyrex

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(a) Evaluation of Bonding Agents as a Means of Improving the Bond Strengths of Binder to Solids

(U) One particular approach to improvement of the binder, ammonium perchlorate bond strength is through the use of bonding agents (alkyloxysilanes and Werner-type chrome complexes), as reported by M. H. Kaufman and J. D. O'Drobinak[7] of the U. S. Naval Ordnance Test Station. In the work conducted, the bonding agents were applied to ammonium perchlorate particles in a water solution.

(U) (b) Volan Coating of Ammonium Perchlorate

(U) Werner-type chrome complexes (Volan's)[8] were received from E. I. du Pont de Nemours & Co., Inc. and the bond strength of unplasticized binder (ZL-437/HX-874) with the chrome complexes to ammonium perchlorate tablets was determined. Several methods of utilizing the chrome complexes were tested and the results are shown below:

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Test No.	Standard Unplasticized Binder (ZL-437/HX-874)	Neat Volan: Added and Mixed With the Standard Binder	Neat Volan: Applied as a Coating to AP Tablet	Neat Volan: Dropped Onto AP Tablet Prior to Standard Binder
1	5.1 psi			
2		5.1 psi		
3			22.3 psi	
4				8.3 psi

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7. Kaufman, M. H., and J. D. O'Drobinak, Improvement of the Oxidizer-Binder Bond in Composite Propellants (U) ICRPG/AIAA Solid Propulsion Conference, Washington, D. C. I p 659 July 1966 (Confidential)

8. Volan (methacrylate chromic chloride) - Trade name for experimental Werner-type chrome complexes supplied by E. I. du Pont de Nemours & Co., Inc.

(U) It may be seen that Test No. 1 (Standard), between ammonium perchlorate and unplasticized binder, without any bonding agent, resulted in a bond strength of 5.1 psi. In Test No. 2 the Volan (8 percent of total binder composition) was added, without solvent, directly to the binder and mixed into it. This method did not improve the bond strength (5.1 psi) over that of the standard.

(U) Test No. 3 simulated the technique reported by Messrs. Kaufman and O'Drobinak, which utilized ammonium perchlorate pressed tablets rather than ammonium perchlorate particles. The "neat" Volan was applied to the ammonium perchlorate tablet as a coating (3 applications). This test resulted in a 22.3 psi bond strength, an increase of 17.2 psi (335 percent).

(U) Test No. 4 was conducted by dropping a single drop of Volan (neat) onto the ammonium perchlorate tablet immediately before the application of the binder to the tablet. This result indicates an improved bond strength (8.3 psi), but not as large an improvement as Test No. 3.

(U) The test results reported are the highest measured values obtained from several measurements of each type test.

(U) Ammonium perchlorate (220 micron) was coated with Volan by a solvent-nonsolvent method. This material was then processed in propellant mixes HS-128 and 143 to determine the effect of the treatment on cured sensitivity. The results of these tests are compared with a standard untreated ammonium perchlorate mix (HS-129) in Table XXIX.

(U) The Volan treated ammonium perchlorate resulted in undercured mixes. Apparently Volan coating interfered with the cure as did complete coating of ammonium perchlorate with ZL-437 (binder) in earlier tests. The uncured impact sensitivities of the treated formulation and untreated formulation are equivalent. A considerable improvement in the cured impact sensitivity of the ammonium perchlorate treated formulations is shown; however, it is believed that the degree of cure of the two propellants is a considerable factor in this difference.

(U) The reported values of the friction sensitivity indicate no significant differences between the untreated and treated ammonium perchlorate formulations. However, it is possible that the degree of cure in mix HS-128 produced a

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TABLE XXIX

EFFECT OF VOLAN ON FRICTION SENSITIVITY

Mix No.	Treatment	Viscosity	Impact (kg-cm) $U^{(a)}$	Impact (kg-cm) $C^{(b)}$	Friction (rpm) U	Friction (rpm) C	Spark (Joules) U	Spark (Joules) C	Friction Screw U	Friction Screw C	Friction Screw lb/inch
HS-129	Standard	"Dry"	11	6	---	2200	0.5	0.5	Pyrex	Pyrex	250
HS-128	Volan	"Dry"	13	14	---	2400	0.5	0.5	Pyrex	Pyrex	100
HS-143	Volan	"Dry"	16	18	4200	2200	0.5	0.5	Pyrex	Pyrex	300

(a). Uncured Results
(b). Cured Results

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more friction sensitive propellant than would have been measured had the propellant properly cured. It has also been determined that Volan, in high concentrations, acts as a cure accelerator for the ZL-437/HX-874/TMETN binder system. This fact then presents the possibility that high concentrations of Volan coating may be of significance in effecting cure. In any event, the Volan coating has not resulted in decreased cured friction sensitivity; however, significant improvements in cured impact sensitivity were recorded.

(U) (c) Volan Coated LMH-1

(U) Tests were conducted to determine the effect of coating LMH-1 with Volan. The "neat" Volan was applied to LMH-1 tablets as a coating (3 applications). This method of application of the Volan is identical to that used for the ammonium perchlorate tests of bond strength with Volan. The results of these tests are shown below:

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Test No.	Standard Binder With Uncoated LMH-1 Bond Strength (psi)	Standard Binder With Volan Coated LMH-1 Bond Strength (psi)
1	29.35[a]	
2		9.4[a]

a. Largest value of 3 tests.

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It may be seen that the standard binder to uncoated LMH-1 has the greater bond strength. The reported values indicate that the application of Volan to the interface between LMH-1 and the ZL-437 binder reduces the bond strength.

(U) 2. Phase II. Sensitivity Improvement

(U) The specific objective of this phase of the program was to employ the factors which were found in Phase I to have a significant effect on LMH-1 propellant sensitivity in order that the optimum insensitivity is achieved. This was to be accomplished within two limiting factors: (1) the propellant was to be a practical, processable formulation, and (2) the performance level of the formulation was to be maintained at 280 lb-sec/lb theoretical specific impulse. Generally, the approaches used in Phase II were:

(U) 1. Use of small particle size ammonium perchlorate.

(U) 2. Partial or complete reduction of TMETN content.

(U) 3. Obtain optimum wetting of solids with the binder through the use of optimum solids packing, wetting agents, better plasticizers, or pasting of the binder and solids.

(U) 4. Coating of the solids with binder ingredients.

(U) 5. Partial substitution of RDX, HMX, or Teflon for ammonium perchlorate.

Twenty-five percent LMH-1, with a particle size of 75 micron or greater, was standard for all formulations in Phase II.

(U) a. Process Studies

(U) Initial propellant studies were conducted to determine the process limitations or effects imposed by the use of pasted ammonium perchlorate or LMH-1. Limited tests were also conducted in an attempt to resolve gassing problems associated with pasting of LMH-1 and improper cures resulting from pasted or coated ammonium perchlorate formulations. A secondary purpose of these tests was to determine the degree of process improvement obtained with pasted solids, in order that higher concentrations of fine ammonium perchlorate particles might be utilized.

(U) (1) Milled LMH-1

(U) Magnesium-doped LMH-1 was mixed with TP-90B plasticizer and ZL-437 polymer. The composition of this blend is as follows.

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	Weight, %
TP-90B	9.395
ZL-437	26.605
LMH-1 (Lot 02106 mg-doped)	64.000

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A semi-fluid mixture resulted, enabling all of the LMH-1 required in the standard formulation to be added. Propellants containing this pasted LMH-1 were prepared and tested as indicated in Table XXX.

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TABLE XXX

PASTED LMH-1 WITH PLASTICIZER

Mix No.	Viscosity KP 124 - 130°F	Density g/cc g/cc	% 6 micron AP	% 400 micron AP	Pasted LMH-1 No.	% TP90B/%TMETN	Sensitivity Test Results: Impact (kg-cm) U[b]	Impact (kg-cm) C[c]	Friction (rpm) U	Friction (rpm) C	Spark (joules) U	Spark (joules) C	Friction Screw (+) Grit 3 Test/Grit U	Friction Screw (+) Grit 3 Test/Grit C	Torque for (+) Test C in-lb
HS-88	4	1.386	24.26	25.24	IV[a]	7/7	8	9	4600	4600	0.1	0.5	Pyrex	Pyrex	150
HS-89	6.4	1.413	33.00	16.5	IV	9/5	10	12	5600	4200	0.5	0.5	Pyrex	Pyrex	200
HS-90	9.6	1.388	39.6	9.9	IV	9/5	12	10	6000	4000	0.5	0.5	Pyrex	(-) all Grits	

a. Paste Blen No. IV: LMH-1 pasted in ZL-437 and TP-90B, with 64 percent being LMH-1, 26.59 percent ZL-437 and 9.395 percent was TP-90B.

b Uncured Results

c. Cured Results

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(U) It can be seen from the sensitivity test results of these mixes that as the concentration of fine ammonium perchlorate increases, the impact sensitivity decreases and the uncured friction sensitivity decreases. However, as the concentration of fine ammonium perchlorate is increased, the propellant viscosity is increased and the cured friction sensitivity increases (becomes more sensitive to friction than the uncured propellant).

(U) Microscopic examination of mixes HS-88, 89 and 90 revealed distinct gassing voids. It may also be noted from Table XXX that the densities of these mixes are significantly changed from the standard measured density of 1.577 g/cc. It is concluded, therefore, that the magnesium-doped LMH-1 does not reduce or eliminate the gassing of pasted LMH-1.

(U) (a) Process Improvement With A High Concentration Of Fine Ammonium Perchlorate Particles

(U) A high concentration of fine ammonium perchlorate particles was successfully incorporated in the formulation by use of pasted LMH-1. Mix HS-90 of Table XXX, which was prepared with 80 percent of the total ammonium perchlorate being the fine particle size, showed an end-of-mix viscosity of 9.6 kilopoise and produced an improved impact sensitivity. The viscosities of mixes HS-88 (49 percent fine ammonium perchlorate) and HS-89 (66.666 percent fine ammonium perchlorate) were 4.0 and 6.4 kilopoise, respectively. Viscosity is compared to the concentration of fine ammonium perchlorate particles for this series of mixes on Figure 18.

(U) These data show that this processing technique offers a method of incorporating high concentrations of fine ammonium perchlorate, if the associated problem of the gassing of pasted LMH-1 can be eliminated. This problem is created by exposing fresh surfaces of LMH-1. Since this pasting technique affords a method of incorporating high concentrations of LMH-1 and fine ammonium perchlorate and, is therefore, a means of improving the impact sensitivity, a method of reducing or eliminating the gassing problem is highly desirable.

