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U.S. Army Toxic and Hazardous Materials Agency

PROPELLANT REUSE/RECOVERY TECHNOLOGY

(TASK ORDER NO. 7)

August 1988
Contract No. DAAK11-85-D-0008

Prepared by:

Arthur D. Little, Inc.
Acorn Park
Cambridge, Massachusetss 02140-2390

Prepared for:

U.S. Army Toxic and Hazardous Materials Agency
Process Development Branch
Aberdeen Proving Ground, MD 21010-5401

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United States Army Toxic and Hazardous Materials Agency
August 1988

Propellant Reuse/Recovery Technology

(Task Order Number 7)

Final Report

A.A. Balasco
Program Manager

C.A. Jake — Task Leader, Hercules (RAAP)
R.C. Bowen
M.L. Hundley (RAAP)
L.H. McDaniel (RAAP)
L.L. Smith (RAAP)
Principal Investigators

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Due primarily to changes in weapon systems, the military has stocks of chemically acceptable propellants which are obsolete. Past disposal practices have been to incinerate or open-burn these stocks; however, extensive research has been conducted in the past at the Radford Army Ammunition Plant (RAAP) for the reclamation/reuse of solvent-based obsolete propellants. A literature review indicated that resolvation of propellant and recovery of selected ingredients from propellant via solvent extraction were the optimal reclamation technologies. This study was conducted in order to demonstrate the feasibility of these technologies. The propellant resolvation studies consisted of both laboratory and bench-scale evaluations; furthermore, appropriate hazards analyses of the procedures and equipment used in the evaluations were performed by the RAAP Hazards Analysis Department. Several operating parameters were assessed including resolvation time, propellant/solvent ratio, solvent/solvent ratio, and propellant particle size.

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22a. NAME OF RESPONSIBLE INDIVIDUAL
Patricia A. Spaine

22b. TELEPHONE *(Include Area Code)*
(301) 671-2054

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CETH-TE-D

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The laboratory-scale studies indicated that obsolete propellant can be successfully resolvated wihin 90 minutes using closely controlled operating parameters. More specifically, the percent nitrogen and viscosity of the nitrocellulose (NC) determine the solvent/solvent and solvent/propellant ratios required to properly resolvate the propellant. It was also demonstrated that single-base propellants resolvate more readily with increased solvent/propellant ratios, i.e., more solvent than is used in the RAAP standard production processes On the other hand, most multi-base propellants resolvate using production-established or slightly increased solvent/propellant ratios.

Bench-scale demonstrations were performed with M1 single-base propellant to optimize the operating parameters. The propellant was ground, dewatered using a Sweco® Vibro-Energy separator, dried in a forced air dry facility, and mixed in a series of thirty iterative trials; the resolvated propellant from the last nine trials was extruded through a 4-in. vertical press. The extrudate was cut to length and processed in the standard RAAP production operations used to manufacture single-base propellant. The finished propellant, which was subjected to the applicable ballistic, chemical, and physical analyses, either met or exceeded military specification requirements.

Propellant ingredient reclamation via solvent extraction was also conducted as a part of this study. Following a preliminary hazards analysis, appropriate solvents were selected based on solubility and distribution coefficient determinations. Laboratory-scale solvent extraction procedures were then developed for single-, double-, and triple-base propellants. Three principal ingredients, i.e., NC, nitroglycerin (NG), and nitroguanidine (NQ), were successfully extracted from single-, double-, and triple-base propellants. NC recovery ranged from 96-100% for single-base, 100% for double-base, and 88% for triple-base propellants. NG recovery from double-base averaged 80% and 100% from triple-base propellants; NQ recovery from triple-base propellant averaged 82%.

Based on the results of the evaluations, design criteria information was developed for both propellant resolvation and solvent extraction of selected propellant ingredients. In addition to the operating parameters defined by these studies, safety and quality were addressed in both designs. Safety-related considerations requiring additional evaluation include remote materials handling, equipment and facility clean-up and containment of potential spillage. Pertinent quality assurance considerations were also addressed in order to ensure the production of specification-grade propellant. For example, the design criteria information generated from these studies provide baseline data which can be used to develop an appropriate quality assurance plan for any follow-on studies.

Using the design criteria information, pilot-scale resolvation studies should be conducted for single-, double-, and triple-base propellant. Additional grinding/screening studies should be performed to obtain propellant particles passing a 12-mesh screen to ensure adequate resolvation. Alternate methods of dewatering and drying of the ground propellant (other than forced air dry) for resolvation should be investigated. Bench-scale solvent extraction studies to optimize the extraction of single-, double-, and triple-base propellant ingredients should be performed. Final users' specification requirements should be delineated to permit the use of resolvated propellant in current military weapon systems.

This report was prepared by Hercules Aerospace Company (Radford Army Ammunition Plant) for Arthur D. Little, Inc. in fulfillment of a requirement for Task Order Number 7 under Contract DAAK11-85-D-0008.

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GLOSSARY

TERM	IDENTIFICATION
Ba^{+2}	Barium cation
$Ba(NO_3)_2$	Barium nitrate
CASBL	Continuous Automated Single-Base Line
DBP	Dibutylphthalate
DNG	Dinitroglycerin
1,2-DNG	1,2-dinitroglycerin
1,3-DNG	1,3-dinitroglycerin
DNT	Dinitrotoluene
DPA	Diphenylamine
EC	Ethyl centralite
FAD	Forced Air Dry
H_2O	Water
HPLC	High-performance liquid chromatography
$KClO_4$	Potassium perchlorate
K_d	Distribution coefficient
K^+	Potassium cation
KNO_3	Potassium nitrate
K_2SO_4	Potassium sulfate
LCL	Lower control limit
N	Nitrogen
NC	Nitrocellulose
NG	Nitroglycerin
N-NDPA	N-nitrosodiphenylamine
2-NDPA	2-nitrodiphenylamine
NQ	Nitroguanidine
Pb^{+2}	Lead cation
$PbCO_3$	Lead carbonate
RAAP	Radford Army Ammunition Plant
RQ	Relative quickness
RF	Relative force
RS	Residual solvents
SpG	Specific gravity
TV	Total volatiles
UCL	Upper control limit

EXECUTIVE SUMMARY

Due primarily to changes in weapon systems, the military has stocks of chemically acceptable propellants which are obsolete. Past disposal practices have been to incinerate or open-burn these stocks; however, extensive research has been conducted in the past at the Radford Army Ammunition Plant (RAAP) for the reclamation/reuse of solvent-based obsolete propellants. A literature review indicated that resolvation of propellant and recovery of selected ingredients from propellant via solvent extraction were the optimal reclamation technologies. This study was conducted in order to demonstrate the feasibility of these technologies. The propellant resolvation studies consisted of both laboratory and bench-scale evaluations; furthermore, appropriate hazards analyses of the procedures and equipment used in the evaluations were performed by the RAAP Hazards Analysis Department. Several operating parameters were assessed including resolvation time, propellant/solvent ratio, solvent/solvent ratio, and propellant particle size.

The laboratory-scale studies indicated that obsolete propellant can be successfully resolvated within 90 minutes using closely controlled operating parameters. More specifically, the percent nitrogen and viscosity of the nitrocellulose (NC) determine the solvent/solvent and solvent/propellant ratios required to properly resolvate the propellant. It was also demonstrated that single-base propellants resolvate more readily with increased solvent/propellant ratios, i.e., more solvent than is used in the RAAP standard production processes. On the other hand, most multi-base propellants resolvate using production-established or slightly increased solvent/propellant ratios.

Bench-scale demonstrations were performed with M1 single-base propellant to optimize the operating parameters. The propellant was ground, dewatered using a Sweco® Vibro-Energy separator, dried in a forced air dry facility, and mixed in a series of thirty iterative trials; the resolvated propellant from the last nine trials was extruded through a 4-in. vertical press. The extrudate was cut to length and processed in the standard RAAP production operations used to manufacture single-base propellant. The finished propellant, which was subjected to the applicable ballistic, chemical, and physical analyses, either met or exceeded military specification requirements.

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Using the design criteria information, pilot-scale resolvation studies should be conducted for single-, double-, and triple-base propellant. Additional grinding/screening studies should be performed to obtain propellant particles passing a 12-mesh screen to ensure adequate resolvation. Alternate methods of dewatering and drying of the ground propellant (other than forced air dry) for resolvation should be investigated. Bench-scale solvent extraction studies to optimize the extraction of single-, double-, and triple-base propellant ingredients should be performed. Final users' specification requirements should be delineated to permit the use of resolvated propellant in current military weapon systems.

1.0 INTRODUCTION

The military currently has stocks of acceptable propellants which are obsolete due to changes in the weapon systems for which the propellants were originally produced. Additional quantities of waste propellant, i.e., propellant that does not conform to ballistic, chemical, or physical specifications, are generated during normal propellant manufacture. According to the Environmental Conference proceedings of the "Hazardous Waste Minimization Interactive Workshop" sponsored by Army Material Command (AMC) in November 1987, 158,000 metric tons of obsolete conventional munitions are in the demilitarization inventory; 249,000 metric tons are projected by the year 1993.

Past disposal practices have been to incinerate or open-burn obsolete or out-of-specification propellants or explosives. For example, at the Radford Army Ammunition Plant (RAAP) alone, 88 metric tons of solvent-based propellants (single-, double-, and triple-base) are slowly being disposed by incineration or open burning. Extensive research has been conducted in the past at RAAP for the reclamation/reuse of these propellants. An engineering evaluation/selection of recovery alternatives was previously conducted in PE-796, "Propellant Reuse Technology Assessment,"[1] to evaluate the existing technologies for reprocessing waste propellants and to develop improvements that would minimize environmental discharge and conserve strategic materials. The results of this study indicated that resolvation of waste propellant and recovery of selected ingredients from waste propellant via solvent extraction were the optimal reclamation technologies.

Based on the engineering evaluation/selection of recovery alternatives previously conducted in PE-796, laboratory-scale propellant resolvation studies were conducted on selected solvent-based propellants. The purpose of these studies was to define the optimum resolvation times necessary to achieve an acceptable colloid for solid propellants. Several operating parameters were also evaluated during the course of these evaluations, including propellant particle size, propellant/solvent ratio, solvent/solvent ratio, ingredient addition, and remixing. The colloided propellant doughs were also evaluated in laboratory-scale mixing and extruding equipment. Using the data generated during these evaluations, bench-scale demonstrations were performed with selected propellant. During the bench-scale evaluations, the operating parameters were optimized. The propellant was ground, mixed, extruded, cut, and dried; the finished propellant was then analyzed for ballistic, chemical, and physical conformance to specification.

As determined by the engineering evaluation in PE-796, a number of processes have been demonstrated for the recovery of propellant ingredients.[1] As a part of this project, certain propellant ingredients were recovered from single-, double-, and triple-base propellants via solvent extraction on a laboratory-scale basis. Following the preliminary hazards analysis, appropriate solvents were selected based on solubility and distribution coefficient determinations. Solvent extraction procedures were developed for the three types of propellant. Two testing procedures were prepared for the solvent extraction studies: high-performance liquid chromatography (HPLC) and atomic absorption spectroscopy. A statistical study was conducted to verify that the HPLC methods developed for these evaluations were comparable to the analytical methods delineated in MIL-STD-286B.

Based on the results of the evaluations, pilot plant design criteria information was developed for propellant resolvation and bench-scale design criteria information was developed for solvent extraction of selected propellant ingredients. Three parameters were addressed in the both designs: operation, safety, and quality.

2.0 LABORATORY-SCALE PROPELLANT RESOLVATION STUDIES

Laboratory-scale propellant resolvation studies were conducted on single-, double-, and triple-base propellants, e.g., M1, M7, and M30. In order to select the optimum resolvation technology, several testing parameters were chosen based on the current production methods used at RAAP for the manufacture of solvent-based propellants. These parameters included colloiding the propellant, defining the various states of solvation to attain the desired colloidal system, and determining resolvation times. Criteria to permit introduction of the resolvated propellants into standard manufacturing processes were established by optimizing the testing parameters via laboratory-scale studies.

2.1 Propellant Selection

Propellant selection was based on three criteria: base ingredients, production-established solvent systems, and grade of nitrocellulose (NC). Selected propellants (chosen to represent the bulk of the propellants available for reclamation) contain at least one of the three base ingredients: NC, nitroglycerin (NG), and/or nitroguanidine (NQ). Single-base propellant contains NC; double-base propellant contains NC and NG; and triple-base propellant contains NC, NG, and NQ. The solvent systems were chosen to be compatible with existing production solvent systems at RAAP. The grade of NC, i.e., nitrogen (N) content, determines the resolvation capability of the propellant; for example, triple-base M30 (12.6%N) propellant more easily resolvates than single-base M1 propellant (13.15%N) which consists of a blend of 12.5%N and 13.4%N NC.

2.2 Solvation of Propellants

The ingredient that mainly affects solvation capability of propellants is NC, a binder yielding gaseous decomposition products and energy during the ballistic cycle. The %N and viscosity (a measure of chain length or molecular weight) of the NC determine the solvent/solvent and solvent/propellant ratios required to properly solvate the propellant ingredients in a mix. Proper ratios are necessary to ensure optimal processing of the propellant in subsequent manufacturing operations, e.g., blocking, extruding, cutting, and solvent removal. Single-base propellant solvent removal is accomplished in the solvent recovery, water dry, and air dry operations with the exception of M10 flake propellant; the solvents in M10, as well as all multi-base propellants, are removed in a forced air dry (FAD) facility.

Various solvent systems can be used in propellant manufacturing. For instance, an ether/ethanol system is used at RAAP for the production of single-base and certain double-base propellants. An acetone/ethanol system is used for other double-base and triple-base propellants. In order to ensure compatibility with standard production processes at RAAP, e.g., solvent removal, only those solvents used in the original manufacture of the propellants were considered in this study. The production solvent systems in use at RAAP were selected on the basis of the NC blends (including %N and viscosity parameters) required to yield specific physical characteristics of the individual propellants.

When certain solvent systems are used, the %N of the NC determines the amount of NC that is soluble. For example, NC having 10 to 12.6%N is soluble in a 2/1 ether/ethanol solvent system, whereas NC having >13%N or <10%N is not soluble. However, acetone dissolves NC having >10%N.[2] Furthermore, as the %N decreases, solubility increases causing the propellant to burn slower, thereby affecting the burning rate of the propellant.

Dilute solutions of NC (low viscosity) exhibit Newtonian behavior in that the rate of flow is proportional to the applied stress or pressure. On the other hand, non-dilute solutions of NC (high viscosity) exhibit non-Newtonian behavior. In non-dilute solutions of NC, the NC micelles (i.e., an ordered collection of submicroscopic fibrils) are more aligned, or parallel, than those in dilute solutions; this alignment is due to the restricted physical space available for the micelles to migrate and possibly become misaligned. The relationship of viscosity to tensile strength and micelle elongation is proportional, i.e., as viscosity increases, the tenacity of the micelle directional alignment also increases. During extension (stretching) of an NC film, which results in elongation of the micelles, additional alignment of the micelles also occurs, e.g., the more amorphous the initial state of the NC film, the greater the tensile strength which is developed by extension because the micelles are aligned in a parallel fashion. NC films prepared with ether/ethanol are more amorphous than NC films prepared with acetone. When acetone is used, the extension is reduced and less opportunity is provided for the micelles to align in a parallel manner, resulting in lower tensile strength; when rupture occurs, a greater portion of the micelles are perpendicular to the axis of stress. As evidence by the above discussion, the strength of NC films can be adjusted by the choice of solvent system.[2]

In the manufacture of propellant at RAAP, NC is blended to specified %N and viscosity to yield desired physical characteristics of the propellants during and following processing. Solvent systems are selected to aid in obtaining these desired characteristics. It must be noted that much of the biological structure of the original cellulose is retained in the NC. Cellulose fibers are comprised of layered structures of fibrils, which are in turn composed of ordered layers of molecules. For example, single-base propellants utilize 13.15%N in the NC blends and an ether/ethanol solvent system of approximately 2/1 to dissolve (gelatinize) the NC. As shown in figure 1, not all of the NC is gelatinized, a desirable characteristic in that a certain quantity of undissolved, intact NC fibers enhance subsequent propellant processing by minimizing mechanical disintegration of the colloid.[2] Since NC is the primary ingredient of single-base propellant, the ether/ethanol solvent system is desirable for ease of solvent removal.

Acetone, on the other hand, has been shown to be the most effective solvent for NC. In the early years of propellant development, acetone was rare and expensive whereas the ether/ethanol system was manufactured from ethanol feedstock. Process developments for acetone production subsequently accelerated the development of multi-base propellants. The interaction between acetone and the NC is not restricted to the external surface (outer layers) of the NC; even when the amount of acetone is relatively small, the acetone is absorbed in the interior and penetrates between the molecular chains, increasing the spacing between them. This phenomenon, termed swelling, takes place at random and is limited by the replacement of the hydroxyl groups by other groups that endow the molecule with solubility. If the physical conditions of the replacement reaction are uneven, the distribution of substituent groups may be so irregular that one section of a chain may be soluble (particularly a section in a disorganized region of a chain) while another section (probably in an organized region of a chain where penetration of the solvent has not been as effective) may not have undergone enough replacements to enable it to dissolve; here the residual hydroxyl groups may be numerous enough to prevent the chains from separating. With a greater amount of acetone, the molecular array becomes confused, the chain alignment is lost, and a gelatinous mass of no regular structure results. Finally, when an excess of solvent has been added, the molecules are completely separated and a true solution is formed.[2]

In the manufacture of double- and triple-base propellants, NG also serves as a plasticizing agent, i.e., solvent. Since varying the content of NG has profound effects on propellant physical properties, e.g., burning rate, brittleness, and tensile strength, F. S. Baker conducted dielectric studies to determine the manner in which the NG is dispersed in the NC matrix.[3] Baker, assuming that the cellulose structure is preserved in the manufacture of NC, further supposed that there existed a limited number of sites possessing high interaction energies. As NG is added to the NC, site occupancy is increased towards monolayer coverage, with monolayer coverage anticipated at an NG concentration of ~25%. Addition of NG in excess of 27% leads to multilayer adsorption; above 30% the available sites are completely filled, indicating that NG is relatively inefficient as a plasticizer. In the production of propellants, therefore, acetone is used to swell the NC, thereby exposing more sites for NG adsorption. Furthermore, since NQ is not solubilized in any of the solvents used at RAAP, the additional swelling provided by the acetone permits the NQ to be interdispersed in the NC/NG triple-base propellant matrix.

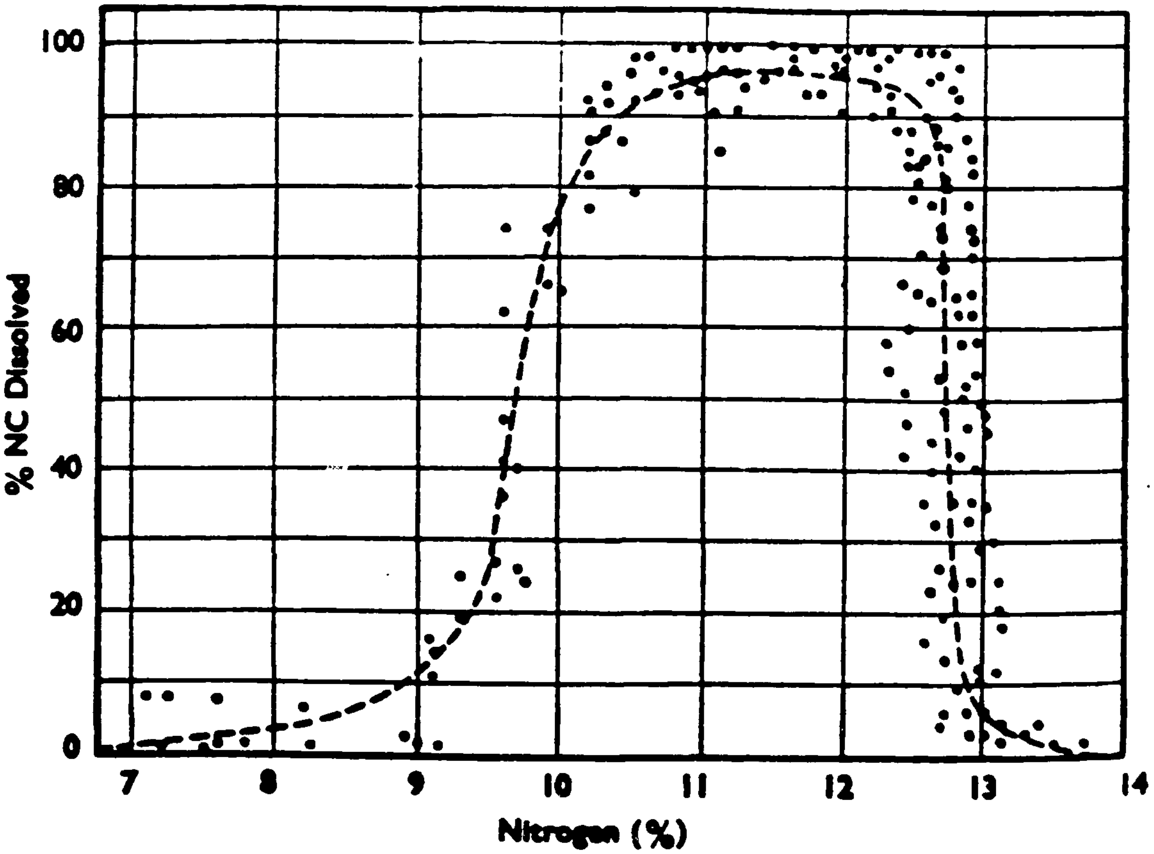

Figure 1. Nitrogen content and solubility in ether/ethanol solvent system (2/1 ratio)

The solvent/propellant ratios are also determined by the NC content of the propellant, i.e., the greater the NC content, the greater the amount of solvent required to dissolve the NC. The solvent/propellant ratios must be closely controlled because of their effect on solvent removal which in turn affects propellant physical characteristics and ballistics. Ethanol is used as a wetting agent to remove water from the NC and to prevent immediate plasticization of the micelles' outer surfaces on the addition of ether or acetone. For single-base propellants, ~10 lb of ethanol is added per 38 lb NC,[4] which dictates the solvent/propellant ratio. For multi-base propellants, the %N in the NC and the NG content determines the solvent/propellant ratio. For multi-base propellants produced at RAAP, the average solvent/propellant ratio is 0.2/1.

A compendium of terms describing the degrees of propellant resolvation is shown in table 1. These terms describe the various states of solvation to attain the desired colloidal system which is the intimate mixture of two substances, one of which, called the dispersed phase or colloid (propellant), is uniformly distributed in a finely divided state throughout the second substance, the dispersion medium (solvents). The terms listed describe the degree of propellant solvation in the order as it occurs in the mixing process. Several terms are combined defining the various stages of solvation. One set of terms occurs twice since the propellant will undergo these stages before and/or after the desired condition of plasticity is attained due to the production mix cycle requiring an over-solvation step and a drydown step (solvent removal by vaporization).

2.3 Resolvation Time

A 90-min time frame for resolvation was considered adequate to permit introduction of the resolvated propellants into the standard manufacturing processes. The average production mix cycle time for single-base propellant is 15 min whereas the average mix cycle for multi-base propellant is 180 min. Mix cycle times of 90 min, i.e., the mean of the single- and multi-base propellant cycle times, were chosen. Furthermore, during normal production, remix of single-base propellant, e.g., press heels and rework from subsequent cutting operations, requires additional mixing time (>15 min) due to the 13.15%N NC and the 87%+ NC content in the propellant whereas multi-base rework usually does not require additional mixing time.

2.4 Operating Parameter Evaluations

Four particle sizes, based on the test plan,[5] were evaluated to assess the effect of particle size on propellant resolvation: whole grain, crushed, coarsely ground, and finely ground. The various particle sizes are defined as follows: whole grain as propellant requiring no preparation; crushed as propellant grain slivers passed through a torn screen on a Wiley mill; coarsely ground as propellant retained on a

Table 1. Compendium of terms describing various states of propellant resolvation

Degree of solvation in order as it occurs in the mixing process	Term	Definition
1	Excess solvent	Solvent not absorbed in propellant.
2	Grainy	Unsolvated propellant pieces having a texture of fine particles determined by tactile quality (for flake, crushed, or ground propellants).
	or	
	Grainy centers	Unsolvated centers of propellant grains having a texture of a small hard particle determined by tactile quality (for whole grain propellants).
3	Poor consistency	Solvent not distributed over propellant evenly, thereby producing various anomalies such as grainy pockets in the propellant sample.
4	Softening depth	Percentage of the grain that contains dispersed solvents which is measured by visual and tactile qualities and by propellant grain length to diameter (OD) at the end of the test (for whole grain propellants).
5	Grainy-plasticity	A combination of grainy and plasticity qualities are observed in the propellant sample (for flake, crushed, or ground propellants).
	or	
	Grainy centers-plasticity	A combination of grainy centers and plasticity qualities are observed in the propellant sample (for whole grain propellants).
6	Poor consistency-plasticity	A combination of poor consistency and plasticity qualities are observed in the propellant sample.

Table 1. (cont)

Degree of solvation in order as it occurs in the mixing process	Term	Definition
7	Doughy	Propellant is a dough free of unsolvated propellant particles but is not pliable or workable due to insufficient solvent in mixing resulting in the dough not having the desired plastic quality.
	or	
	Spongy	Swelling of the propellant from the absorption of solvent resembling elastic, porous, and absorbent characteristics due to the propellant being over-solvated.
	Plasticity	Propellant is pasty (soft mixture capable of being molded or modeled of uniform composition) or elastic (capable of being flexible by being pliable when molded or modeled) forming a colloidal system that resembles a pliable, workable dough free of unsolvated propellant particles. This condition is the desired end product of resolvating propellants.
8	0-75 %	
	or	
9	75-100%	
10	Doughy or Spongy	See degree of solvation number 7.

20-mesh screen; and finely ground as propellant passed through a 20-mesh screen and retained on a 50-mesh screen. Figures 2 through 5 are representative photographs of the four particle sizes evaluated in this study.

The evaluations of production-established solvent/propellant ratios showed that increasing the amount of solvent enhanced propellant resolvation. The original intent was to vary the established RAAP production ratios in incremental steps of ± 5%; however, single-base propellants resolvated more easily with increased (i.e., greater than production-established ratios) solvents whereas most of the multi-base propellants resolvated using production-established or slightly increased solvent/propellant ratios. Established production solvent/solvent ratios, i.e., ether/ethanol and acetone/ethanol, are used at RAAP for the manufacture of single- and multi-base propellants, respectively; these ratios, of course, are dependent on the specific formulation of propellant to be produced. As in the solvent/propellant ratio evaluations, the original intent was to vary the production-established ratio (i.e., 70/30 ether/ethanol) in incremental steps of ± 5%. However, preliminary testing of the worst-case propellant, M10, which has the greatest NC content, indicated that deviation from the production-established ratio was not necessary since a solvent/propellant ratio of 1.25/1 successfully resolvated the propellant. A solvent/propellant ratio of 1.5/1, i.e., additional solvent, was required for resolvation of the propellant using a solvent/solvent ratio of 65/35 ether/ethanol. Based on these results, all propellants were resolvated using production-established solvent/solvent ratios.

Prior to resolvation, all propellants were analyzed for applicable formulation-specific chemical ingredients; lists of single- and multi-base propellant ingredients and their functions are presented in tables 2 and 3, respectively. The chemical analyses of M1, M6, and M10 single-base propellants are presented in tables 4, 5, and 6, respectively. The only propellant ingredient out of specification according to MIL-STD-652D is diphenylamine (DPA) in two of the single-base propellants: M1 multi-perforated propellant for the 155-mm gun system (designated M3A1, lot number 60710) and M6 multi-perforated propellant for the 155-mm gun system (designated M119, lot number 69877). Since these propellants are old lots and the DPA level is not below 0.2%, these are acceptable propellants in that the amount of DPA loss is well within the limits established in the storage specifications delineated in the applicable US Army/Hercules Incorporated contractual agreement.

The chemical analyses of M2, M7, and M9 double-base propellants are presented in tables 7, 8, and 9, respectively. NG content is 0.05% low for the M2 propellant lot, which is not a problem due to storage specification requirements, i.e., a certain percentage of NG loss is permissible during storage. The ethyl centralite (EC) content for the M7 propellant lot was low; however, since this propellant is a current production item, this lot was blended to meet military specifications.

The chemical analyses of M30, M30A1, and M31A1 triple-base propellants are presented in tables 10, 11, and 12, respectively. As shown, none of the propellant ingredients were out of specification.