(U) In an attempt to minimize or eliminate the gassing of pasted LMH-1, the composition shown below was prepared and placed in a vacuum oven for 5 days at 100°F.

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	Weight, %
TP-90B	5.350
ZL-437	27.769
LMH-1, Lot 02106	66.881

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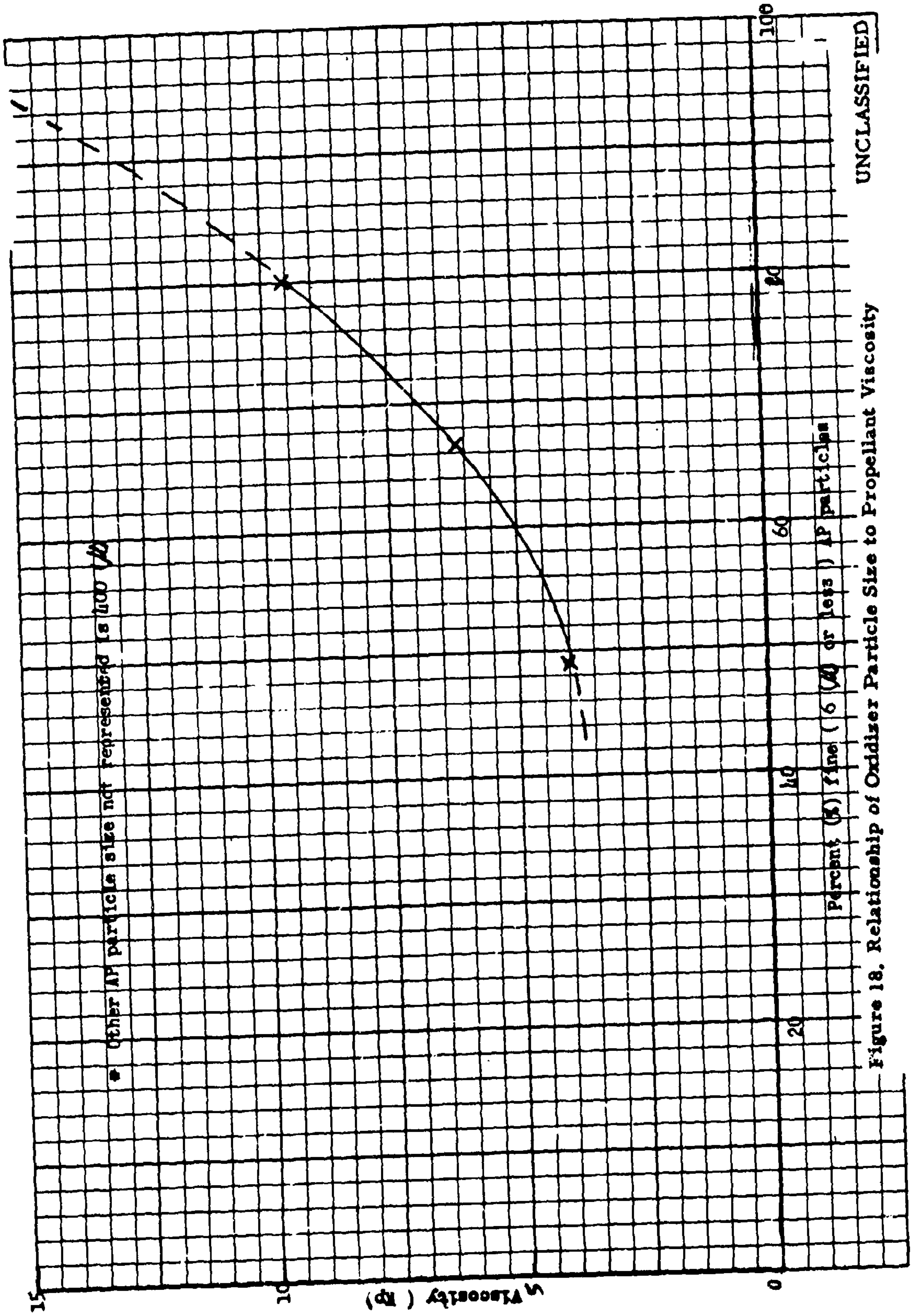

Figure 18. Relationship of Oxidizer Particle Size to Propellant Viscosity

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This bleud was then used in mix HS-108 to determine if this treatment has any effect on the propellant gassing. The results of this test and mix HS-88 are given in Table XXXI. The measured density of mix HS-108 is within the normal range of measured densities for propellants made without pasted LMH-1 and shows considerable reduction in propellant porosity. The normal range is 1.51 to 1.60 g/cc, with the average measured density being 1.577 g/cc. This density is 0.134 g/cc, or 9.7 percent, higher than mix HS-88. On the basis of these density measurements, it is indicated that the vacuum oven treatment decreased the amount of gassing during propellant cure. However, microscopic examination of mix HS-108 revealed some gassing voids as were found in mix HS-88. The lower concentration of TMETN plasticizer of mix HS-88 gave generally less sensitive propellant than mix HS-108.

(U) (2) Pasted Ammonium Perchlorate

(U). Ammonium perchlorate was pasted with a mixture of binder (ZL-437) and plasticizer (TP-90B). The formulation of this blend, which was used in the standard formulation, is shown below.

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	Weight, %
TP-90B	8.16
ZL-437	18.14
AP (6 micron)	73.70

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The use of this mixture allowed 84.99 percent of the total ammonium perchlorate to be added as fine ($<$ 6 micron) particle pasted material.

(U) As shown on Table XXXII , the use of all fine (6 micron or less) ammonium perchlorate particles (HS-92A) resulted in a mix viscosity of 20 kilopoise or less. This processing technique is an effective means of utilizing a high concentration of fine ammonium perchlorate particles; however, as previously reported, the use of coated or pasted ammonium perchlorate does not allow normal cures of the standard formulation. Mixes HS-91, 92, and 92A failed to cure. Methods of eliminating this problem include using excess curing agent and/or cure catalysts.

TABLE XXXI

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EFFECT OF VACUUM OVEN ON PASTED LMH-1

Mix No.	Viscosity (124 - 130°F) K P	Density g/cc	Percent TP-90B	Percent TMETN	Sensitivity Results: Impact (kg-cm) U (b)	Impact (kg-cm) C (c)	Friction (rpm) U	Friction (rpm) C	Spark (Joules) U	Spark (Joules) C	Friction Screw (+) Test 3 Test/grit U	Friction Screw (+) Test 3 Test/grit C	Torque for (+) Test cured in/lb
HS-88[a]	4	1,386	5	7	8	9	4600	4600	0.1	0.5	Pyrex	Pyrex	150
HS-108[a]	38	1,520	2	12	3	11	3000	2600	0.1	0.1	Pyrex	Pyrex	250

a. Formulation is same for both mixes with the exception of plasticizers and LMH-1 paste blend

b. Uncured results

c. Cured results

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TABLE XXXII

PASTED AMMONIUM PERCHLORATE WITH PLASTICIZER

Mix No.	Viscosity (kp) at 124 - 130°F	LMH-1 Particle Size	% 400 micron AP	% Pasted AP	Sensitivity Test Results: Impact (kg-cm)	Friction (rpm)	Spark (joules)	Friction Screw (+) Grit
					Uncured	Uncured	Uncured	Uncured
HS-91	9.6	76	7.43	42.07	9	6000	0.5	Pyrex
HS-92	8.0	118	7.43	42.07	5	6600	0.5	Pyrex
HS-92A[b]	Est. <20	118	7.43[a]	42.07	9	3600	0.1	Pyrex

a. 7.43 Percent 6 micron ammonium perchlorate added as untreated.

b. Viscosity not measured due to size of mix.

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(U) The results of the sensitivity tests of the uncured propellant (Table XXXII) indicate the pasted ammonium perchlorate was not as effective in reducing propellant sensitivity as the coating or pasting of LMH-1.

(U) A series of tests were initiated to determine the extent of adjustments necessary for proper cures when pasted ammonium perchlorate is used. The following blend was prepared for these tests.

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	Weight, %
AP (6 microm)	73.507
ZL-437	20.553
TP-90B	5.940

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Five 5-gram mixes utilizing varying curing agent and catalyst concentrations were prepared with this blend. These mixes and their resultant penetrometer measurements are given in the following table.

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Mix No.	A	B	C	D	E
LMH-1 (02106) -gms	1.250	1.250	1.250	1.250	1.250
Pasted AP - gms	2.525	2.525	2.525	2.525	2.525
AP (6 micron) - gms	0.619	0.619	0.619	0.619	0.619
TMETN - gms	0.550	0.550	0.550	0.550	0.550
HX-874 - gms	0.056	0.050	0.060	0.056	0.056
FeAA - gms	--	--	--	0.025	0.075
Penetrometer (mm/sec)					
24 hrs	--	--	22.0	19.6	3.85
48 hrs	26.0	19.6	16.0	5.0	1.07
72 hrs	26.0	18.1	22.0	11.2	1.15
96 hrs	27.0	26.4	18.0	5.2	1.20
Comments	soft cure after 8 days	soft after 8 days	fair cure after 7 days	good cure after 7 days	hard cure after 7 days

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(U) Mix A is the standard formulation, in which 15.00 percent of the total ammonium perchlorate was untreated. This mix had a soft cure after 48 hours and the cure did not significantly improve within 8 days. Mix B was made with less curing agent (HX-874), therefore increasing the acid/imine cure ratio. The cure characteristics of this mix are not significantly different from Mix A. Mix C was made with excess curing agent. This mix attained an improved state of cure in 7 days. Mix D is the standard formulation with ferric acetylacetonate (FeAA) added (0.50 percent) as the cure catalyst. The cure of this mix is rated as good after 4 days. In Mix E, 1.50 percent of FeAA was used as the cure catalyst. This mix cured in less than 2 days to a low strength propellant.

(U) Impact sensitivities were measured on cured mixes C, D and E. No other sensitivity tests were conducted on these propellants due to the limited quantity of the propellant available. Mix C was the least sensitive to impact with 16 kg-cm, mix D measured 12 kg-cm, and mix E measured 10 kg-cm.