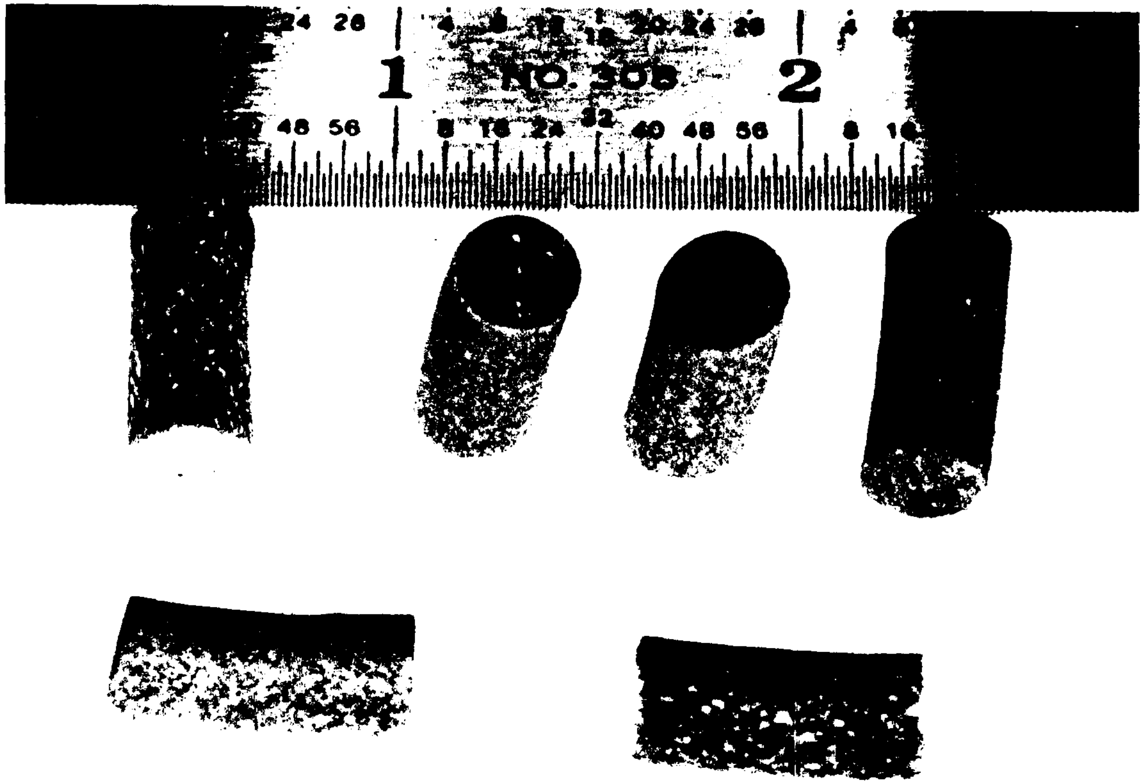

Figure 2. Whole grain M6 single-base propellant

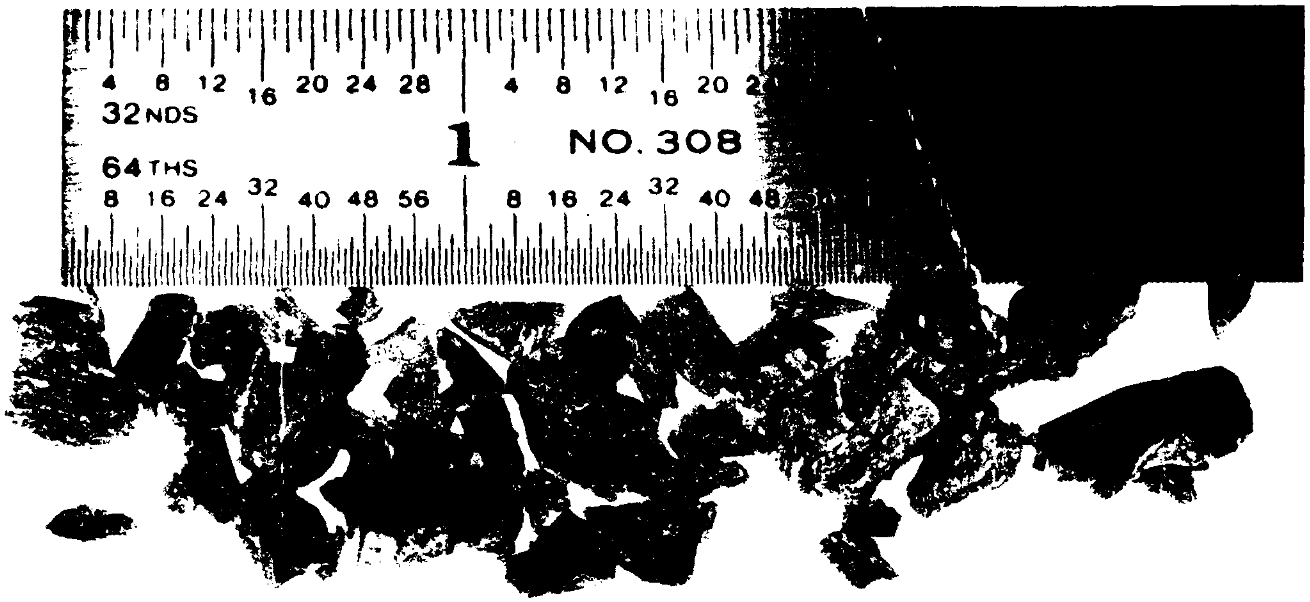

Figure 3. Crushed M6 single-base propellant (passed through torn screen)

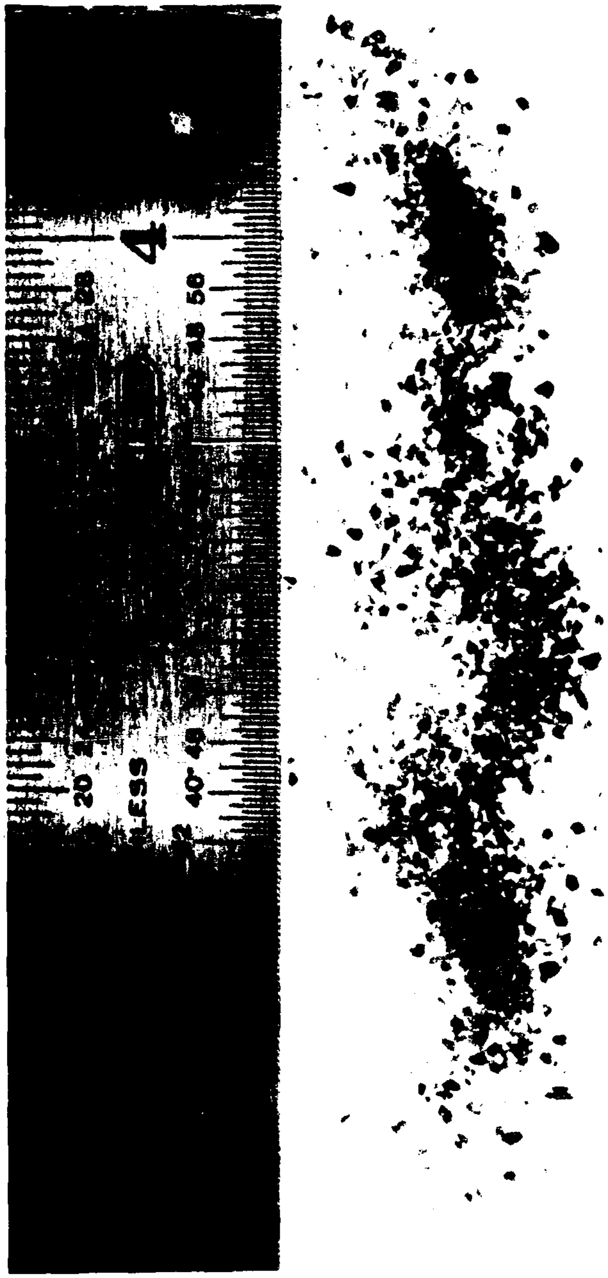

Figure 4. Coarsely ground M6 single-base propellant (retained on 20-mesh screen)

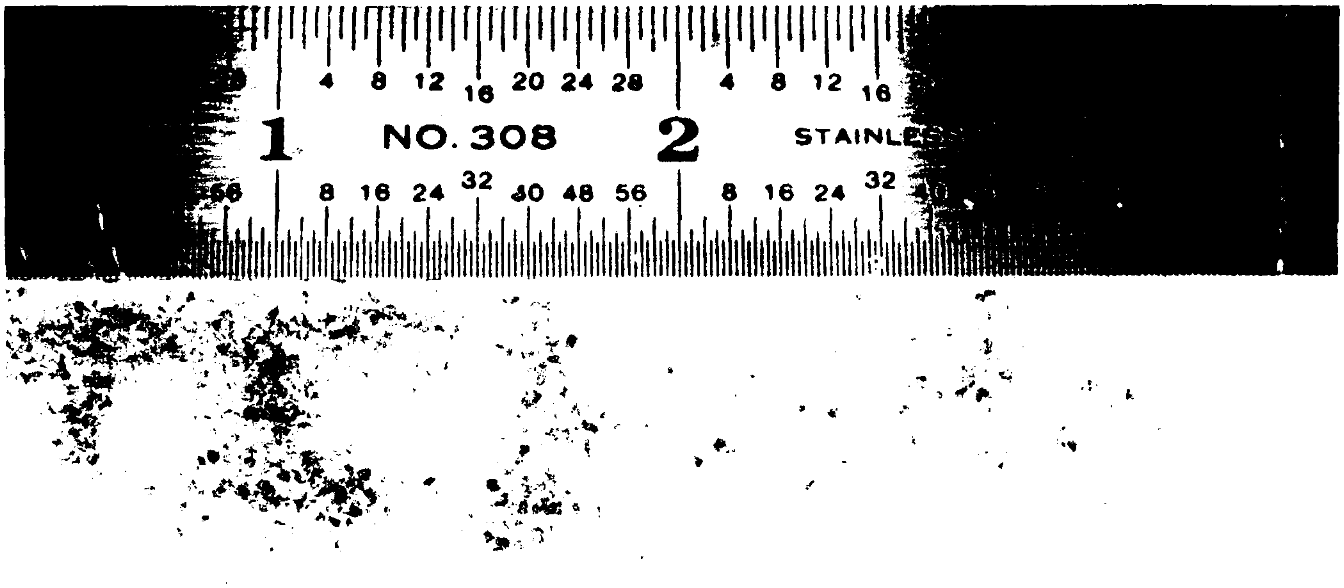

Figure 5. Finely ground M6 single-base propellant (passed through 20-mesh screen and retained on a 50-mesh screen)

Table 2. Single-base propellant ingredients and functions

Ingredient	Function
Nitrocellulose (NC)	A base ingredient that is a binder. Yields gaseous decomposition products and energy.
Dibutylphthalate (DBP)	Plasticizer. Peptizes binders such as NC so that fibers form plastics such as propellant. Improves mechanical properties such as promoting increased elongation. Decreases energy. Decreases hygroscopicity.
Dinitrotoluene (DNT)	Like DBP, it acts as a high boiling plasticizer-solvent, which aids in conferring upon the propellant its properties of non-hygroscopicity and flashlessness.
Diphenylamine (DPA)	Stabilizer. Acquires decomposition products to inhibit decomposition and decreases energy.
Potassium sulfate (K_2SO_4)	Flash and smoke reducers to inhibit completion of combustion and reduce flash (associated with radar detection). Particle size is important. Provides some energy.
Graphite	Acts as a lubricant, thereby increasing loading density. Also acts as a conductor for static electricity.
Ethanol (ethyl alcohol)	Used in propellant manufacturing to gelatinize 12.6% N NC. Ether is required with ethanol for NC having a higher nitrogen content.
Ether (diethyl ether)	Used in propellant manufacturing required with ethanol to gelatinize NC so that other ingredients can be bound into it. Ether alone will not dissolve NC with any nitrogen content.
Water (H_2O)	Used in propellant manufacturing to keep NC wet and to purify. Keeps NC fibers from becoming tightly knit. Aids in cross linking NC so that processing is facilitated.

Table 3. Multi-base propellant ingredients and functions

Ingredient	Function
Nitrocellulose (NC)	A base ingredient that is a binder. Yields gaseous decomposition products and energy.
Nitroglycerin (NG)	A base ingredient that yields gaseous decomposition products and energy.
Nitroguanidine (NQ)	A base ingredient that yields gaseous decomposition products and energy. Gases are cool and much less gun barrel erosion is obtained than with other propellant bases.
Dibutylphthalate (DBP)	Plasticizer. Peptizes binders such as NC so that fibers form plastics such as propellant. Improves mechanical properties such as promoting increased elongation. Decreases energy. Decreases hygroscopicity.
2-nitrodiphenylamine (2-NDPA)	Stabilizer. Acquires decomposition products to inhibit decomposition and decreases energy. (Also acts as rate modifier.)
Ethyl centralite (EC)	Stabilizer. Acquires decomposition products to inhibit decomposition and decreases energy.
Potassium perchlorate ($KClO_4$)	A burning rate modifier that promotes high rate for rockets. Also contributes energy.
Potassium sulfate (K_2SO_4) and barium nitrate [$Ba(NO_3)_2$]	Flash and smoke reducers to inhibit completion of combustion and reduce flash (associated with radar detection). Particle size is important. Provides some energy.
Cryolite	Flash reducer, insoluble in water. Therefore, cryolite is good for slurry mix operations.
Graphite (glaze)	Acts as a lubricant, thereby increasing loading density. Also acts as a conductor for static electricity.

Table 3. (cont)

Carbon black	Increases rate of burning. Opacifies and prevents subsurface burning.
Ethanol (ethyl alcohol)	Used in propellant manufacturing to gelatinize NC.
Acetone	Gelatinizes (peptizes) NC so that other ingredients can be bound into it.
Water (H_2O)	Used in propellant manufacturing to keep NC wet and to purify. Keeps NC fibers from becoming tightly knit. Aids in cross linking NC so that processing is facilitated.

Table 4. Chemical analyses of M1 single-base propellant

Propellant ingredient/ characteristic	Specification requirement	M1 f/155mm M3A1 lot no. 60710[a]	M1 f/155mm M3A1 lot no. 65418[b]
Nitrocellulose (NC)	85.00 ± 2.00%	85.09%	84.75%
Dinitrotoluene (DNT)	10.00 ± 2.00%	10.09%	9.46%
Dibutylphthalate (DBP)	5.00 ± 1.00%	4.62%	4.77%
Diphenylamine (DPA)	1.00 + 0.20, -0.10%	0.85%	1.04%
Potassium sulfate (K_2SO_4)	1.00 ± 0.30%	1.07%	1.02%
Hygroscopicity	-	0.81%	0.86%
Total volatiles (TV)	-	0.96%	0.60%
Moisture (H_2O)	0.60 ± 0.20%	0.68%	0.52%
Residual solvent (RS)	0.80% maximum	0.28%	0.08%
Stability			
Color change	No color change in 40 min (minimum)	55 min	>60 min
Explosivity	Shall not explode in <5 h	>5 h	>5 h

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[a] Multi-perforated.
[b] Single-perforated.

Table 5. Chemical analyses of M6 single-base propellant

Propellant ingredient/ characteristic	Specification requirement	M6 f/155mm M119 lot no. 69877*
Nitrocellulose (NC)	87.00 ± 2.00%	87.55%
Dinitrotoluene (DNT)	10.00 ± 2.00%	9.54%
Dibutylphthalate (DBP)	3.00 ± 1.00%	2.91%
Diphenylamine (DPA)	1.00 + 0.20, -0.10%	1.16%
Potassium sulfate (K_2SO_4)	1.00 ± 0.30%	0.93%
Hygroscopicity	-	0.80%
Total volatiles (TV)	-	1.57%
Moisture (H_2O)	0.60 ± 0.20%	0.41%
Residual solvent (RS)	1.10% maximum	1.16%
Stability		
Color change	No color change in 40 min (minimum)	>60 min
Explosivity	Shall not explode in <5 h	>5 h

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* Multi-perforated.

Table 6. Chemical analyses of M10 single-base propellant

Propellant ingredient/ characteristic	Specification requirement	M10 flake f/60mm M720 lot no. 7950018047
Nitrocellulose (NC)	98.00 ± 1.00%	98.24%
Diphenylamine (DPA)	1.00 ± 0.30%	0.82%
Potassium sulfate (K_2SO_4)	1.00 ± 0.30%	0.94%
Glaze (graphite)	0.20% maximum	0.09%
Hygroscopicity	-	1.66%
Total volatiles (TV)	1.80% maximum	0.93%
Moisture (H_2O)	-	0.87%
Residual solvent (RS)	-	0.06%
Stability		
Color change	No color change in 60 min (minimum)	>60 min
Explosivity	Shall not explode in <5 h	>5 h

Table 7. Chemical analyses of M2 double-base propellant

Propellant ingredient/ characteristic	Specification requirement	M2 f/165mm lot no. PE-132-S
Nitrocellulose (NC)	77.45 ± 2.00%	78.79%
(13.25 ± 0.05% N)		
Nitroglycerin (NG)	19.50 ± 1.00%	18.45%
Barium nitrate ($BaNO_3$)	1.40 ± 0.25%	1.31%
Potassium nitrate (KNO_3)	0.75 ± 0.25%	1.01%
Ethyl centralite (EC)	0.60 ± 0.15%	0.41%
Graphite	0.30 ± 0.10%	0.37%
Hygroscopicity	-	0.38%
Total volatiles (TV)	2.10% maximum	*
Moisture (H_2O), %	-	*
Residual solvent (RS)	-	*
Stability		
Color change	No color change in 40 min (minimum)	No color change detected >60 min
Explosivity	No fumes detected in 1 h	No fumes detected in 1 h

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* TV analyses in progress.