(U) This series of mixes illustrates the concept of using a higher imine/acid cure ratio, or the use of cure catalyst, such as FeAA, to obtain cures with pasted or coated ammonium perchlorate.

(U) b. <u>Task 1. Investigation of Surface Treatments and Coatings</u>

(U) It was determined in Phase I of this program that surface treatments did not affect the sensitivity of LMH-1 propellants, therefore, this variable was eliminated from consideration in the Phase II sensitivity improvement investigation. The investigation of solid coatings had, however, resulted in significant decreases in propellant sensitivity. In the Phase II investigation, solid coatings of four different concentrations were studied to determine the effect of coating concentration on propellant sensitivity.

(U) (1) <u>LMH-1 Coating Concentration</u>

(U) Lot 02106 LMH-1 (magnesium-doped, 76 micron) was coated with 2, 3, 4 and 5 percent of ZL-437/HX-874 and ZL-327 alone. The coating was accomplished by the solvent-nonsolvent technique. The ZL-437/HX-874 coating (same ratio as used in standard formulation) was cured in place on the LMH-1 in a 100°F oven for 5 days. These two coatings of LMH-1 were then processed in the standard formulation, using the standard process, with constant materials. The results of these propellant mixes and tests are shown in Tables XXXIII and XXXIV.

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TABLE XXXIII

ZL-437/HX-874 COATED LMH-1

Mix No.	Viscosity KP 124 - 130 °F	Density g/cc	Percent of ZL-437 & HX-874 Coating	Sensitivity Test Results: Impact (kg-cm)		Friction (rpm)		Spark (joules)		Friction Screw (+) Grit 3 Test/Grit		Torque For (+) Test
				U[a]	C[b]	U	C	U	C	U	C	C in-lb
Standard HS-94	14.4	1.534	0	8	10	2400	3000	0.5	0.5	Pyrex	Pyrex	250
HS-99	16.0	1.560	2	7	5	4200	4000	0.5	0.5	Pyrex	Pyrex	100
HS-100	15.2	1.531	3	5	5	3000	4000	0.5	0.5	Pyrex	Pyrex	200
HS-101	15.1	1.543	4	7	5	3200	4600	0.5	0.5	Pyrex	Pyrex	100
HS-102	14.6	1.491	5	7	6	3600	4600	0.5	0.5	Pyrex	Pyrex	50

a. Uncured Results

b. Cured Results

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TABLE XXXIV

ZL-437 COATED LMH-1

Mix No.	Viscosity KP 124 - 130 °F	Density g/cc	Percent ZL-437 Coating on LMH-1	Sensitivity Test Results: Impact (kg-cm)		Friction (rpm)		Spark (joules)		Friction Screw (+) Grit 3 Test/Grit		Torque For (+) Test
				U[b]	C[c]	U	C	U	C	U	C	C in-lb
Standard HS-94	14.4	1.534	0	8	10	2400	3000	0.5	0.5	Pyrex	Pyrex	250
HS-95	16.0	1.549	2	7	8	4200	4000	0.5	0.5	SIC	Pyrex	250
HS-96[a]	8.0		3	7	No Cure	3600		0.5		Pyrex		
HS-97	10.4	1.495	4	6	5	3000	4000	0.5	0.5	Pyrex	Pyrex	250
HS-98	16.8	1.560	5	7	6	3800	3800	0.5	0.5	Pyrex	Pyrex	back-off

a. Failed to cure.

b. Uncured Results

c. Cured Results

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(U) (a) ZL-437/HX-874 Coated LMH-1

(U) The results of the ZL-437/HX-874 coating are evaluated in Table XXXIII. Mix HS-94, the standard mix for this series of tests, contained no coated solids. There was no improvement in either uncured or cured impact sensitivity as the coating concentration was increased. There was no significant difference between the uncured impact sensitivity of the standard and the 4 test mixes; however, a decrease of 4 to 5 kg-cm is shown in the values of the 4 cured test mixes as compared to the standard. It is also noted that the viscosities of these mixes were equivalent.

(U) The friction sensitivity results of the 4 test mixes indicated no improvement in the uncured propellant as a result of an increased coating. In the cured propellant, the values obtained indicated slight improvement as a result of a higher coating concentration; however, this was not considered a significant decrease. A comparison of the test mixes to the standard mix indicates that improvements of 800 to 1600 rpm were generally realized in the friction sensitivity of both the uncured and cured propellants.

(U) (b) ZL-437 Coated LMH-1

(U) The results of the tests with ZL-437 coated LMH-1 are shown in Table XXXIV. Mix HS-94 is again given as the standard. Mixes HS-95 through 98 were coated with 2, 3, 4 and 5 percent of the binder (ZL-437), respectively. The results of this series of tests are very similar to those of the ZL-437/HX-874 coating tests. No improvement was shown in impact or friction sensitivity, in either the uncured or cured propellants, as a result of the increased coating of LMH-1. However, as was the case with the ZL-437/HX-874 coating, an increase in cured propellant impact sensitivity occurred with the coated LMH-1 when compared to the standard. The friction sensitivity of the ZL-437 coated LMH-1 was generally improved over the standard in both the uncured and cured friction sensitivity. The range of improvement was from 600 to 1800 rpm for uncured propellant and from 800 to 1000 rpm for the cured propellant.

(U) (2) Ammonium Perchlorate Coating Concentration

(U) The investigation of ammonium perchlorate coating was conducted with ZL-437/HX-874. The coating was applied by a solvent-nonsolvent technique and then cured on the particle. In this series of tests, mix HS-94 was again used as the standard. The results are given in Table XXXV.

(U) The uncured or cured impact sensitivity is not significantly changed due to the increased coating of the ammonium perchlorate particle. The impact sensitivity of the mixes containing coated oxidizer is from 4 to 5 kg-cm for the uncured propellant and, 6 to 10 kg-cm for the cured propellant. The impact

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TABLE XXXV

ZL-437/HX-874 COATED AMMONIUM PERCHLORATE

Mix No.	Viscosity KP 124 - 130 °F	Density g/cc	Coating ZL-437/HX-874 (%)	Sensitivity Test Results: Impact (kg-cm)		Friction (rpm)		Spark (joules)		Friction Screw (+) Grit 3 Test/Grit		Torque For (+) Test Cured
				U[a]	C[b]	U	C	U	C	U	C	in-lb
Standard HS-94	14.4	1.534	0	8	10	2400	3000	0.5	0.5	Pyrex	Pyrex	250
HS-103	12.8	1.546	2	5	8	3600	3800	0.5	0.5	Pyrex	Pyrex	100
HS-104	11.2	1.496	3	5	8	3400	1800	0.5	0.5	Pyrex	Pyrex	200
HS-105	8.0	1.48	4	4	6	2600	2600	0.5	0.5	Pyrex	Pyrex	250
HS-106	11.2	1.538	5	5	10	2000	2600	0.5	0.5	Pyrex	Pyrex	250

(a) Uncured Results
(b) Cured Results

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sensitivity, as compared to the standard, is 3 kg-cm lower in the uncured propellant and slightly more sensitive, to no change, in the cured propellant.

(U) The friction sensitivity data indicates that as the coating percentage increases, the friction sensitivity increases. This trend is depicted more clearly for the uncured propellant than for the cured propellant. This could be the result of more intimate contact between ammonium perchlorate and ZL-437. It had been previously determined that mixtures of ammonium perchlorate (84.18 percent) and TMETN (15.82 percent) gave a friction sensitivity of 6800 rpm and an impact sensitivity of 195 kg-cm, while a mixture of ammonium perchlorate (86.63 percent) and ZL-437/HX-874 (13.37 percent) gave a friction sensitivity of 4600 rpm and an impact sensitivity of 240 kg-cm. Furthermore, a similar test of LMH-1 and ZL-437/HX-874 (13.37 percent) resulted in a friction sensitivity of >7000 rpm and an impact sensitivity of >250 kg-cm.

(U) From these and small scale tests, it is indicated that when a fuel (such as the binder) and an oxidizer (ammonium perchlorate) are in intimate contact, sensitivity to friction is increased. Also, when two fuels (such as LMH-1 and binder) are in intimate contact, the sensitivity to both impact and friction is reduced. In this system the oxidizer may either be ammonium perchlorate or TMETN and the fuel may be the polyester binder ZL-437 or LMH-1. Various degrees of sensitivity result, depending upon the oxidizer or fuel energy of the two materials in intimate contact.

(U) c. Task 2 - Interrelationship Among Propellant Variables

(U) The purpose of this task was to improve propellant sensitivity after having, in Phase I, identified the variables that affected sensitivity. Experimental work conducted under this task was directed toward establishing the interrelationship among the variables, and combining these variables to minimize sensitivity. The variables that had demonstrated improvements in propellant sensitivity, and which were selected for use in the factorial experiments conducted, are shown below:

1. Increased ZL-437 content
2. Decreased TMETN concentration
3. Pasting of 45 percent of oxidizer (ammonium perchlorate) in ZL-437
4. Coating of LMH-1 with ZL-437 (3 percent)
5. Substitution of RDX (10 percent) for ammonium perchlorate content.

(U) Three series of mixes were prepared and tested. All mixes had a constant 74.5 percent by weight solids. The first series of mixes combined 2 of the above variables. The more promising techniques of the Series I mixes were combined as 3-variable formulations in Series II. Series III formulations were a combination of the results of Series I and II to give the most insensitive, processable mix, taking into consideration theoretical impulse and O/F ratio.

(U) (1) Series I (2 Variable) Formulations

(U) The propellant composition, theoretical specific impulse, density and O/F ratio of the Series I formulations are shown in Table XXXVI, and are compared to a standard mix (HS-112, Code 6). The mixes are coded to identify variables incorporated; i.e., mix HS-115 is coded 613 [standard formulation (6) with increased ZL-437 content (1) and 45 percent of the ammonium perchlorate premilled in ZL-437 (3)].

(U) The test results of the Series I formulations (see Table XXXII) indicate an improvement in uncured impact sensitivity. The sensitivity test results for mixes HS-114, 118, 119 and 120 show a 65 to 100 percent decrease in uncured impact sensitivity when compared to the standard. One variable was common in these formulations; decreased TMETN content.

(U) The cured impact sensitivity test results of mixes HS-117 and 122 indicate decreased sensitivity. The sensitivity variables combined in these formulations are shown below.

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Mix HS-117 (E_o = 12 kg-cm)

Increased binder
Substitution of RDX for ammonium perchlorate

Mix HS-122 (E_o = 10 kg-cm)

Pasted ammonium perchlorate
Substitution of RDX for ammonium perchlorate

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TABLE XXXVI

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SERIES 1 FORMULATIONS AND PROPERTIES OF THE INVESTIGATION OF SENSITIVITY VARIABLES

Mix No.	Mix Code	% AP	% ZL-437	% TMETN	% TP-90B	% RDX	% LMH-1	Theoretical I_{sp} lb-sec/lb	Density g/cc	O/F Ratio
HS-112	6	49.50	11.50	14.00	---	---	25.00	280.07	1.6156	1.172
HS-113	61	49.50	12.50	13.00	---	---	25.00	278.63	1.6113	1.153
HS-114	612	49.50	12.50	8.00	5.00	---	25.00	278.12	1.5666	1.059
HS-115	613	49.50	12.50	13.00	---	---	25.00	278.63	1.6113	1.153
HS-116	614	49.50	12.50	13.00	---	---	25.00	278.63	1.6113	1.153
HS-117	615	39.50	12.50	13.00	---	10.00	25.00	278.83	1.6017	1.048
HS-118	623	49.50	11.50	9.00	5.00	---	25.00	279.26	1.5707	1.076
HS-119	624	49.50	11.50	9.00	5.00	---	25.00	279.26	1.5707	1.076
HS-120	625	39.50	11.50	9.00	5.00	10.00	25.00	278.51	1.5616	0.992
HS-121	634	49.50	11.50	14.00	---	---	25.00	280.07	1.6156	1.172
HS-122	635	39.50	11.50	14.00	---	10.00	25.00	280.80	1.6060	1.069
HS-123	645	39.50	11.50	14.00	---	10.00	25.00	280.80	1.6060	1.069

Key to Mix Code:

1. Increased ZL-437 Content
2. Decreased TMETN Concentration
3. 45 Percent of Oxidizer (AP) was pasted in ZL-437
4. Coated LMH-1 with ZL-437 (3%)
5. RDX Substitution
6. Standard Formulation

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TABLE XXXVII

SENSITIVITY RESULTS OF SERIES I, TASK 2, PHASE II FORMULATIONS

Mix No.	Mix Code	Impact Sensitivity (kg-cm) U[a]	Impact Sensitivity (kg-cm) C[b]	Friction Sensitivity (rpm) C	Spark Sensitivity (joules) U	Spark Sensitivity (joules) C	Friction Screw U (+) Grit	Friction Screw U Lb/In	Friction Screw C (+) Grit	Friction Screw C Lb/In	Viscosity at 124 (kp)
HS-112	6	3	7	2600	1.0	1.0	Pyrex	150	Pyrex	150	12
HS-113	61	3	8	3600	1.0	0.5	Pyrex	50	Pyrex	Back-Off	14
HS-114	612	6	5	3600	1.0	0.5	Pyrex	75	Pyrex	300	4
HS-115	613	3	6	3400	1.0	0.5	Pyrex	300	Pyrex	250	24
HS-116	614	3	8	3200	0.5	0.5	Pyrex	250	Pyrex	225	16
HS-117	615	4	12	2600	0.5	1.0	Pyrex	225	Pyrex	Back-Off	18
HS-118	623	5	7	3200	0.5	1.0	Pyrex	250	Pyrex	250	2
HS-119	624	5	7	4200	0.5	1.0	Pyrex	250	Pyrex	250	4
HS-120	625	6	7	3600	0.5	0.5	Neg. (-)	--	Pyrex	Back-Off	4
HS-121	634	3	7	3400	0.5	0.5	Pyrex	Back-Off	Pyrex	150	8
HS-122	635	2	10	4200	0.5	0.5	Pyrex	100	Pyrex	200	8
HS-123	645	4	7	4000	1.0	1.0	Pyrex	200	Pyrex	150	12

a. Uncured Results
b. Cured Results

Key to Mix Code.
1. Increased ZL-437 Content
2. Decreased TMETN Content
3. 45 % of Total Oxidizer (AP) Prepasted in ZL-437
4. Coated LMH-1 with 3% (LMH-1 wt.) ZL-437
5. RDX Substitution
6. Standard

The common variable used in these two mixes was the substitution of RDX for ammonium perchlorate. Other propellants containing RDX and reduced TMETN (HS-120) and coated LMH-1 (HS-123) did not have improved impact sensitivity. The cured impact sensitivity improvement of mixes HS-117 and 112 is also dependant upon factors other than the substitution of RDX.

(U) The uncured friction sensitivity, as measured with the friction screw tester [9], indicates mix HS-120, which included as variables the reduction of TMETN content and the substitution of RDX for ammonium perchlorate content, to be superior. It had been concluded from the investigations conducted during Phase I that both of these variables, individually, had shown significant effects on friction sensitivity.

(U) The cured friction sensitivity is improved by at least 800 rpm in 8 of the 11 tests conducted. Three mixes (HS-119, 122 and 123), which included the common variable of a coated solid, show an improvement of 1400 rpm (54 percent) when compared to the standard. The solid was coated by either the solvent-nonsolvent method or pasting. All variables, with the exception of increased binder, were utilized during the processing of these 3 mixes. It may be concluded, therefore, that the use of any of the variables, with the exception of increased binder, gives some improvement in cured friction sensitivity. The electrostatic discharge sensitivity (spark) was not affected by any of the variables of this series.

(U) Mixes processed during the Phase I studies indicated that when the oxidizer was completely coated, either by pasting or solvent-nonsolvent coating, the propellant cure was inhibited. Since the SEries I mixes showed satisfactory propellant cure, propellant mixes were prepared incorporating a wetting agent together with coated (or pasted) ammonium perchlorate. These mixes were made to determine the effect of a combination of wetting agents and pasted oxidizer on propellant cure, processing and sensitivity. The standard mix in these tests was HS-114 (see Table XXXVIII), which incorporated an increased binder content and reduced TMETN content. The wetting agents used in the test mixes were Armeen SZ, Armeen Z and G-2684. The mixes processed well and proper cures were obtained.

(U) The sensitivity test results indicated that an improvement in both impact and friction sensitivity results with the use of wetting agents. Mix HS-126 (G-2684 wetting agent) is the least sensitive to impact, both uncured and cured (8 and 9 kg-cm, respectively).

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9. The friction screw tester was utilized for the uncured friction tests of these mixes due to damage of the rotating friction tester.

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TABLE XXXIII

EFFECT OF WETTING AGENTS ON SENSITIVITY

Mix No.	Mix Code	Impact Sensitivity (kg-cm)		Friction Sensitivity (rpm)	Spark Sensitivity (joules)		Friction Screw				Viscosity at 124 - 129°F (kp)
							U		C		
		U[a]	C[b]	C	U	C	(+) Grit	Lb/In	(+) Grit	Lb/In	
HS-114	612	6	5	3600	1.0	0.5	Pyrex	75	Pyrex	300	4
HS-124	612 with Armeen (SZ)	5	8	4600	0.5	1.0	Pyrex	150	Pyrex	275	4
HS-125	612 with Armeen (Z)	8	8	3400	0.5	1.0	Pyrex	200	Pyrex	300	3
HS-126	612 with G-2684	8	9	4000	0.5	0.5	Pyrex	300	Pyrex	250	3

a. Uncured Results
b. Cured Results

Key to Mix Code:
1. Increased ZL-437 Content
2. Decreased TMETN Content
3. 45% of Total Oxidizer (AP) Pasted in XL-437
4. Coated LMH-1 with 3% (LMH-1 wt.) ZL-437
5. RDX Substitution
6. Standard

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(U) These mixes also show an improvement in uncured friction sensitivity as determined by the torque requirements of the friction screw tests. The cured friction sensitivity shows little if any improvement by tests with the friction screw, but does indicate some friction improvement (HS-124) in tests on the rotating disc tester.

(U) (2) Series II (3-Variable) Formulations

(U) As a result of the testing of the Series I mixes, increased binder (ZL-437) was omitted as a variable in the Series II (3-variable) formulations. Since the addition of wetting agents had resulted in decreases of propellant sensitivity, it was concluded that this variable would be further evaluated in the Series II formulations. It may be seen from the sensitivity test results of these mixes (see Table XXXIX) that slight improvement in the uncured impact sensitivity is achieved when compared to the standard. The cured impact sensitivity was not generally affected. The most improved mix for impact purposes was mix HS-130, which measured a higher end-of-mix viscosity than did the standard. Mix HS-130, a decreased TMETN, RDX-substitution, pasted ammonium perchlorate formulation, produced a 3 (100 percent) and 4 kg-cm (57 percent) improvement in uncured and cured impact sensitivity, respectively.

(U) As was the case in the Series I mixes, friction sensitivity was improved in most of the tests. The most improvement resulted with mix HS-133, a decreased TMETN, coated - LMH-1, RDX-substitution formulation using fine particles of RDX, on which the cured friction sensitivity was decreased 3000 rpm, or 115 percent.

(U) (3) Series III (4 - 5 Variable) Formulations

(U) The propellants of Series III combined the variables of Series II with the wetting agent G-2684.

(U) The sensitivity test results for this series of mixes are shown in Table XL. These data show that mix HS-136 (decreased TMETN, milled ammonium perchlorate, coated LMH-1 and 1 percent wetting agent formulation), when compared to the standard, resulted in no significant improvement in uncured impact sensitivity, a slight increase in cured impact sensitivity, and a 1000 rpm improvement (or 38 percent) in the cured friction sensitivity.

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TABLE XXXIX

SENSITIVITY TEST RESULTS OF PHASE II, TASK 2, SERIES II (3-VARIABLE) FORMULATIONS

Mix No.	Mix Code	Mix Viscosity @ 124-129°F	I_{sp} lb-sec/lb	O/F Ratio	Impact (kg-cm) U [b]	Impact (kg-cm) C [c]	Friction (rpm) U	Friction (rpm) C	Spark (Joules) U & C	Friction Screw in/lb to (+) Tests on Pyrex Grit U	Friction Screw in/lb to (+) Tests on Pyrex Grit C
HS-112	6	12	280.07	1.172	3	7	---	2600	1.0	150	150
HS-130	6235	18	278.51	0.992	6	11	---	4600	0.5	250	300
HS-132	6245	4	278.51	0.992	5	8	3400	3200	0.5	200	75
HS-133	6245[a]	4	278.51	0.992	5	6	3600	5600	0.5	200	300
HS-134	6345	4	280.8	1.069	4	7	3600	4200	0.5	200	225
HS-135	6234	4	279.26	1.076	5	6	4000	3600	0.5	250	

(a) Fine RDX used in place of coarse RDX
(b) Uncured results
(c) Cured results

Key to Mix Code:

2. Decreased TMETN concentration
3. 15 percent of oxidizer (AP) was pasted in the binder (ZL-437)
4. Coated LMH-1 with 3 % of weight of LMH-1 by ZL-437.
5. RDX (10%) substitution for AP
6. Standard Fomulation
7. Wetting agent (G-2684).