Table 8. Chemical analyses of M7 double-base propellant

Propellant ingredient/ characteristic	Specification requirement	M7 f/TOW launch lot no. current HPC lot (HPC65)
Nitrocellulose (NC) (13.15% N Lint.)	54.60% (nominal)	53.72%
Nitroglycerin (NG)	35.50% (nominal)	36.77%
Potassium perchlorate ($KClO_4$)	7.80% (8.05% maximum)	7.55%
Carbon black	1.20% (nominal)	1.17%
Ethyl centralite (EC)	0.90% (0.80% minimum)	0.72%
Hygroscopicity	-	0.65%
Total volatiles (TV)	0.80% maximum	0.36%
Moisture (H_2O)	-	-
Residual solvent (RS)	-	-
Stability		
Color change	No color change in 40 min (minimum)	No color change detected in >60 min
Explosivity	No fumes in 1 h	No fumes detected in 1 h

Table 9. Chemical analyses of M9 double-base propellant

Propellant ingredient/ characteristic	Specification requirement	M9 flake lot no. 65110
Nitrocellulose (NC) (13.25% N, visc. 8-25 s, solubility 36% maximum)	57.75 ± 1.5%	56.00%
Nitroglycerin (NG)	40.00 ± 1.5%	41.54%
Potassium nitrate (KNO_3)	1.50 ± 0.50%	1.67%
Ethyl centralite (EC)	0.75 ± 0.10%	0.74%
Glaze (graphite)	0.2% maximum	0.08%
Hygroscopicity	-	0.61%
Total volatiles (TV)	0.5% maximum	0.16%
Moisture (H_2O)	-	0.13%
Residual solvent (RS)	-	0.03%
Stability		
Color change	No color change in 40 min (minimum)	No color change detected in >60 min
Explosivity	No fumes detected in 1 h	No fumes detected in 1 h

Table 10. Chemical analyses of M30 triple-base propellant

Propellant ingredient/ characteristic	Specification requirement	M30 f/M490 lot no. 69903
Nitrocellulose (NC) (12.6% N)	28.0%	28.29%
Nitroglycerin (NG)	22.5%	22.51%
Nitroguanidine (NQ)	47.7%	47.49%
Ethyl centralite (EC)	1.5%	1.23%
Cryolite	0.3%	0.35%
Glazed (added)	0.2% maximum	0.19%
Hygroscopicity	-	0.42%
Total volatiles (TV)	0.50% maximum	0.18%
Moisture (H_2O)	-	-
Residual solvent (RS)	-	-
Stability		
Color change	No color change in 40 min (minimum)	No color change detected in >60 min
Explosivity	No fumes in 1 h	No fumes detected in 1 h

Table 11. Chemical analyses of M30A1 triple-base propellant

Propellant ingredient/ characteristic	Specification requirement	M30A1 f/155mm lot no. P0004
Nitrocellulose (NC) (12.6% N, visc. 8-20 s)	28.0%	27.14%
Nitroglycerin (NG)	22.5%	23.11%
Nitroguanidine (NQ)	47.0%	47.16%
Ethyl centralite (EC)	1.5%	1.41%
Potassium sulfate (K_2SO_4)	1.0%	1.08%
Glaze (added)	0.15%	0.13%
Hygroscopicity	-	0.38%
Total volatiles (TV)	0.50% maximum	0.16%
Moisture (H_2O)	-	-
Residual solvent (RS)	-	-
Stability		
Color change	No color change in 40 min (minimum)	No color change detected in >60 min
Explosivity	No fumes in 1 h	No fumes detected in 1 h

Table 12. Chemical analyses of M31A1 triple-base propellant

Propellant ingredient/ characteristic	Specification requirement	M31A1 f/8 in. lot no. 70077
Nitrocellulose (NC) (12.6% N, visc. 8-20 s)	20.0%	19.65%
Nitroglycerin (NG)	19.0%	19.53%
Nitroguanidine (NQ)	54.0%	53.78%
Dibutylphthalate (DBP)	4.5%	4.20%
2-nitrodiphenylamine (2-NDPA)	1.5%	1.72%
Potassium sulfate (K_2SO_4)	1.0%	1.00%
Glaze (added)	0.15% maximum	0.12%
Hygroscopicity	-	0.35%
Total volatiles (TV)	0.30% maximum	0.19%
Moisture (H_2O)	-	-
Residual solvent (RS)	-	-
Stability		
Color change	No color change in 40 min (minimum)	No color change detected in >60 min
Explosivity	No fumes in 1 h	No fumes detected in 1 h

2.5 Resolvation Testing Procedure

Prior to the propellant resolvation tests, hazards analysis evaluations were performed to assure proper handling and safety techniques of propellants. Applicable operating procedures were reviewed by the RAAP Hazards Analysis Department to ensure that specific safety precautions and controls were applied to each step of the laboratory resolvation studies. The detailed hazards analysis is included as appendix A.

Resolvation tests were conducted on each propellant by weighing a 50-g sample and placing the sample into a transparent polyethylene sample bag. The propellant sample bags (6-in. x 6-in. x 6-mil) have vapor seals that fold down for taping to prevent solvent losses. Preweighed solvents for testing solvent/propellant ratios in the specified solvent/solvent ratios of ether/ethanol or acetone/ethanol were then added to the sample and the bag sealed. The sample bag was then placed in a bottle on a viscosity mixer that continuously tumbled the sample at a rate of 3.5 rpm to assure coating of the propellant by the solvents; the laboratory mixing equipment used for these studies is shown in figure 6. The propellant/solvent sample was inspected at 15-min intervals to record the time and degree of resolvation.

The degree of resolvation was recorded per the terminology described in table 1. If necessary, grainy pockets in the propellant/solvent sample were removed by manually massaging the sample bag to assure an even distribution of solvents throughout the sample since no internal mixing, i.e., shearing action (work) imparted to the propellant via mixer blades, could be accomplished without solvent losses. Sample resolvation was discontinued when the sample attained the desired degree of resolvation or after 90 min of resolvation. Photographs of partially resolvated and acceptably resolvated M6 propellant are presented in figures 7 through 12; resolvation parameters are listed on the individual figures. If the sample resolvated, the density and flow characteristics (extrusion pressure and flow) of the sample were determined.

The density and flow characteristics of the resolvated propellant sample were determined using a plastic extruder (syringe), shown in figure 13, using the following known parameters: (1) volume, (2) weight, (3) total volatiles (TV), and (4) diameter as area of nozzle. The density of the sample was obtained by blocking the sample at 20 psig, which was the measured pressure applied to the air cylinder. Flow characteristics were determined by measuring the time required to extrude a strand and the length of the strand over predetermined pressure ranges. Propellant flow curves were generated and compared to actual production mixes (baseline data) to aid in determining if the sample was over- or under-solvated. Examples of these curves are shown in figures 14 and 15 for M1 and M6 propellants, respectively.

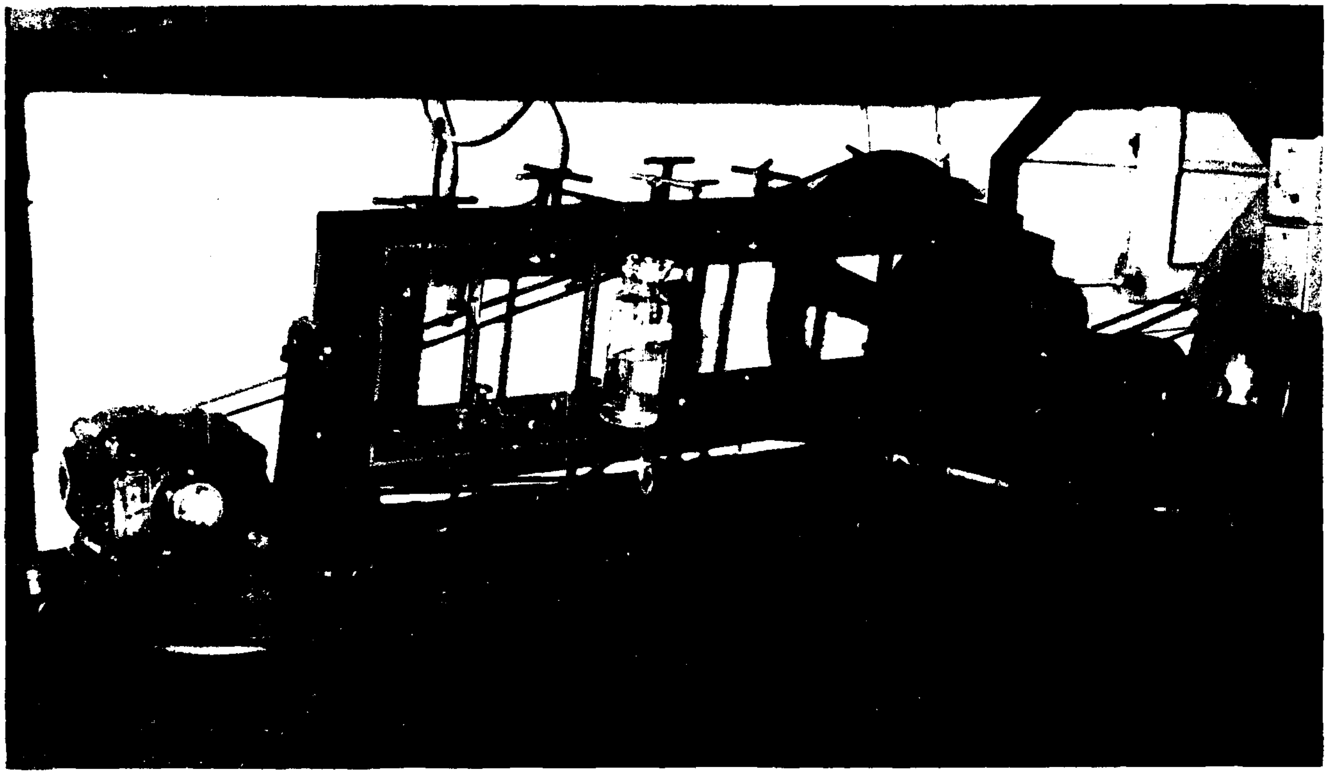

Figure 6. Laboratory mixing equipment used in resolvating propellant samples

Figure 7. Partially resolvated whole grain M6 propellant (1/1 solvent/propellant ratio and 65/35 ether/ethanol ratio after 90 min)

Figure 8. Partially resolvated crushed M6 propellant (1/1 solvent/propellant ratio and 65/35 ether/ethanol ratio after 90 min)

Figure 9. Resolvated coarsely ground M6 propellant (1/1 solvent/propellant ratio and 65/35 ether/ethanol ratio after 90 min)

Figure 10. Resolvated coarsely gorund M6 propellant (1/1 solvent/propellant ratio and 65/35 ether/ethanol ratio after 90 min) showing desired plasticity

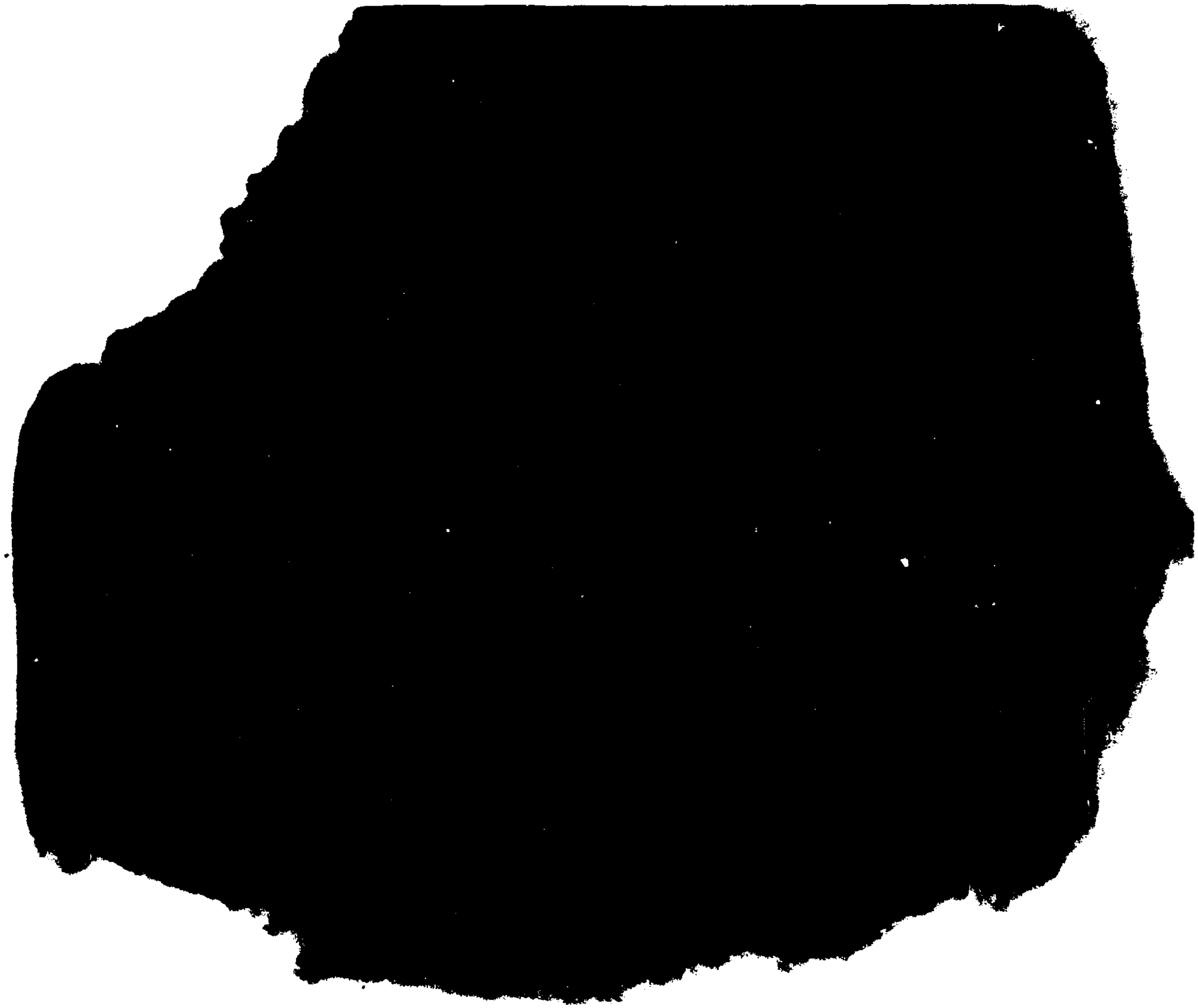

Figure 11. Resolvated finely ground M6 propellant (1/1 solvent/propellant ratio and 65/35 ether/ethanol ratio after 90 min)