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TABLE XL

SENSITIVITY RESULTS OF PHASE II, TASK 2, SERIES III (4-5 VARIABLE) FORMULATIONS

Mix No.	Mix Code	Mix Viscosity @ 124-129°F	I_{sp} lb-sec/lb	O/F Ratio	Impact (kg-cm) U[a]	Impact (kg-cm) C[b]	Friction (rpm) U	Friction (rpm) C	Spark (Joules) U & C	Friction Screw in/lb to (+) Tests on Pyrex Grit U	Friction Screw in/lb to (+) Tests on Pyrex Grit C
HS-112	6	12	280.07	1.172	3	7	---	2600	1.0	150	150
HS-136	62347	4	279.26	1.076	4	5	2600	3600	0.5	300	300
HS-137	62457	4	278.51	0.992	6	7	2600	4000	0.5	150	275
HS-138	623457	4	278.51	0.992	7	6	4000	6000	0.5	50	125

(a) Uncured Results
(b) Cured Results

Key to Mix Code:
2. Decreased TMETN concentration
3. 45 percent of oxidizer (AP) was pasted in the binder (ZL-437).
4. Coated LMH-1 with 3 percent of weight of LMH-1 by ZL-437.
5. RDX (10%) substitution for AP
6. Standard Formulation
7. Wetting agent (G-2684).

(U) Mix HS-137 (decreased TMETN, coated LMH-1, RDX and 1 percent wetting agent), when compared to the standard, indicates an improvement in uncured impact sensitivity of 3 kg-cm, with no change of cured impact sensitivity. The uncured and cured friction sensitivity is equivalent to mix HS-136. Mix HS-138 incorporated all the variables being considered (decreased TMETN, pasted ammonium perchlorate, coated LMH-1, RDX and 1 percent wetting agent). The uncured impact was 7 kg-cm, which is, by comparison, a 130 percent improvement over the standard. The cured impact sensitivity, however, shows little difference. This mix produced one of the most insensitive tests to friction of all mixes tested. These results were 4000 and 6000 rpm in the uncured and cured propellant, respectively, and an improvement of 130 percent in the cured propellant as compared to the standard.

(U) In summary, the tests results of Series I, II and III show that:

(U) 1. The improvement in impact sensitivity of uncured propellant was generally associated with the reduction of TMETN content.

(U) 2. The improvement in impact sensitivity of cured propellant was generally associated with the substitution of RDX.

(U) 3. The improvement in friction sensitivity of uncured propellant was generally associated with the reduction of TMETN content and the coating of LMH-1.

(U) 4. The improvement in friction sensitivity of cured propellant was generally associated with the reduction of TMETN content, the coating of LMH-1, or substitution of RDX for ammonium perchlorate.

(U) d. Task 3 - Effect of Ammonium Perchlorate and LMH-1 Particle Size

(U) It was shown early in the investigation of sensitivity variables of Phase I, Task 1 that improvements in impact sensitivity could be obtained with control of the solids particle size. It was also shown in tests of other sensitivity variables, such as increase or decrease of LMH-1 or TMETN, that impact sensitivity was affected. The mix viscosity, which is effected by the above variables, also has an effect on impact sensitivity.

(U) A series of mixes, as described in Table XLI, was made in which variations in oxidizer and LMH-1 particle sizes were evaluated in combination with other variations in propellant composition. The results of these tests indicate that changes in ammonium perchlorate particle sizes resulted in a

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TABLE XLI

SENSITIVITY TEST RESULTS OF PHASE II, TASK 3 MIXES
(Effect of Solids Particle Size)

Mix No.	Mix Code	% Pasted AP	% 400 (μ) AP	LMH-1 WMD (μ)	Viscosity @ 124-129°F	Impact (kg-cm) U[(a)]	Impact (kg-cm) C[(b)]	Friction (rpm) U	Friction (rpm) C	Spark (Joules) U & C	Friction Screw in/lb to (+) Tests on Pyrex Grit U	Friction Screw in/lb to (+) Tests on Pyrex Grit C
HS-138[(c)]	623457	22.27	17.23	118	4	7	6	4000	6000	0.5	50	125
HS-139	623457	39.5	0	118	11	4	7	3200	3200	0.5	300	100
HS-140	623457	13.17	26.33	118	8	10	11	3000	4600	0.5	150	125
HS-141	623457	26.33	13.17	118	2	5	9	4000	4200	0.5	150	back-off
HS-142	623457	39.5	0	83	14	4	10	4000	6200	0.5	back-off	275

(a). Uncured Results
(b). Cured Results
(c). Standard Mix

Key to Mix Code
2. Decreased TMETN concentration
3. 45 percent of oxidizer (AP) was pasted in the binder (ZL-437).
4. Coated LMH-1 with 3 percent of weight of LMH-1 by ZL-437.
5. RDX (10%) substitution for AP
6. Standard Formulation
7. Wetting agent (G-2684).

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range of 4 to 10 kg-cm for uncured propellant and 6 to 11 kg-cm for the cured propellant. The change of LMH-1 particle size of mixes HS-139 and 143 produced no change in uncured impact sensitivity, but did give a 3 kg-cm improvement in cured impact sensitivity. The most impact sensitive propellant was mix HS-139, which contained all small particle size ammonium perchlorate.

(U) A reevaluation of the AP/LMH-1 dry blend mixture data was made. The results of this analysis, with some new data included, indicates that a critical particle size ratio and diameter of solid particles does exist for impact sensitivity. The results of this evaluation are graphically illustrated on Figure 19. Impact sensitivity is plotted against the ratio of LMH-1 particle size/oxidizer particle size. A 2/1 ratio by weight of AP/LMH-1 was used. It can be seen that ratios of 1 or less using 85 micron LMH-1 or less, gave E_o's of 50 ± 10 kg-cm and as the ratio increased to the range of 3 to 10, the E_o values reached a maximum of 100 kg-cm. The mixtures become more sensitive at ratios larger than 10, probably becoming asymptotic, to a minimum impact sensitivity in the 30 kg-cm range. The values for large (138 micron) LMH-1 are somewhat different and will be discussed further in the section which follows.

(U) This analysis indicates that the ratio of LMH-1/AP particle size is a more precise control factor for impact sensitivity than the specific particle sizes of either ammonium perchlorate or LMH-1.

(U) Since the solids particle size and particle size ratios are intervariables of the microstructure of propellant, it is believed that the propellant microstructure more clearly defines the physical parameter in control of impact sensitivity. In a broad application, one may see that similarities, within the limitations imposed by differences of particle geometrical shapes, exist between the optimum particle size ratios for improved impact sensitivities and Dallavalle[10] optimum solids packing theory. In addition, it can be stated that the propellant microstructure changes as the ratio of solid particle sizes change if the concentrations, by weight, of the propellant components are held constant.

(U) It is indicated that the impact sensitivity can be controlled within a range by proper selection of the solid particle size ratio. The range of impact sensitivity is limited by the materials of the propellant formulation.

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10. Dallavalle, J. M., Micromeritics - The Technology of Fine Particles, Chapter 6, Pitman Publishing Corp., New York and London, 1948.

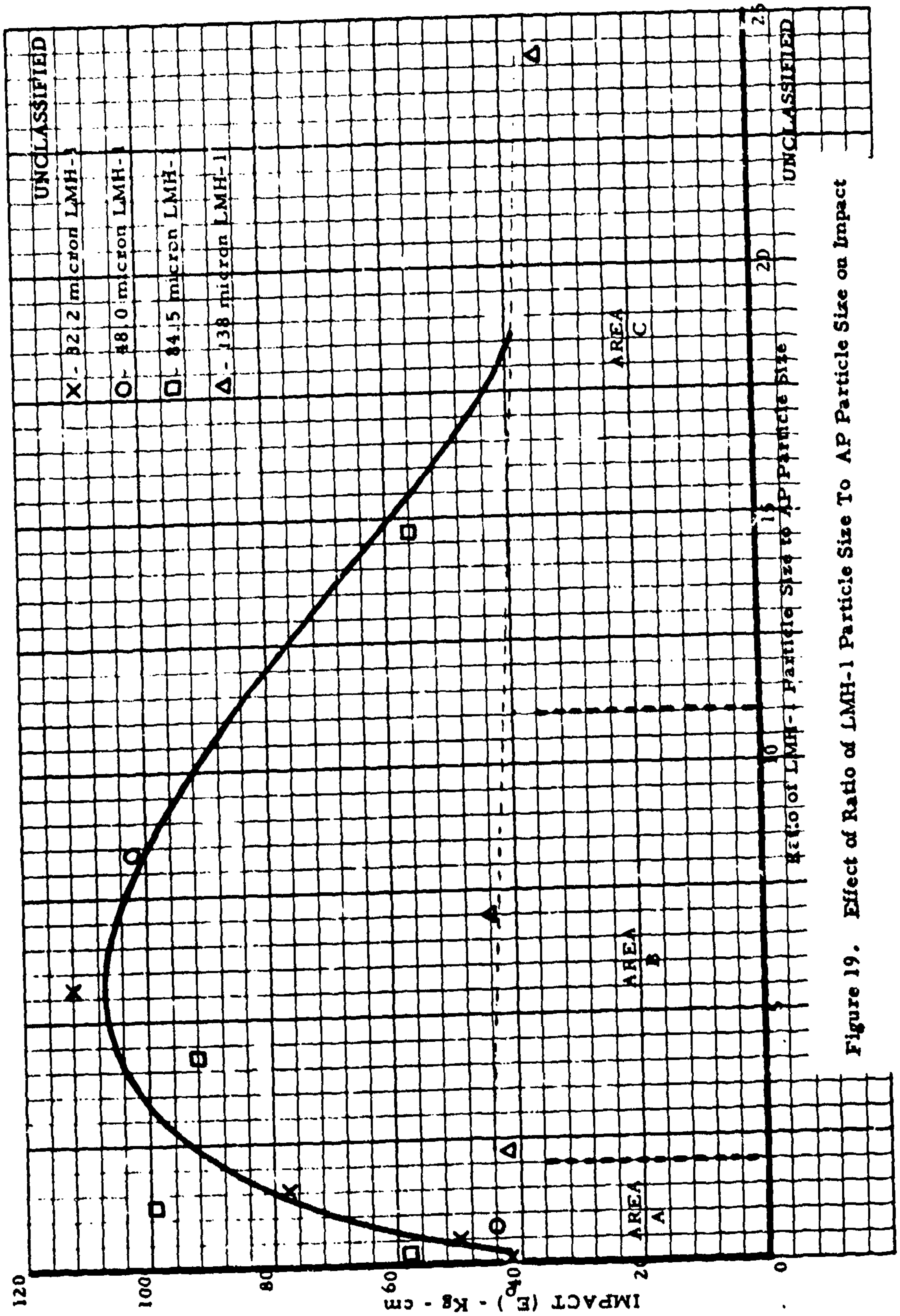

Figure 19. Effect of Ratio of LMH-1 Particle Size To AP Particle Size on Impact

(U) (1) Critical Particle Diameter

(U) Three conclusions may be drawn from the data of Figure 19:

(U) 1. At very low ratios of LMH-1/AP particle size, very sensitive mixtures result regardless of the range of either solid particle size.