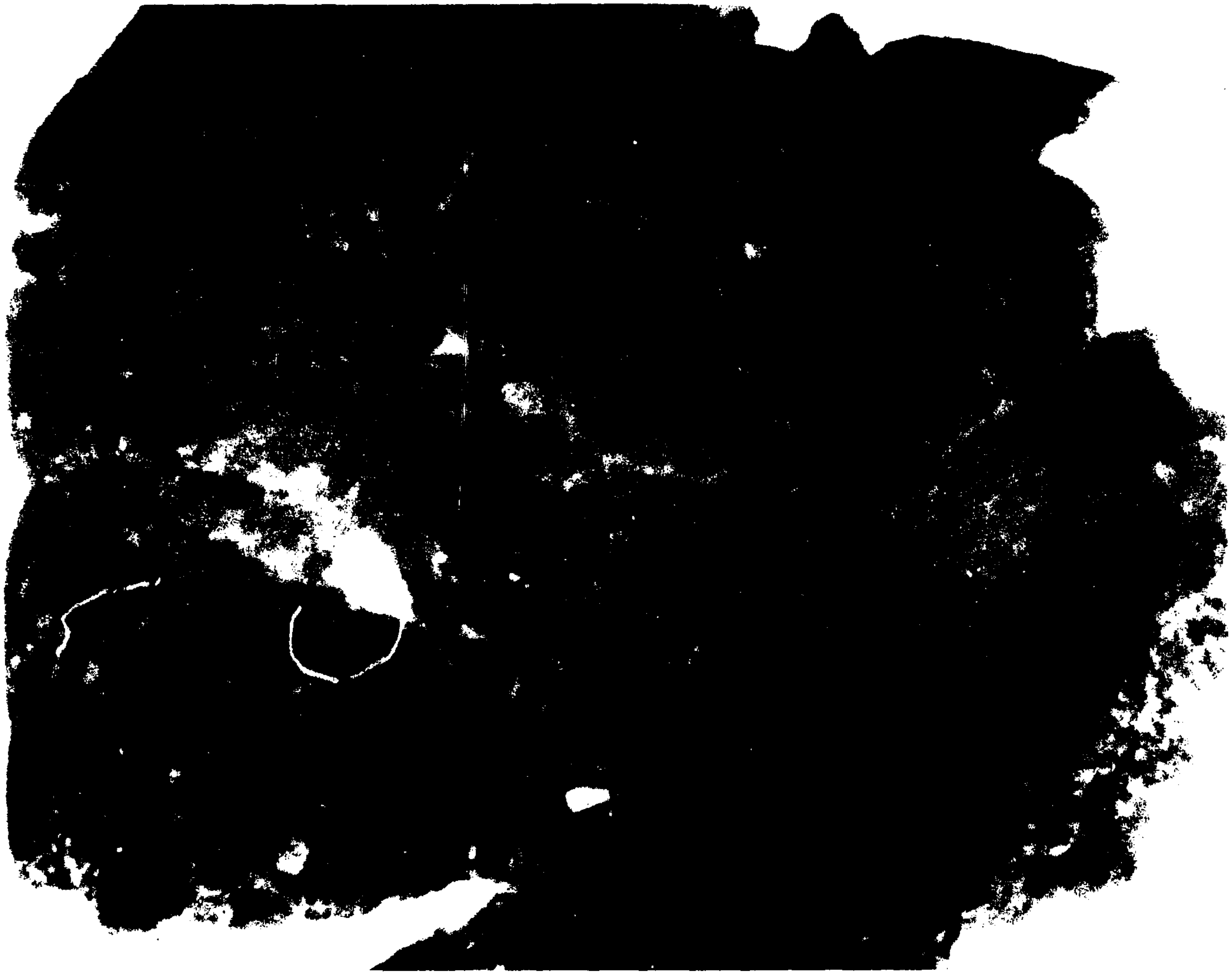

Figure 12. Resolvated finely ground M6 propellant (1/1 solvent/propellant ratio and 65/35 ether/ethanol ratio after 90 min) showing desired plasticity

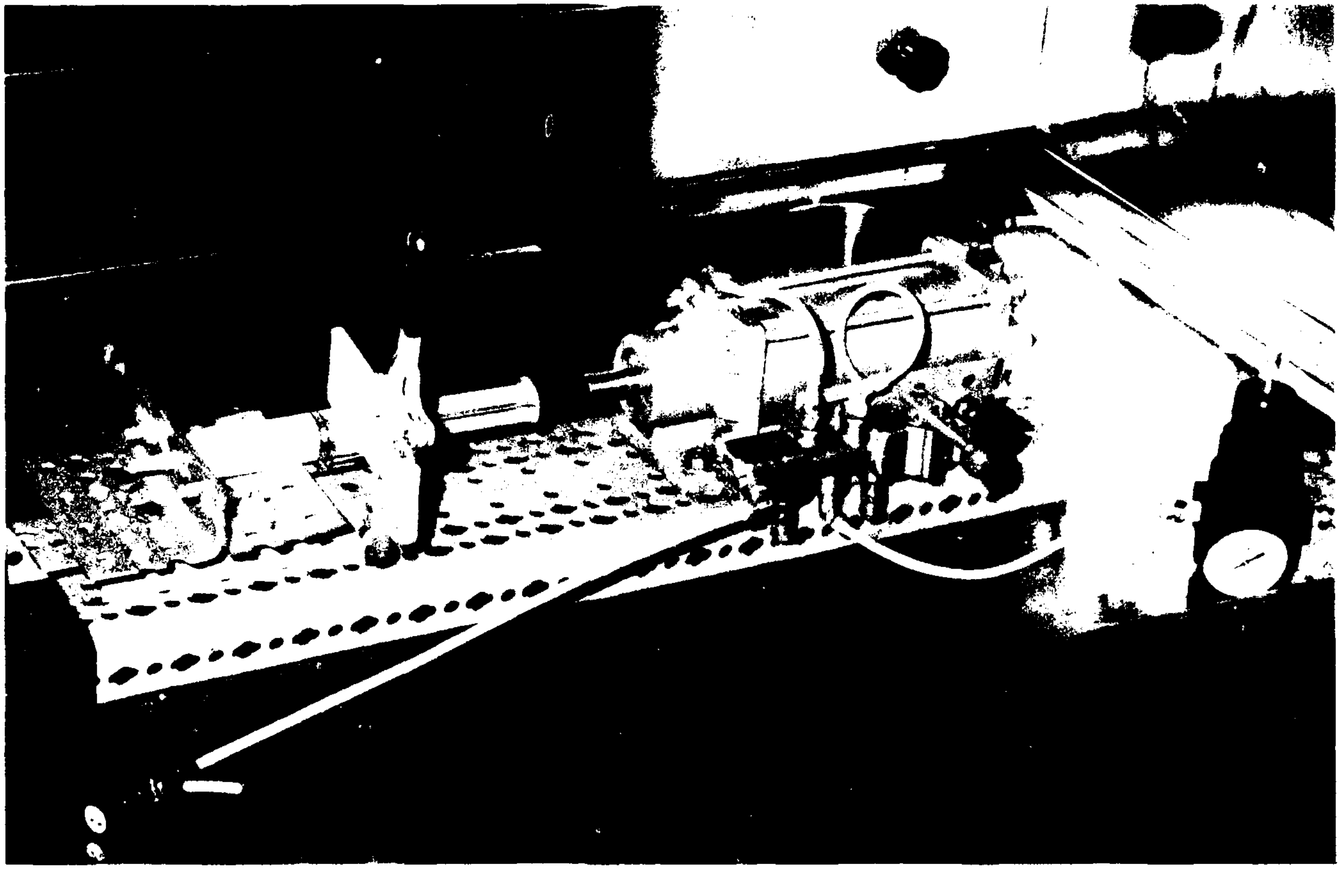

Figure 13. Plastic extruder for determining density and flow characteristics of resolvated propellant

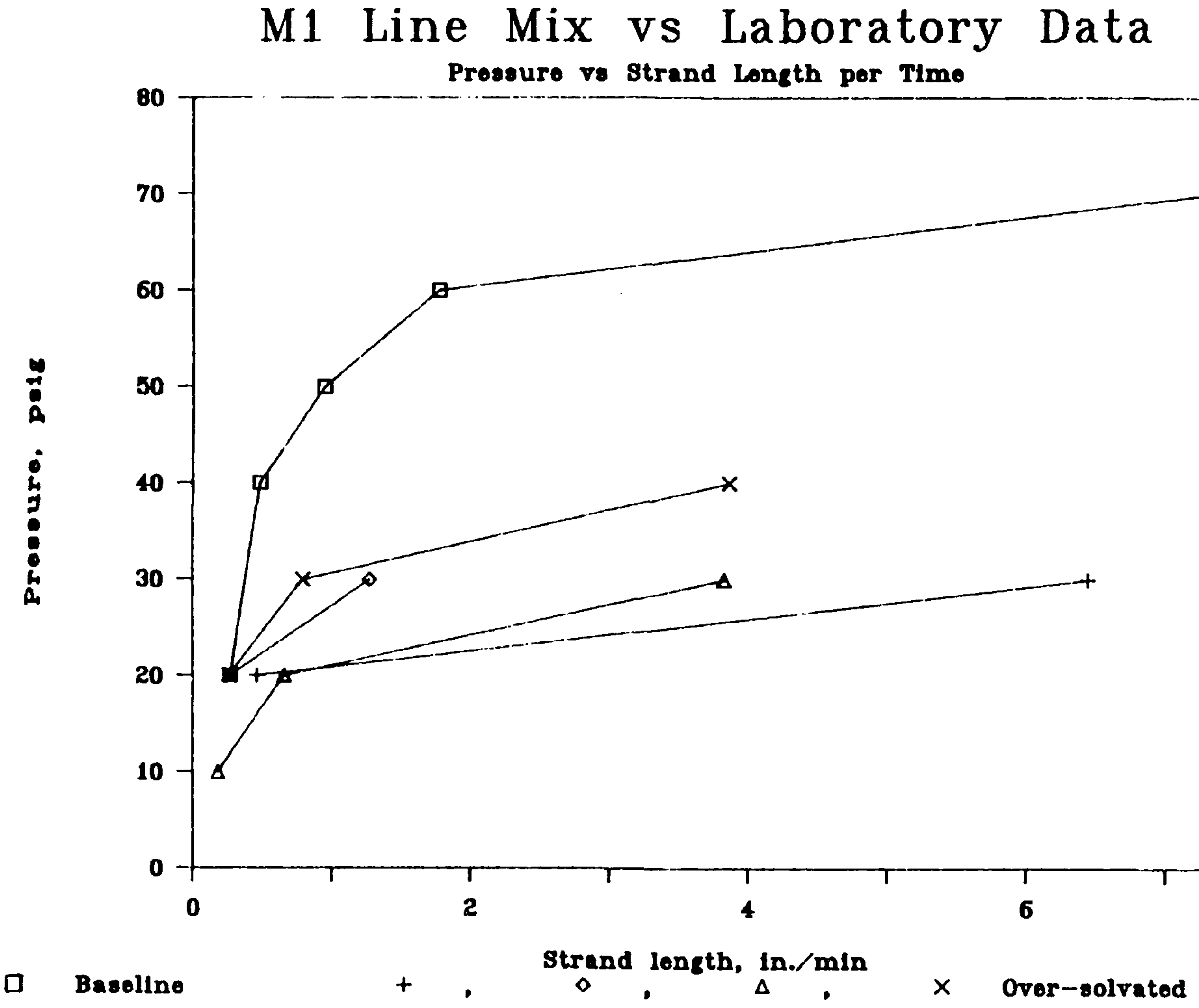

Figure 14. Flow characteristics of M1 single-base propellant

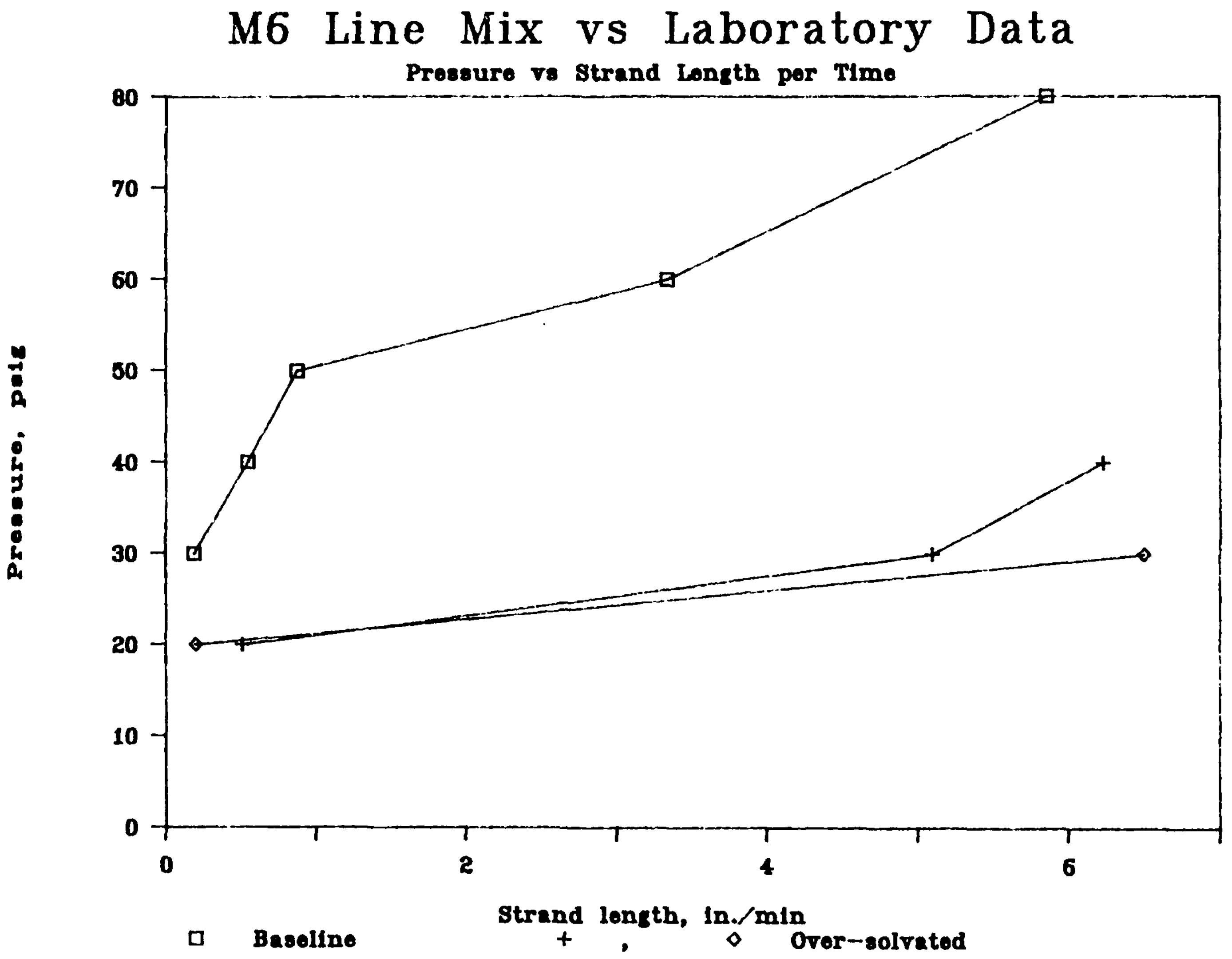

Figure 15. Flow characteristics of M6 single-base propellant

2.6 Results

Propellant resolvation tests were conducted with single-, double-, and triple-base propellants. The resolvation tests for single-base propellants were conducted using production-established solvent/solvent ratios of ether/ethanol designated for each individual propellant. The resolvation tests for the double- and triple-base propellants were conducted using formulation-specific, production-established solvent/solvent ratios of acetone/ethanol. The complete laboratory resolvation results for the four propellant particle sizes of each of the propellants have been summarized in table 13 to facilitate the following discussions. For each of the propellants discussed below, the degree of solvation attained is presented graphically in an accompanying figure; a description of each degree of solvation is presented in table 1. The degrees of solvation described in this table were delineated in order to accurately describe the stages of solvation which normally occur during mixing of propellants in the standard manufacturing processes. The desired degree of solvation, i.e., the plasticity necessary to introduce the resolvated propellant into the standard manufacturing processes, shown in each figure is 9.

The single-base M1 propellant (both single- and multi-perforated) whole grains were not crushed because the whole grain itself is representative of the crushed sample size (fig. 16). The resolvation of M1 multi-perforated propellant was conducted at solvent/propellant ratios of 1/1, 1.25/1, and 1.5/1. The coarsely and finely ground samples resolvated in 90 min at the production-established solvent/solvent ratio of 65/35 (ether/ethanol) for solvent/propellant ratios of 1/1 and 1.25/1. As evidenced by the degree of solvation represented by the y-axis in figure 17, only 60% plasticity or resolvation of the whole grain/crushed M1 multi-perforated sample occurred in 90 min. As shown in figure 18, the resolvation of M1 single-perforated propellant occurred for the whole grain/crushed and ground samples within 90 min for the solvent/propellant ratio of 1/1 at the production-established solvent/solvent (ether/ethanol) ratio of 65/35 except for one ground sample. For the whole grain/crushed and ground M1 single-perforated samples at a solvent/propellant ratio of 1.25/1 and whole grain/crushed sample at a solvent/propellant ratio of 1.5/1, resolvation did not occur within 90 min due to inadequate mixing (figs. 19 and 20); therefore, these tests were repeated. The whole grain/crushed samples did not resolvate whereas the ground samples resolvated within the 90-min time frame for solvent/propellant ratios of 1/1 (table 13).

The resolvation of M6 single-base propellant occurred for the coarse and finely ground samples within the allotted 90-min time frame for all three solvent/propellant ratios of 1/1, 1.25/1, and 1.5/1 (figs. 21 through 24) for the production-established solvent/solvent ratio of 65/35 (ether/ethanol). Only one each of the coarse and finely ground samples did not resolvate in 90 min for the solvent/propellant ratio of 1/1. These tests were repeated since inadequate mixing occurred; the samples resolvated within the 90-min time frame. The whole grain and crushed M6 propellant samples did not completely resolvate in 90 min at various solvent/propellant ratios (table 13).

Table 13. Results of laboratory resolvation study for various propellant particle sizes

Product	Propellant type	Solvent/solvent ratio[a]	Whole grain		
			Solvent/propellant ratio	No. of tests	Status
M10 (flake)	single-base	70/30	1/1	2	US[b]
			1.25/1	3	R[c]
			1.5/1	1	R
M6	single-base	65/35	1/1	1	US
			1.25/1	1	US
			1.5/1	1	US
			1.75/1	1	US
M1 single-perf	single-base	65/35	1/1	4	R
			1.25/1	3	R(b)[d]
			1.5/1	1	US
M1 multi-perf	single-base	65/35	1/1	2	US
			1.25/1	1	US
			1.5/1	1	US
M2	double-base	56/44	0.4/1	1	US
			0.6/1	1	US
			0.8/1	1	US
M9 (flake)	double-base	44/56	0.4/1	3	R
			0.6/1	2	R
			0.8/1	1	OS[e]
M7 (stick)	double-base	49/51	Whole grain particle size is stick; therefore, sample had to be crushed.		
M30	triple-base	40/60	0.4/1	1	US
			0.6/1	1	US
			0.8/1	1	US
			1/1	1	US

Table 13. (cont)

Product	Propellant type	Solvent/solvent ratio[a]	Whole grain		
			Solvent/propellant ratio	No. of tests	Status
M30A1	triple-base	40/60	0.4/1	1	US
			0.6/1	1	US
			0.8/1	1	US
			1/1	1	US
M31A1	triple-base	45/55	0.6/1	1	US
			0.75/1	1	US
M10 (flake)	single-base	70/30	Whole grain particle size also represents crushed particle size.		
M6	single-base	65/35	1/1	1	US
			1.25/1	1	US
			1.5/1	2	US
			1.75/1	1	US
M1 single-perf	single-base	65/35	Whole grain particle size also represents crushed particle size.		
M1 multi-perf	single-base	65/35	Whole grain particle size also represents crushed particle size.		
M2	double-base	56/44	0.8/1	1	US
			1/1	1	US
M9 (flake)	double-base	44/56	Whole grain particle size also represents crushed particle size.		
M7 (stick)	double-base	49/51	0.4/1	3	R(b)
			0.6/1	1	R
			0.8/1	1	R

Table 13. (cont)

Product	Propellant type	Solvent/solvent ratio[a]	Whole grain Solvent/propellant ratio	 No. of tests	 Status
M30	triple-base	40/60	0.4/1	1	US
			0.5/1	1	US
M30A1	triple-base	40/60	0.4/1	1	R(b)
			0.8/1	1	US
M31A1	triple-base	45/55	0.6/1	1	US
			0.7/1	1	R(b)
			0.75/1	1	US
			0.8/1	1	US
M10 (flake)	single-base	70/30	Whole grain particle size also represents coarsely ground particle size.		
M6	single-base	65/35	1/1	3	R
			1.25/1	1	R
			1.5/1	1	R
M1 single-perf	single-base	65/35	1/1	2	R(b)
			1.25/1	1	OS
M1 multi-perf	single-base	65/35	1/1	3	R(b)
			1.25/1	2	R
M2	double-base	56/44	0.4/1	1	US
			0.6/1	1	US
			0.8/1	3	R
M9 (flake)	double-base	44/56	Whole grain particle size also represents coarsely ground particle size.		
M7 (stick)	double-base	49/51	0.2/1	1	US
			0.4/1	3	R(b)
			0.6/1	2	R

Table 13. (cont)

Product	Propellant type	Solvent/solvent ratio^a	Finely ground		
			Solvent/propellant ratio	No. of tests	Status
M30	triple-base	40/60	0.2/1	1	US
			0.3/1	1	OS
			0.35/1	1	OS
			0.4/1	1	OS
			0.8/1	1	OS
			1/1	1	OS
M30A1	triple-base	40/60	0.2/1	1	US
			0.4/1	3	R
M31A1	triple-base	45/55	0.2/1	3	R(b)
			0.4/1	2	OS(b)^f
M10 (flake)	single-base	70/30	Whole grain particle size also represents finely ground particle size.		
M6	single-base	65/35	1/1	3	R(b)
			1.25/1	1	R
			1.5/1	1	R
M1 single-perf	single-base	65/35	1/1	4	R(b)
			1.25/1	2	OS(b)
			1.5/1	1	OS
M1 multi-perf	single-base	65/35	1/1	3	R(b)
			1.25/1	2	R
M2	double-base	56/44	0.4/1	1	US
			0.6/1	3	R(b)
			0.8/1	1	R
M9 (flake)	double-base	44/56	Whole grain particle size also represents finely ground particle size.		

Table 13. (cont)

Product	Propellant type	Solvent/solvent ratio[a]	Finely ground Solvent/propellant ratio	No. of tests	Status
M7 (stick)	double-base	49/51	0.2/1	1	US
			0.4/1	3	R(b)
			0.6/1	1	OS(b)
M30	triple-base	40/60	0.2/1	1	US
			0.3/1	1	US
			0.4/1	1	OS
			0.8/1	1	OS
			1/1	1	OS
M30A1	triple-base	40/60	0.2/1	1	US
			0.4/1	3	R
M31A1	triple-base	45/55	0.2/1	3	R(b)
			0.4/1	2	OS(b)

---

[a] Production-established solvent/solvent ratio for single-base propellants is ether/ethanol; production-established solvent/solvent ratio for multi-base propellants is acetone/ethanol.

[b] US = under-solvated propellant.

[c] R = resolvated propellant.

[d] R(b) = resolvated propellant having a borderline sample as one of the tests.

[e] OS = over-solvated propellant.

[f] OS(b) = over-solvated propellant having a borderline sample as one of the tests.

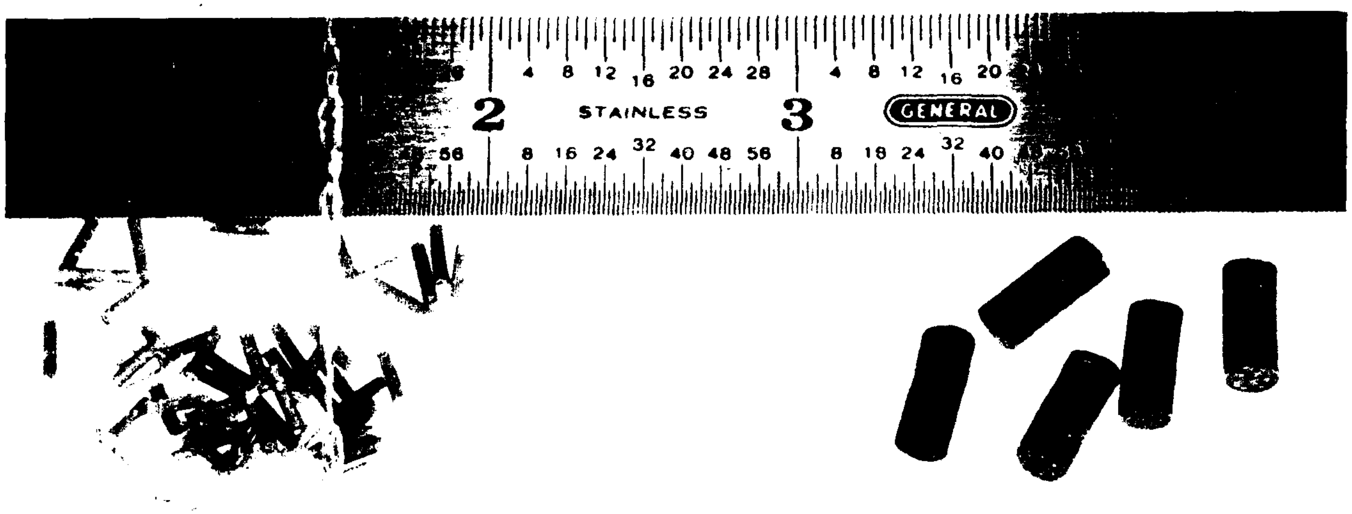

Figure 16. Single- and multi-perforated whole grain M1 single-base propellant

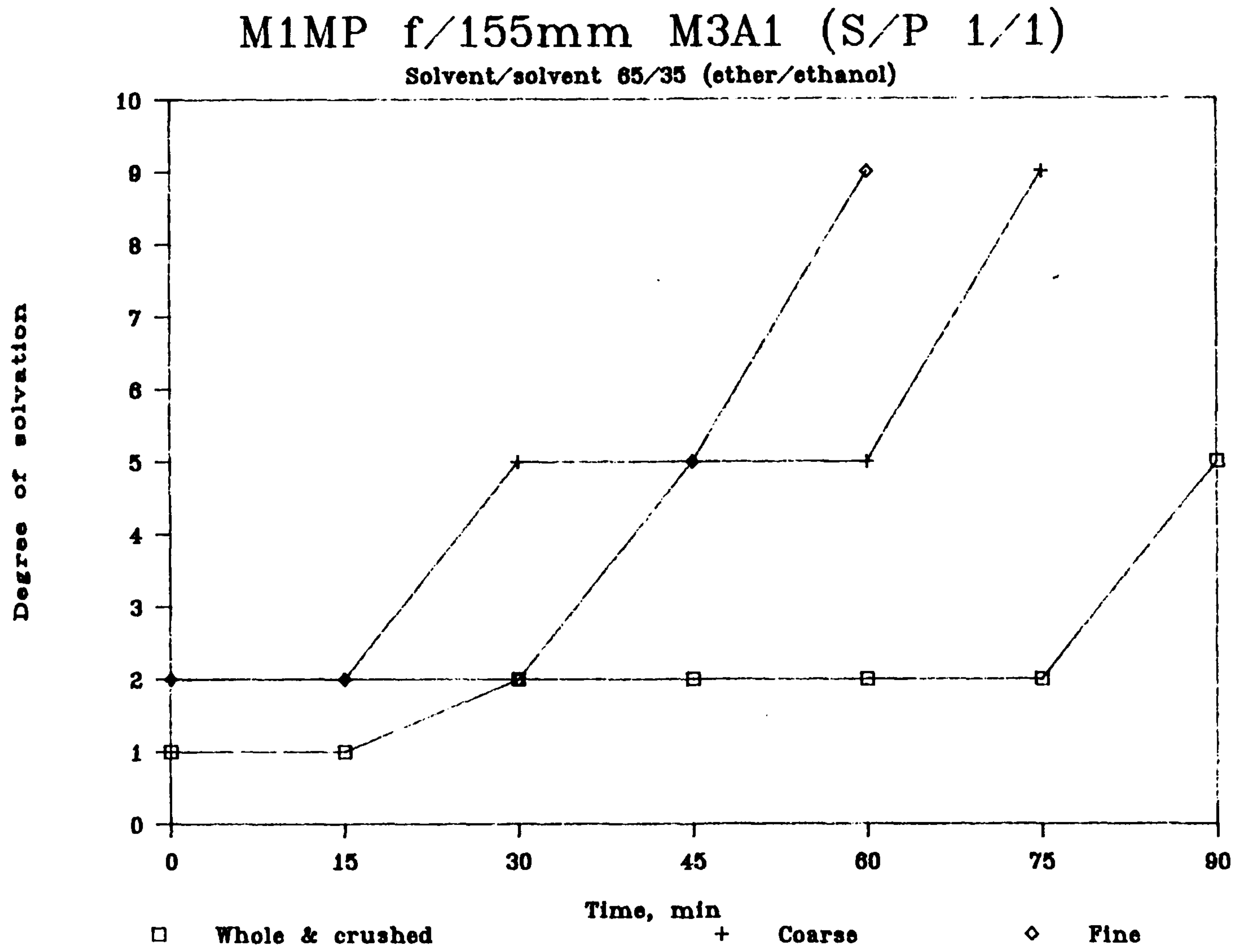

Figure 17. Degree of solvation vs time for M1 multi-perforated propellant (1/1 solvent/propellant ratio and 65/35 ether/ethanol ratio)