(U) 2. At very high ratios of LMH-1/AP particle size, very sensitive mixtures result regardless of the range of either solid particle size.

(U) 3. At intermediate ratios of LMH-1/AP particle size, insensitive mixtures may be obtained, but the absolute particle size of LMH-1 is a major factor to be considered.

(U) The data of Figure 19 and Table XLII show that when large (138 micron) LMH-1 is used, relatively sensitive mixtures result with the smaller particle sizes of ammonium perchlorate. The precise reason for this phenomenon with large LMH-1 is not known, but it is believed to be related to a significant change of the solid LMH-1 particle geometrical shape, which is assumed constant for discussion purposes. The change of particle shape would account for a change of propellant packing structure and therefore a change of impact sensitivity.

(U) In this respect, the critical diameter is defined as the solid particle size (or particle size grouping) of an individual material that deviates at some point from the general relationship between impact sensitivity and particle size ratio.

(U) (2) Dry Blend and Propellant Sensitivity Interrelation

(U) Experiments with dry blends of LMH-1 and ammonium perchlorate have resulted in a method for predicting impact sensitivities of uncured propellants from data obtained by use of dry blends of the solid components. For any given formulation, this method is capable of quantitatively predicting changes in impact sensitivity due to changes in particle sizes of the solid components. The restrictions placed upon the calculation of sensitivity is that a known dry blend with a fixed weight ratio of AP/LMH-1 and a standardized propellant formulation, using the same fixed weight ratio of AP/LMH-1 and the same particle sizes of solids as used in the dry blend, must have established impact sensitivity values. A second (candidate formulation) dry blend, again using the same weight ratio of AP/LMH-1 may be selected with different particle sizes of AP and/or LMH-1 (different particle size ratio), but all material concentrations must be constant. The impact sensitivity of the candidate

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TABLE XLII

IMPACT SENSITIVITY TEST RESULTS - DRY BLEND MIXTURES

Test No.	AP $\overline{WMD}$ (μ) (66.44%)	LMH-1 $\overline{WMD}$ (μ) (33.56%)	LMH-1/AP Particle Size Ratio	Impact (E_o^o) (kg-cm)
db-1	5.7/400 (2/3)	32.2	0.10	59
db-2	5.7/220 (2/1)	48.0	0.60	66
db-3	5.7	32.2	5.65	112
db-4	5.7	48.0	6.42	102
db-5	5.7	84.5	14.82	56
db-6	5.7	133	24.21	36
db-7	20	32.2	1.61	78
db-8	20	138	6.90	44
db-9	61	32.2	0.53	50
db-10	61	84.5	1.38	99
db-11	61	138.0	2.26	42
db-12	220	32.2	0.15	42
db-13	220	84.5	0.38	58

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propellant can be calculated from these values (within the limits of the impact tester). The simple relationship

$$\frac{d_1}{P_1} = \frac{d_2}{P_2}$$

may be used to predict E_o for P_2 where

d_1 = known E_o for a given weight ratio and particle size ratio of LMH-1/AP

P_1 = known E_o for a propellant containing the same weight ratio and particle size ratio as used in d_1.

d_2 = known E_o of dry blend of new particle sizes of LMH-1 and AP in the same weight ratio as used in d_1 and P_1.

P_2 = unknown E_o for propellant with the same particle sizes used in d_2 and the same overall formulation used in P_1.

(U) Examples of the accuracy of the calculation are given below. In these examples, propellant sensitivity data from Phase I, Task 1 were used and are given in Table III. The impact sensitivity results of several dry blend mixtures (Table XLII) are repeated for information.

(U) <u>Example No. 1</u>

d_1 = 102 kg-cm (db-4, Table XLII)

P_1 = 18 kg-cm (HS-18, Table III)

d_2 = 56 kg-cm (db-5, Table XLII)

P_2 = (X) kg-cm (HS-19, Table III)

$$\frac{102}{18} = \frac{56}{P_2}$$

$$102\ (\text{kg-cm})\ P_2 = 1008\ (\text{kg-cm})^2$$

$$P_2 = 10\ \text{kg-cm}$$

The uncured impact sensitivity of HS-19 was measured at 11 kg-cm.

(U) Example No. 2

d_1 = 102 kg-cm (db-4)
P_1 = 18 kg-cm (HS-18)
d_2 = 66 kg-cm (db-2)
P_2 = (X) kg-cm (HS-22)

$$\frac{102}{18} = \frac{66}{P_2}$$

$$102\ (\text{kg-cm})\ P_2 = 1188\ (\text{kg-cm})^2$$

$$P_2 = 12\ \text{kg-cm}$$

The uncured impact sensitivity of HS-22 (a bimodal ammonium perchlorate mix) was measured at 11 kg-cm.

(U) Example No. 3

d_1 = 66 kg-cm (db-2)
P_1 = 11 kg-cm (HS-22)
d_2 = 44 kg-cm (db-8)
P_2 = (X) kg-cm (HS-24)

$$\frac{66}{11} = \frac{44}{P_2}$$

$$66\ (\text{kg-cm})\ P_2 = 484\ (\text{kg-cm})^2$$

$$P_2 = 7\ \text{kg-cm}$$

The uncured impact sensitivity of HS-24 was measured at 7 kg-cm.

(U) Example No. 4

d_1 = 44 kg-cm (db-8)
P_1 = 7 kg-cm (HS-24)
d_2 = 56 kg-cm (db-5)
P_2 = (X) kg-cm (HS-19)

$$\frac{44}{7} = \frac{56}{P_2}$$

$$44\ (kg\text{-}cm)\ P_2 = 392\ (kg\text{-}cm)^2$$

$$P_2 = 9\ kg\text{-}cm$$

The uncured impact sensitivity of HS-19 was measured at 11 kg-cm.

(U) As a final example, a dry blend sensitivity without a known matching propellant sensitivity is choosen.

$$d_1 = 102\ kg\text{-}cm\ (db\text{-}4)$$
$$P_1 = 18\ kg\text{-}cm\ (HS\text{-}18)$$
$$d_2 = 59\ kg\text{-}cm\ (db\text{-}1)$$
$$P_2 = (X)\ kg\text{-}cm$$

$$\frac{102}{18} = \frac{59}{P_2}$$

$$102\ (kg\text{-}cm)\ P_2 = 1062\ (kg\text{-}cm)^2$$

A propellant formulation, with the solids particle size ratio of db-1, holding the percent of LMH-1 and ammonium perchlorate constant with HS-18, would predict an impact sensitivity of 10 kg-cm.

(U) These sample calculations show the direct correlation between solid particle size of dry blends and the uncured propellant impact sensitivity. The accuracy of these calculations are, of course, dependant on the accuracy of the test results.

SECTION V

EXPERIMENTAL EQUIPMENT

(U) During the course of this investigation, a duplicate of the Esso Research and Engineering Company friction screw device was manufactured by the Huntsville Division of Thiokol Chemical Corporation. This friction test device was used in the evaluation of the friction sensitivity of the propellants of this program and the results obtained were compared with these of the Thiokol rotating disc friction tester. The operating procedure for both the Esso-type friction screw and Thiokol's rotating disc testers is given in Appendix A of this report.

(U) A comparison of the sensitivity test results obtained using the two friction testers are given in Table XLIII for "neat" materials, material combinations and propellant formulations. These data show that a mixture of LMH-1 and ammonium perchlorate is quite sensitive by tests with the rotating disc tester (~500 rpm), and positive (+) with both the CaF_2 grit (hardness = 4) and Pyrex (hardness = 5.5) when tested on the friction tester. The propellants using these ratios of AP/LMH-1 (HS-3, 8 and 11) gave F_o (rotating friction sensitivity) of 1400 to 1600 rpm and was (+) to the Pyrex grit [negative (-) to CaF_2)] on the friction screw tester. The friction screw tester indicates a slight difference in friction sensitivity of the dry AP/LMH-1 mixture in comparison to the complete propellant formulation of HS-3.

(U) Measurements were run on a number of propellants including TP-H8126 Nike Zeus propellant. This standard propellant had an F_o of 3500 rpm and was negative on the friction screw with all grits. The only material to give a negative test with Pyrex and then a positive test with SiC was P-BEP polymer. The only propellant to give a positive test with bare tools was a P-BEP/B/AP propellant. However, this same propellant had an F_o of 2200 rpm. In this case boron (Mohs hardness = 9.5) is a harder grit than SiC, and is probably causing the extreme sensitivity on the screw. This propellant contains a high percentage (9 percent) of boron. It may be seen in other propellants in the table that boron increases the friction sensitivity (rotating disc tester), even when low boron levels are present.

(U) It appears that the main difference in the two tests is that the friction screw is a combination of friction and compression, whereas there is no compression in the rotating disc tester. It was noted in a number of tests on the friction screw, with the most friction sensitive materials (disc test), that a positive test was obtained at a very low (< 100 in/lb) torque. Also, some of the less sensitive materials (disc test) gave positive tests only when the screw was backed off. From these observations, it appears that a positive test with a certain grit on the friction screw covers a wide range of rpm on the rotating disc tester.