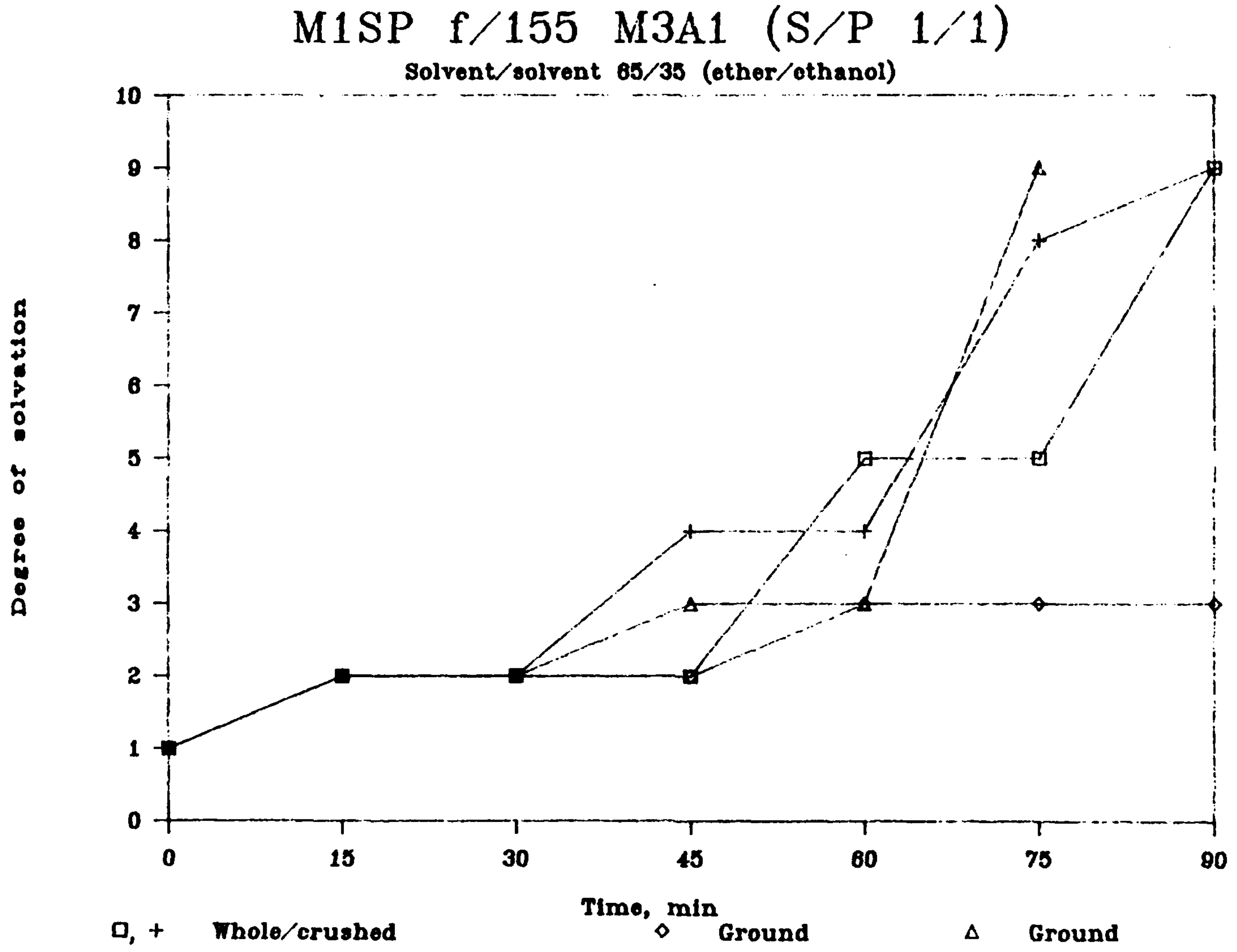

Figure 18. Degree of solvation vs time for M1 single-perforated propellant (1/1 solvent/propellant ratio and 65/35 ether/ethanol ratio)

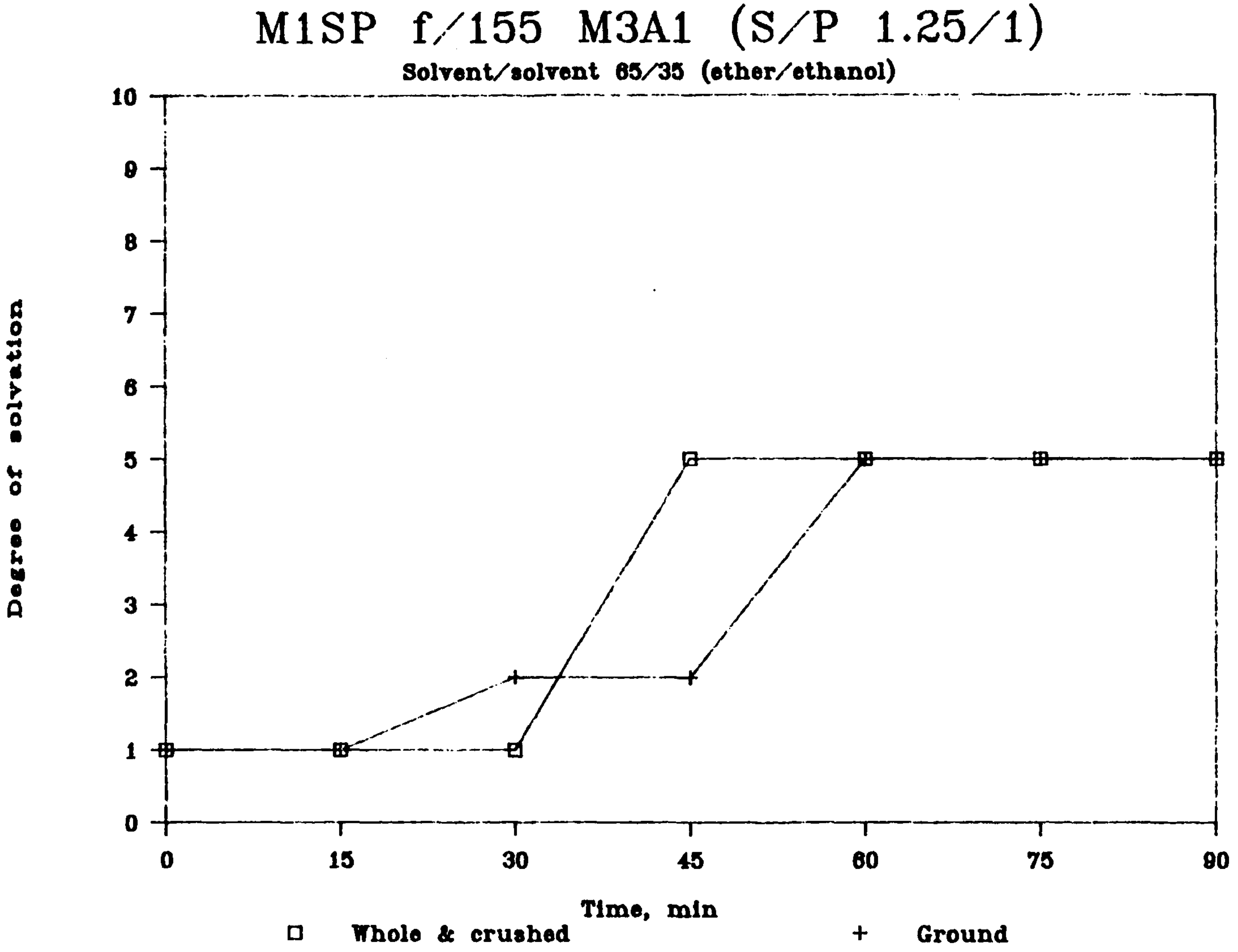

Figure 19. Degree of solvation vs time for M1 single-perforated propellant (1.25/1 solvent/propellant ratio and 65/35 ether/ethanol ratio)

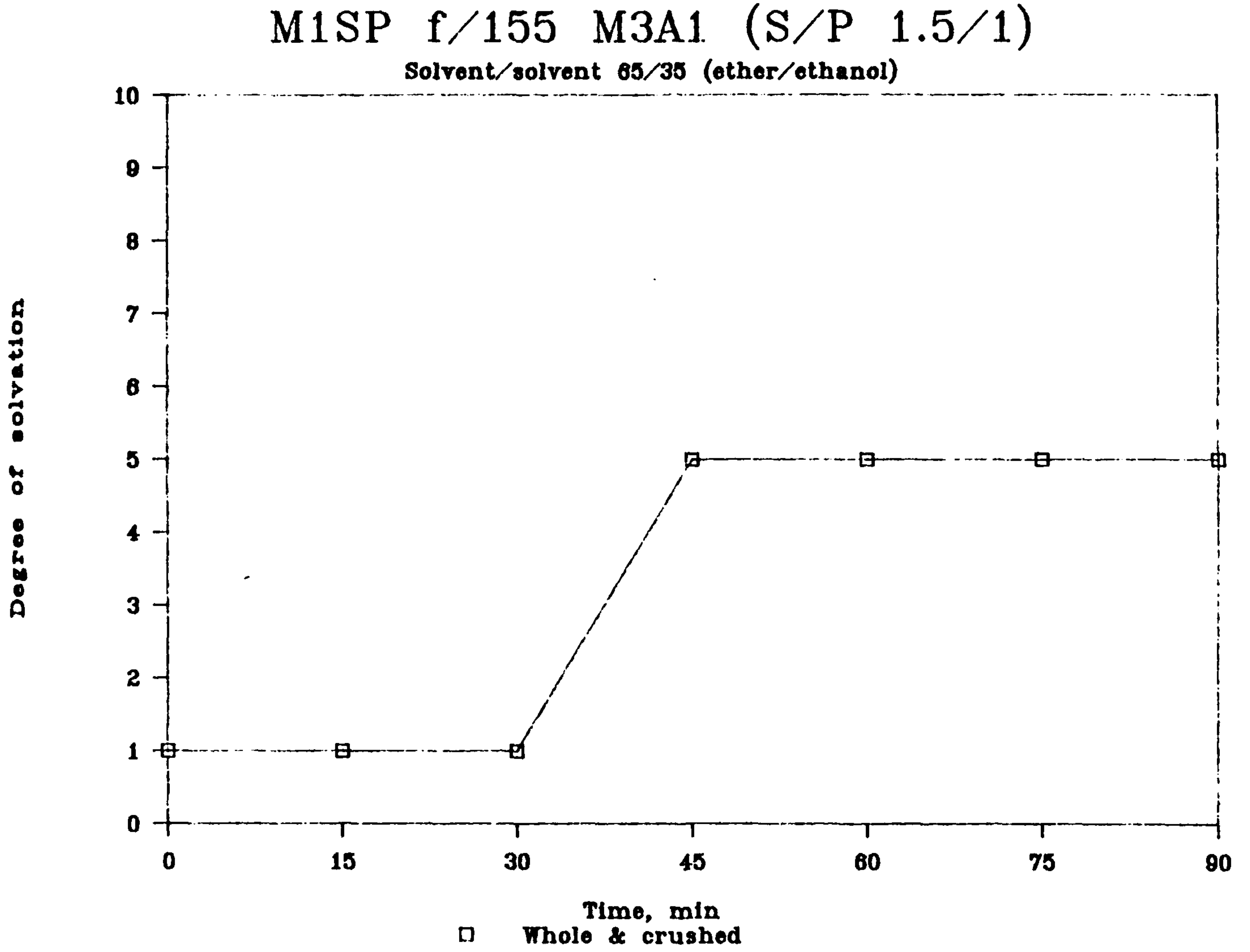

Figure 20. Degree of solvation vs time for M1 single-perforated propellant (1.5/1 solvent/propellant ratio and 65/35 ether/ethanol ratio)

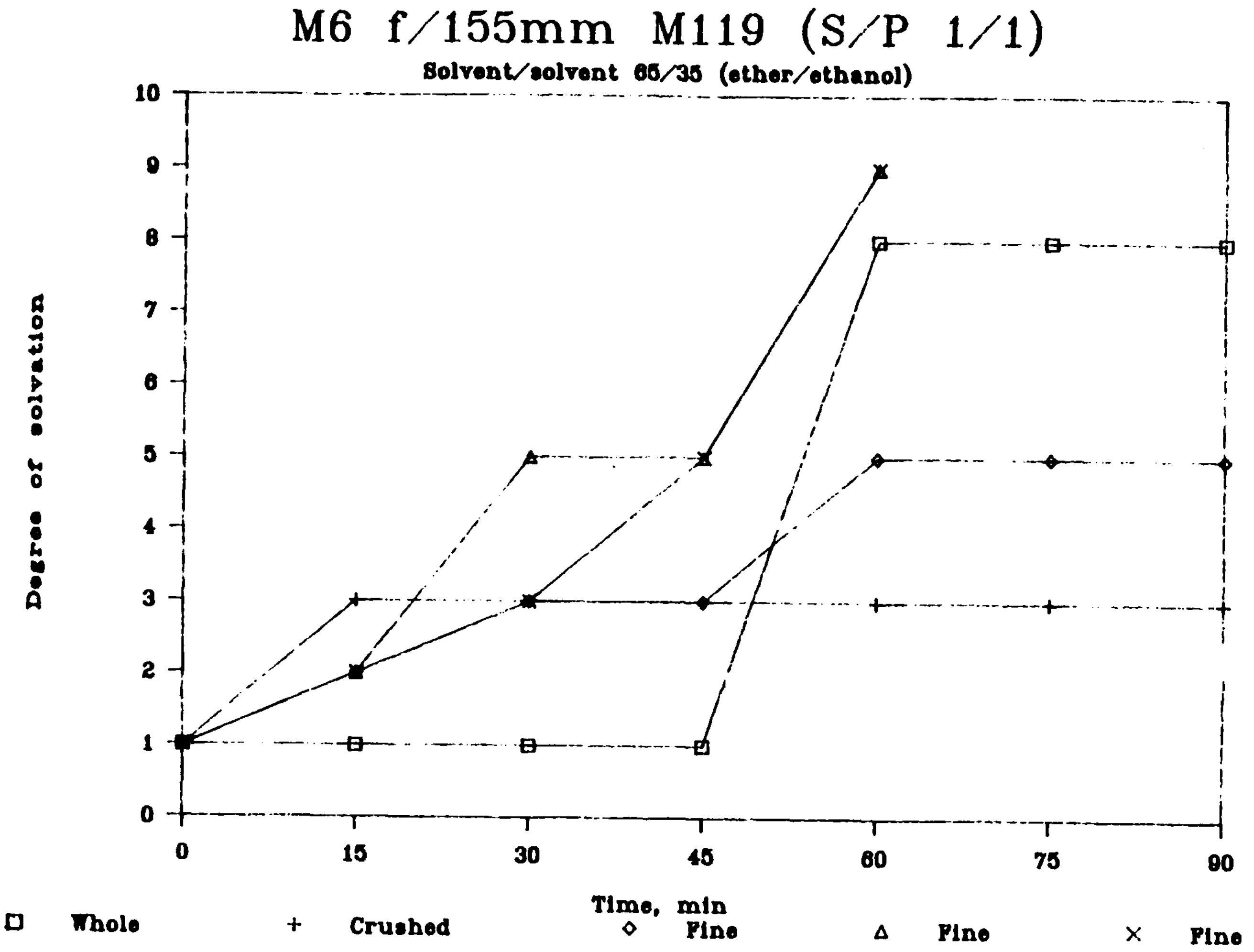

Figure 21. Degree of solvation vs time for M6 propellant (1/1 solvent/propellant ratio and 65/35 ether/ethanol ratio)