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TABLE XLIII

COMPARISON OF SENSITIVITY TESTS ESSO-TYPE FRICTION SCREW TESTER AND THIOKOL'S ROTATING DISC TESTER

	Friction Screw				F_o Rotating Disc
	No Grit (0)	CaF_2 (4.0)	Pyrex (5.5)	SiC (9.0)	(rpm)
AP	-		-	-	>7000
AP + Al	-		-	-	>7000
AlH_3 (32 μ)	-	-	-	-	>7000
AlH_3 (138 μ)	-	-	-	-	>7000
AlH_3 32 μ + 200 μ AP	-	+	+		500
AlH_3 138 μ + 200 μ AP	-	+	+		500
P-BEP	-		-	+	1900
TVOPA	-		-	-	2700
NFPA	-		-	-	>7000
Carboxyl Terminated NFPA/TVOPA, 1/1	-		-	-	>7000
TP-H8126	-		-	-	3500
NFPA-Al-AP Propellant	-		-	-	2600
P-BEP-Al-AP Propellant	-		+		1600
NFPA-AlH_3-AP Propellant	-		+		2200
P-BEP-AlH_3-AP Propellant	-		+		1600
NFPA-AP Propellant	-		+	+	1700
P-BEP-B-AP Propellant	+		+	+	2200
NFPA-RDX	-		-	-	>7000
NFPA-RDX-B 3%	-		-	-	5700
P-BEP-RDX	-		-	-	3500
P-BEP-RDX-B 3%	-		-	-	3200
HS-3 AP-AlH_3 Propellant (Cured)	-	-	+		1600
HS-8 AP-AlH_3 Propellant (Cured)	-	-	+		1400
HS-11 AP-AlH_3 Propellant (Uncured)	-	-	+		1600

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(U) The continued use of the friction screw in the program revealed unusual results with the HS- series (ZL-437/TMETN/AP/LMH-1) of propellants. In some cases, positive (+) results have been obtained with the Pyrex grit, which has a Mohs' hardness of 5.5, and negative results with the SiC grit, with a Mohs' hardness of 9.0, using the same propellant sample.

(U) Table XLIV shows a comparison of the detailed results of the tests of a randomly selected group of mixes for the friction screw tester and the rotating disc tester. These mixes are considered to be typical of the results of testings conducted under this program. It is to be noted that a maximum of three tests with each grit were obtained. More tests may have produced a positive test of the example with SiC (mix HS-50); however, the number of tests to be conducted is an undefined variable.

(U) There is one question as yet unanswered in reports dealing with the friction screw tester; what effect do multiple grits have on the test. Fuels such as aluminum, LMH-1, boron, and others, behave as grits in the testing of propellants. Also, the oxidizers themselves may act as grits. It has been reported that a Mohs' hardness of 4.3 to 6 was measured for LMH-1, 1.5 to 2, for ammonium perchlorate, and 2 to 3 for RDX.

(U) The comparable results of the friction test devices indicate that the use of multiple materials, and thus variables in propellant formulations, will require a more quantitative test of friction sensitivity than is available presently with the design of the friction screw test device. However, it appears that this device may be successfully used to determine the sensitivity properties of individual ingredients.

TABLE XLIV UNCLASSIFIED

RESULTS OF FRICTION SCREW TEST

Mix No.	Propellant State[e]	F_o[d] Friction Sensitivity (rpm)	Pyrex Grit (5.5) N[a]	Pyrex Grit (5.5) P[b]	Pyrex Grit (5.5) Torque[f] (in-lb) at Initiation	SiC Grit (9.0) N	SiC Grit (9.0) P	SiC Grit (9.0) Torque (in-lb) at Initiation
HS-49	U	2200	2[c]	1	Back-Off	3	0	---
HS-49	C							
HS-50	U	2800	0	1	150	3	0	---
HS-50	C	2600	0	1	150	3	0	---
HS-55	U	3000	3	0	---	1	1	300
HS-55	C	3600	0	1	200	0	1	250
HS-57	U	2400	3	0	---	3	0	---
HS-57	C	2600	0	1	100	3	0	---
HS-59	U	2600	0	1	Back-Off	3	0	---
HS-59	C							
HS-60	U	4200	0	1	Back-off	0	1	250
HS-60	C	2800	0	1	200	0	1	Back-Off
HS-62	U	4400	2	1	250	3	0	---
HS-62	C	3000	0	1	Back-Off	3	0	---
HS-65	U	4600	0	1	200	3	0	---
HS-65	C	2400	0	1	200	3	0	---
HS-69	U	3000	0	1	150	3	0	---
HS-69	C	6000	1	1	Back-Off	3	0	---

(a) Negative Test
(b) Positive Test
(c) Number of Tests in that category
(d) F_o (10 consecutive negative tests)
(e) (U)-Uncured; (C)-Cured
(f) Torque is measured by torque wrench to a maximum of 300 in-lbs

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SECTION VI

CONCLUSIONS

PHASE I. SENSITIVITY DEFINITION

(U) 1. Intermediate particle sizes (50 to 80 micron) of LMH-1 were least sensitive to impact in the uncured state. Cured propellants were essentially the same. Dry blends of ammonium perchlorate and LMH-1 confirmed these sensitivity results.

(U) 2. Sensitivity to friction increases as LMH-1 particle size increases (becomes more sensitive) in the uncured state; however, in the cured state, only a slight difference exists.

(U) 3. Dry blends of AP/LMH-1 were extremely friction sensitive and not dependent on oxidizer or LMH-1 particle size.

(U) 4. Propellant sensitivity, especially to impact, was decreased using small oxidizer ammonium perchlorate particle sizes.

(U) 5. The use of dry lubricants (MoS_2, graphite) gave significant improvements in the impact and friction sensitivity of LMH-1/AP dry blends.

(U) 6. Dry lubricants, such as graphite and Molykote, result in decreases in specific impulse too large to consider their use. Powdered Teflon appears to be more promising, giving only a 1.1 lb-sec/lb loss at the 3 percent level.

(U) 7. Three percent powdered Teflon gives significant decreases in propellant sensitivity; however, large increases in propellant viscosity also occur due to the particle shape of Teflon.

(U) 8. The use of small ammonium perchlorate particles in a formulation substituting aluminum for LMH-1 also gave improved impact sensitivities.

(U) 9. The substitution of 10 percent RDX for ammonium perchlorate in LMH-1 propellants has resulted in a significant decrease in friction sensitivity, without loss of performance.

(U) 10. HMX resulted in desensitization similar to that obtained with RDX. Theoretical ballistic calculations are also similar.

(U) 11. Desensitization with RDX, HMX, and other materials such as bibenzyl, p-terphenyl, and graphite appears to be caused by the lubricating properties of these compounds.

(U) 12. A 3 percent, by weight solids, coating of LMH-1 with ZL-437 produced improved friction sensitivities. Coating with Viton A and Hypalon were less effective.

(U) 13. The coating of LMH-1 with a mixture of HX-874 and ZL-437, and then curing the coating, results in decreases in friction sensitivity, especially in the uncured state. Sensitivities were not significantly different from coating with ZL-437 only.

(U) 14. A less viscous mix using ZL-437 and HX-874 coated LMH-1 (with the coating cured) resulted in a large improvement in cured friction sensitivity. An increase in impact sensitivity, due to the large size ammonium perchlorate used, was also realized.

(U) 15. Coatings of ammonium perchlorate gave only slight changes in propellant sensitivity.

(U) 16. Both ammonium perchlorate and LMH-1 were successfully pasted in ZL-437. Hydrogen losses from the LMH-1 were negligible, as determined by carbon and hydrogen analyses.

(U) 17. LMH-1 pasted in ZL-437 gave significant improvements in both impact and friction sensitivity. Large size ammonium perchlorate was needed to give good processing. Coated ammonium perchlorate had no effect in conjunction with pasted LMH-1. The LMH-1 propellants have much lower densities (88 percent), due to the increased reactivity of the pasted material.

(U) 18. Large concentrations of fine ammonium perchlorate may be processed in the standard formulation by use of a preblend made by pasting LMH-1 or ammonium perchlorate in a mixture of binder and plasticizer.

(U) 19. Pasting of magnesium-doped LMH-1 failed to prevent propellant gassing probably as a result of the new surface areas created by pasting.

(U) 20. Vacuum treatment of pasted LMH-1 does not prevent propellant gassing.

(U) 21. Mixes with coated or pasted ammonium perchlorate do not cure as normal. Higher cure ratios, or the addition of a cure catalyst, will, however, produce cures.

(U) 22. Four different wetting agents were found to lower the contact angle of the binder to oxidizer or binder to LMH-1.

(U) 23. MAPO, used as a wetting agent, had no effect on propellant sensitivity or viscosity.

(U) 24. Wetting agents Armeen SZ and G-2684 failed to improve the propellant viscosity. Propellant friction sensitivities were improved with these wetting agents.

(U) 25. Some small improvement in cured friction sensitivity was obtained with mixes processed in the ARC 2 CV mixer, when compared to those processed in the Plastograph mixer.

(U) 26. Early addition of LMH-1 to the mixer results in some increase in friction sensitivity.

(U) 27. Reduction of the LMH-1 content resulted in a decrease in friction sensitivity and an increase in impact sensitivity.

(U) 28. Both impact and friction sensitivity are improved when the TMETN content is reduced. Cured propellants were usually less sensitive than uncured.

(U) 29. Chemical treatments of the surface of LMH-1 did not produce sensitivity improvements.

(U) 30. The probable reason for differences in cured and uncured propellant friction sensitivities is that LMH-1 and oxidizer particles are completely wet in the uncured state, but are easily dewet or broken loose from the cured binder.

(U) 31. A considerable improvement in binder-ammonium perchlorate bond strength is realized when Volan is applied as an ammonium perchlorate coating.

(U) 32. Volan coating of LMH-1 results in a large reduction of LMH-1 to binder bond strength.

(U) 33. The anti-static agents, STATIKILL or NEUTRO-STAT, did not reduce the electrostatic discharge sensitivity of LMH-1 or LMH-1 propellants.

(U) 34. Extensively dried ammonium perchlorate does improve the uncured friction sensitivity of propellant.

PHASE II. SENSITIVITY IMPROVEMENT

(U) 1. Improved cures of milled ammonium perchlorate propellants were obtained using higher imine/acid ratios and a cure catalyst.

(U) 2. The friction sensitivity of propellant containing coated LMH-1 was improved in comparison to the uncoated LMH-1 formulation.

(U) 3. Higher concentrations of coatings on LMH-1 did not significantly affect the propellant friction or impact sensitivities.

(U) 4. Higher concentrations of coatings on ammonium perchlorate particles had no significant effect on impact sensitivity.

(U) 5. Increased concentrations of binder coating on ammonium perchlorate particles produced a propellant that was more sensitive to friction.

(U) 6. Intimate contact between a fuel (ZL-437 or LMH-1) and an oxidizer (ammonium perchlorate or TMETN) increases friction sensitivity.

(U) 7. The reduction of TMETN concentration in the standard formulation is a significant variable in reducing uncured impact sensitivity.

(U) 8. The use of RDX as a partial substitute for ammonium perchlorate is effective in reducing cured propellant impact sensitivity.

(U) 9. The use of RDX as a partial substitute for ammonium perchlorate and decreased TMETN content were effective in reducing uncured friction sensivity.

(U) 10. The coating of LMH-1 with the binder, reduced TMETN content, and substitution of RDX for ammonium perchlorate in the formulation were effective variables in reducing the cured propellant friction sensitivity.

(U) 11. The use of the wetting agent G-2684 complimented sensitivity improvements with other included variables.

(U) 12. A mix insensitive (comparatively) to friction was obtained when all variables of Phase II, with the exception of the effect of ammonium perchlorate and/or LMH-1 particle size, were combined in a formulation.

(U) 13. Both LMH-1 and ammonium perchlorate particle sizes have significant effects on impact sensitivity.

(U) 14. The ratio of LMH-1 particle size to ammonium perchlorate particle size is critical to the degree of impact sensitivity improvement. The critical particle size ratio for maximum improvement is from 2 to 11; however, intermediate particle sizes of LMH-1 must be used (30 - 85 microns).

(U) 15. The effect on E_o of particle size variations of LMH-1 and ammonium perchlorate in a set formulation can be predicted quantitatively mathematically.

(U) 16. The electrostatic discharge (ESD) or spark sensitivity of the LMH-1 propellant was not effected by the variables of this program. No increase or decrease of spark sensitivity was observed.

(U) 17. The method of physically decreasing friction sensitivity is by separating the fuel from the oxidizer by inert or less energetic materials, or by reducing the friction generated between the solids.

(U) 18. The apparent underlying cause of impact sensitivity is the propellant packing structure.

APPENDIX A

SENSITIVITY TESTING PROCEDURES

Four procedures for sensitivity testing are presented herein:

(1) Spark Testing Procedure
(2) Impact Testing Procedure
(3) Friction Testing Procedure
(4) Friction Screw Procedure

SPARK TESTING PROCEDURE

THIOKOL SPARK TESTER

1. Propellant or powder samples are prepared and kept in a desiccator until tests are conducted.

2. Use a sample of uncured propellant or powder which is approximately 0.020 grams.

3. Cured propellant samples are prepared by microtoming a large sample of propellant to a thickness of 0.022 ± 0.01 inch and samples are then cut from microtome by a No. 3 cork borer (≈ 0.5 mm).

4. The desired electrostatic charge in joules is stored on a capacitor by selecting the proper capacitor and voltage from a prepared chart.

5. A dry (blank) run is made at each energy level in order to watch and observe the loudness of the spark as recorded by the microphone - decibel meter system.

6. The sample is placed on the ground pole and the tester is charged. The upper pole is lowered slowly until the capacitor discharges. The degree of participation is determined by observing the color change of spark and change of loudness of spark as indicated on decibel meter. A greenish or yellow color of spark indicates a positive test, or a decibel meter reading above that of the blank reading indicates a positive test.

7. When a positive test is obtained the energy is lowered one level. Steps 4 and 5 are repeated until five negative tests are obtained.

IMPACT TESTING PROCEDURE

OLIN MATHIESON DROP-WEIGHT TESTER

1. Use 0.020 gram sample weight for powders. For cured propellant samples a sample 0.5 mm (0.02") thick and 5mm in diameter. Such is accomplished by microtoming a 0.02 inch slab of propellant and stamping out the samples with a No. 2 cork borer.

2. For granulated material,, use particle size which will pass No. 50 and be retained by No. 100 U. S. Standard Sieve.

3. Prepared samples should be kept desiccated, as moisture content will affect sensitivity. (Dry material is normally more sensitive).

4. A brass cup containing sample is placed on the anvil, and the plunger tip is carefully inserted into cup.

5. Place the Sample Holder on the Drop-Weight Tester and gently lower the two kilogram weight into the plunger in order to make certain the sample is compacted and all parts are in contact.

6. Place 2 kilogram weight at 50 centimeters height, and drop weight.

7. If a "fire" results, then the height of the weight is lowered by one centimeter, a new sample is placed in the tester and the weight is dropped from this new height. If a "fire" is obtained in this height, then the weight is lowered by one centimeter and the test repeated with the new sample. This general procedure of lowering the weight one centimeter is repeated until a "no-fire" is obtained. After the first "no-fire", the drop height is increased by 0.5 cm and the test repeated. With each successive "no-fire", the drop height is increased until a "fire" is obtained. The weight and the height at which 10 successive "no-fires" are obtained is recorded as the E_0.

8. For the determination of E_{50}, a positive test and a negative test are first obtained. Bracketing the 50 percent point is carried out by increasing the height after a negative test, and decreasing it after a positive test. A minimum of twenty trials should be made, again increasing the weight by the selected minimum increment wherever a negative test occurs and decreasing it when a positive test occurs. E_{50} is then determined by interpolation.

9. All tests should be made at a standard temperature as in the Test Method for Liquids.

10. Care should be used in removing the brass cup after a negative test. In the case of sensitive materials the entire holder should be submerged in water and the cup removed with a suitable spreader-tool.

11. The plunger and anvil are made of hardened tool steel. The flat surfaces should be kept clean and free of pits and erosion. This is more important in the case of the plunger since it is in direct contact with the sample. These surfaces may be reground as necessary. A fine grind should be specified, and surfaces must be kept flat and parallel.

FRICTION TESTING PROCEDURE

THIOKOL ROTATING DISC TESTER

1. Use a 0.020 gram sample for uncured propellant or powders. For cured propellant a sample 0.5 mm thick and 5 mm in diameter is prepared by microtoming a larger sample of propellant. Prepared samples should be kept in a desiccator.

2. The faces of both the upper and lower discs are thoroughly cleaned with solvent and soft cloth (methylene chloride or benzene). A constant 200 g weight is used on the upper face. The faces are then put in contact and rotated at 5000 RPM to ascertain that all foreign objects are removed and that the solvent is evaporated. This procedure must be repeated after each test. The faces are refinished if pitting or scars appear.

3. The sample is placed between the two discs and the discs are rotated slowly by hand to ascertain if good contact is made between the discs. The rotating disc is brought up to a speed of 2000 rpm. As soon as this speed is reached, the timer is started. Time to ignition is then measured. A new sample is used for each test.

4. A positive test is one in which ignition occurs in less than 120 seconds.

5. If the test at 2000 RPM's is negative, a new sample is placed in the tester. The speed is raised in increments of 500 RPM's until a positive test is obtained. After the positive test, the speed on the next sample is lowered by 100 RPM's and such is continued until speed is reached where ten successive no-fires in 120 seconds can be obtained. This value of RPM is reported as the F_0 friction sensitivity.

6. If the test at 2000 RPM's is positive, the speed is lowered in increments of 100 RPM's until two successive negative tests are obtained. This value of RPM is reported as the F_0 friction sensitivity.

FRICTION SCREW PROCEDURE

ESSO FRICTION SCREW TESTER

1. Approximately 0.005 grams of propellant, powder or liquid, is used for friction testing with the Esso Friction Screw.

2. Before each test, the plates of the friction screw is wiped clean to insure no residual grit.

3. The propellant, powder or liquid sample, is placed on the bottom plate of the tester, approximately one-quarter (1/4) of an inch from the plate center. Then the grit, if any used, is placed directly on top of sample. The grit quantity should be approximately the same as the sample quantity.

4. A separate plate is used for each grit (CaF_2, Pyrex, or SiC) in order to minimize the effect of rough surfaces.

5. The top plate is tightened to a point of sample contact by turning the screw. Then a torque wrench is used to gage and tighten the screw to a uniform force.

6. The torque wrench is tightened to 300 inch-pounds, if the sample does not detonate under this torque or upon "back-off", the test is negative. If the sample detonates, the grit name (or bare plate) and torque under which it detonated is recorded. This is a positive test.

7. The sequence of test grits are: first, bare plate (0); second, CaF_2(4); third, pyrex (5.5), and fourth, SiC (9). If the sample fails to detonate with the SiC grit, it is considered insensitive to the Friction Screw Tester.

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13. ABSTRACT Thiokol's program to define the cause of LMH-1 propellant sensitivity and, in turn, to decrease the sensitivity characteristics of these propellants was divided into two phases: Phase I - Sensitivity Definition, and Phase II - Sensitivity Improvement. Factors affecting the sensitivity of both cured and uncured LMH-1 propellant have been investigated and defined. Studies which were conducted with regard to sensitivity definition indicated that both LMH-1 and ammonium perchlorate, separately, are insensitive to both impact and friction. The friction sensitivity of LMH-1 propellants is due to the relative ease of reaction of LMH-1 with oxidizer, and that to desensitize these propellants, contact between the two must be prevented or limited. Various methods of sensitivity improvement were examined. Some of these were surface treatments and coatings, binder solid bond studies, pasting techniques, and interrelationships between propellant variables. The friction sensitivity of the LMH-1 formulation tests varied from 1200 to 6000 rpm. The application of techniques to physically limit the contact of fuel to oxidizer, or to reduce the friction produced by the contact were responsible for these large decreases of sensitivity. These results were far beyond the established goals of the program. Impact sensitivity of propellants was found to be significantly affected by changes in ingredient particle size of solid ingredients.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
AlH_3 (C) - Aluminum Hydride (C)						
LMH-1 (U) - Code name for Aluminum Hydride (C)						
AP (U) - Ammonium Perchlorate (U)						

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It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS)*, *(S)*, *(C)*, or *(U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.