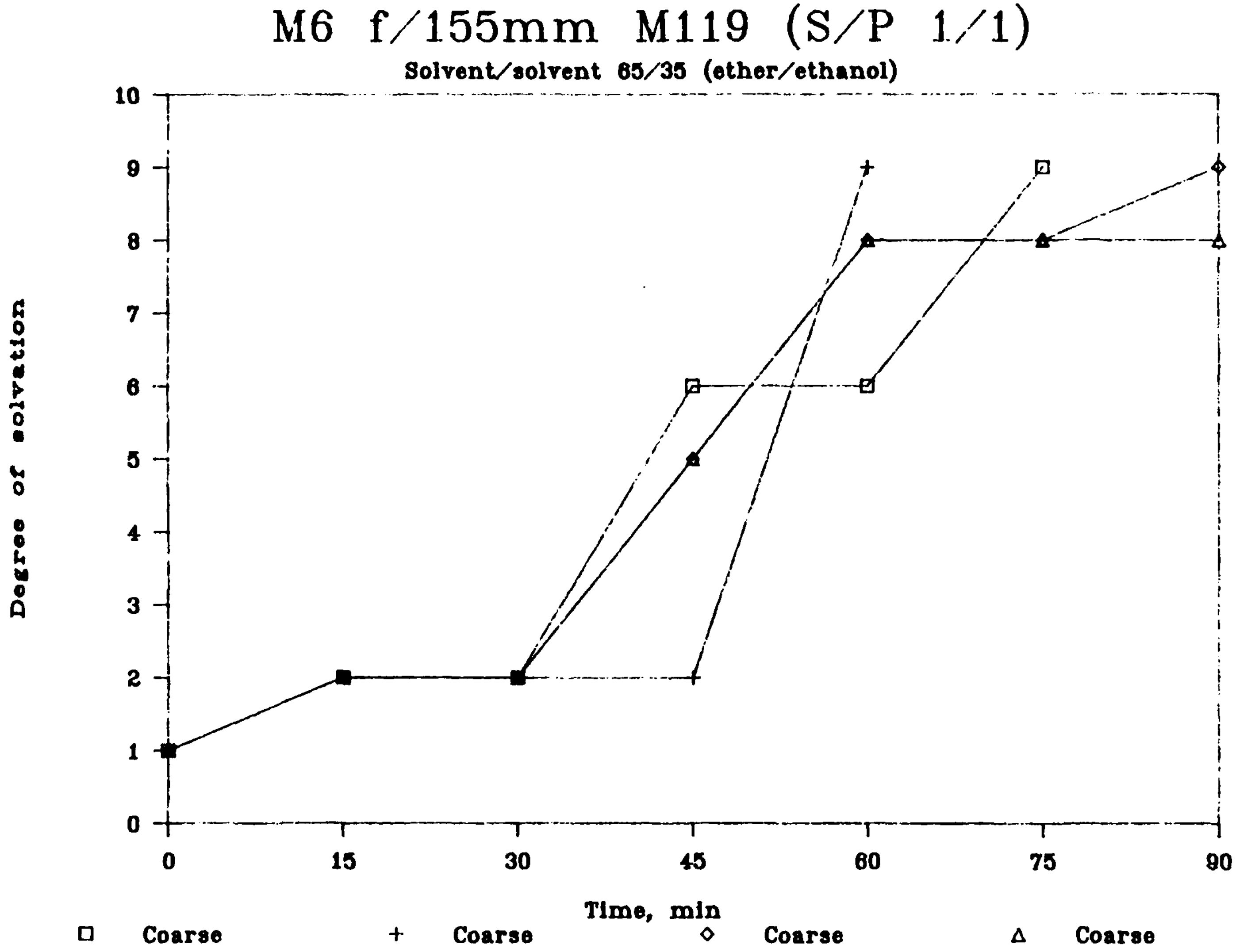

Figure 22. Degree of solvation vs time for M6 coarsely ground propellant (1/1 solvent/propellant ratio and 65/35 ether/ethanol ratio)

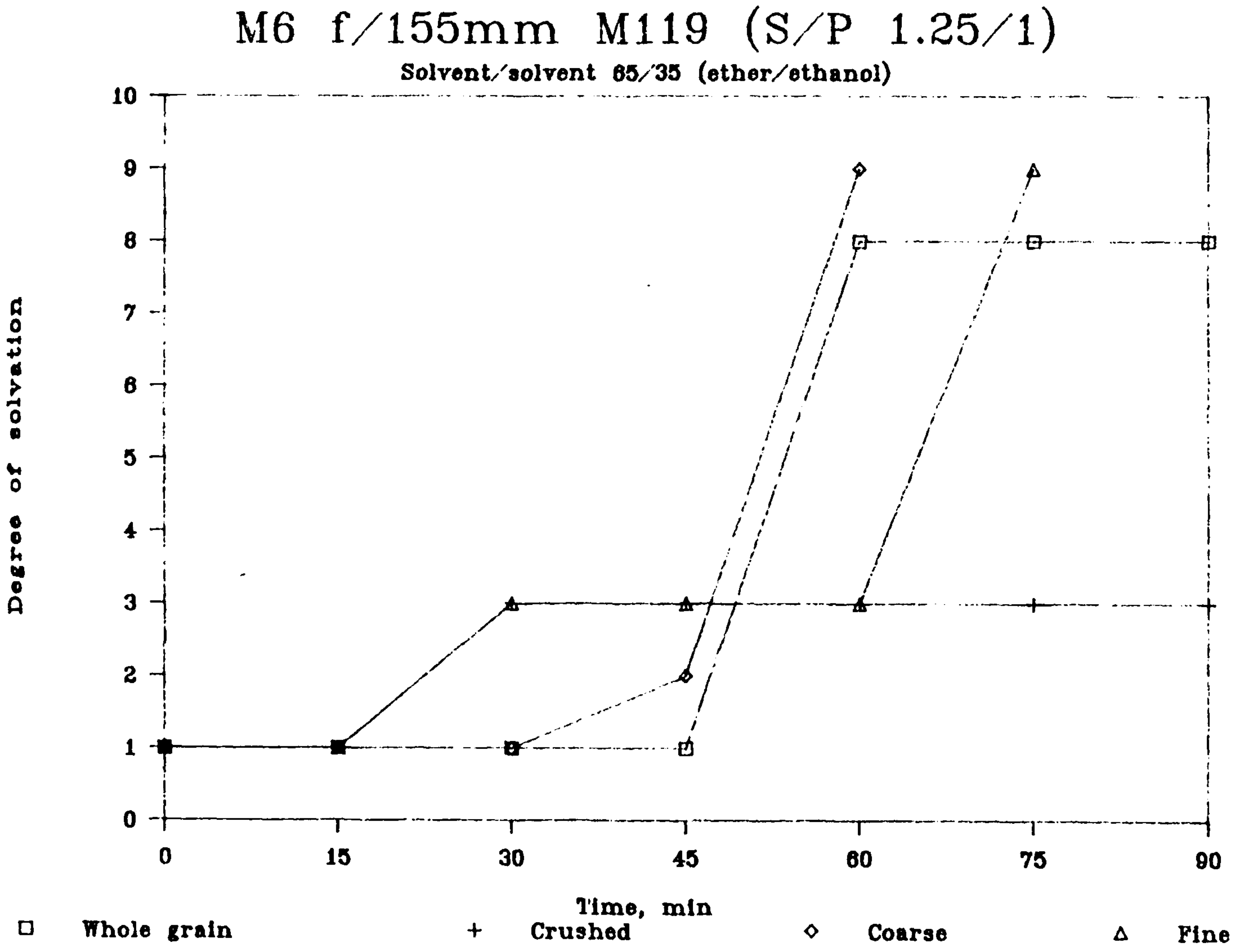

Figure 23. Degree of solvation vs time for M6 propellant (1.25/1 solvent/propellant ratio and 65/35 ether/ethanol ratio)

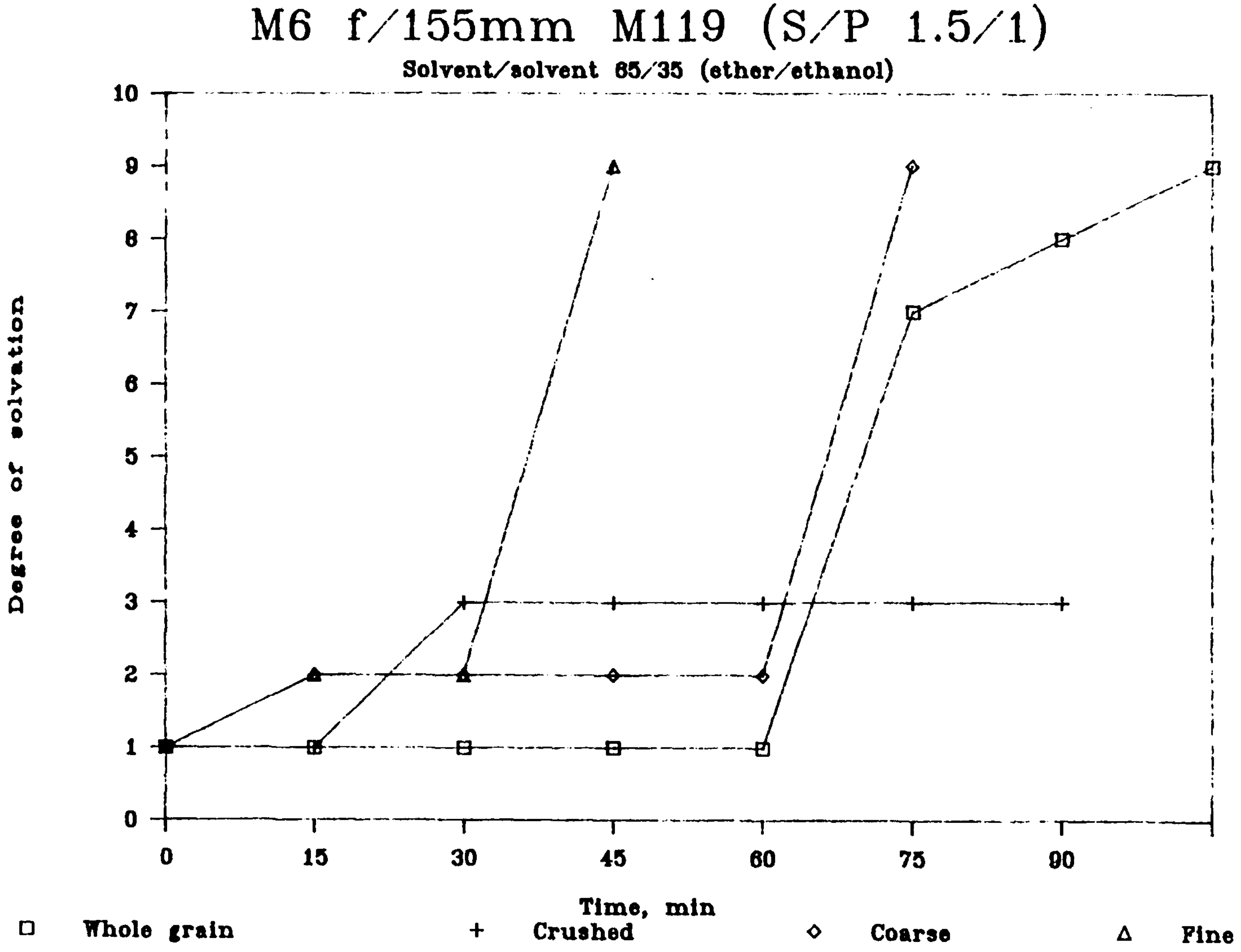

Figure 24. Degree of solvation vs time for M6 propellant (1.5/1 solvent/propellant ratio and 65/35 ether/ethanol ratio)

M10 is a single-base flake in which a sample represents whole grain, crushed, and ground particle sizes (fig. 25). As shown in figures 26 through 28, resolvation of the M10 propellant occurred for the solvent/propellant ratios of 1.25/1 and 1.5/1 for the solvent/solvent ratio of 70/30 (ether/ethanol).

Whole grain and ground samples of M2 double-base propellant did not resolvate within the allotted 90-min time frame when the solvent/propellant ratio was 0.4/1 (figs. 29 through 31). The whole grain sample resulted in "grainy centers" of unsolvated propellant grains. The ground samples, both coarse and fine, resulted in "poor consistency" due to the solvent not being evenly distributed over the propellant, thus forming grainy pockets in the samples. Greater solvent/propellant ratios of 0.6/1 and 0.8/1 resolvated the finely and coarsely ground samples, respectively. However, increased solvent/propellant ratios did resolvate the whole grain and crushed samples (table 13).

M7 double-base propellant resolvated within the 90-min time frame at a solvent/propellant ratio of 0.4/1. The crushed particle sizes contain case-hardened propellant pieces which require additional solvent (0.6/1) for resolvation; case hardening of the propellant granules occurs during the drying operations (primarily the water dry process). Ground samples of M7 propellant resolvated within the allotted 90-min time frame at the solvent/propellant ratio of 0.4/1, resulting in the same resolvation curve for both coarsely and finely ground samples (figs. 32 and 33).

M9 is a double-base flake propellant in which a sample represents whole grain, crushed, and ground particle sizes. The M9 propellant resolvated within the allotted 90-min time frame for solvent/propellant ratios of 0.4/1 and 0.6/1. The greater ratio (0.6/1) resolvated the propellant in 30 min whereas the lesser ratio (0.4/1) resolvated the propellant in 90 min (fig. 34).

The resolvation of whole grain and ground samples of M30 triple-base propellant also showed that particle size reduction of the propellant is a necessary requirement to obtain resolvation within the allotted 90-min time frame (figs. 35 through 37). Resolvation testing over a range of solvent/propellant ratios (0.4/1 to 1/1) for the whole grain samples resulted in all samples having "excess solvent" not being absorbed into the propellant. The whole grain sample having a solvent/propellant ratio of 1/1 started to resolvate after 90 min, resulting in a sample having "poor consistency." The coarsely and finely ground samples overly solvated, resulting in a "spongy" mixture above the desired degree of plasticity. Decreasing the solvent/propellant ratio from 0.4/1 to 0.2/1-0.3/1 resolvated the ground samples to a more acceptable degree of plasticity (figs. 36 and 37) since these propellant samples attained borderline plasticity within 30 min. The crushed samples would not resolvate due to the greater amount of exposed case-hardened surface area which precludes solvent penetration in the NC matrix.

The resolvation of whole grain and ground samples of M30A1 triple-base propellant also showed that particle size reduction of the propellant is a necessary requirement to obtain resolvation within the

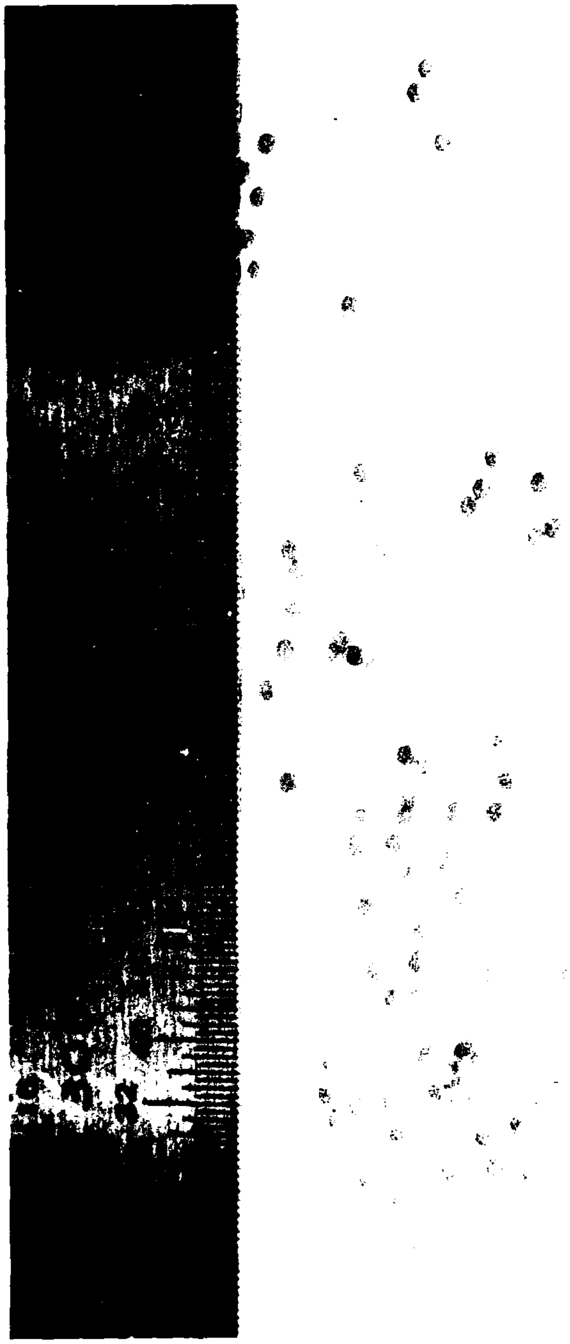

Figure 25. M10 single-base flake propellant

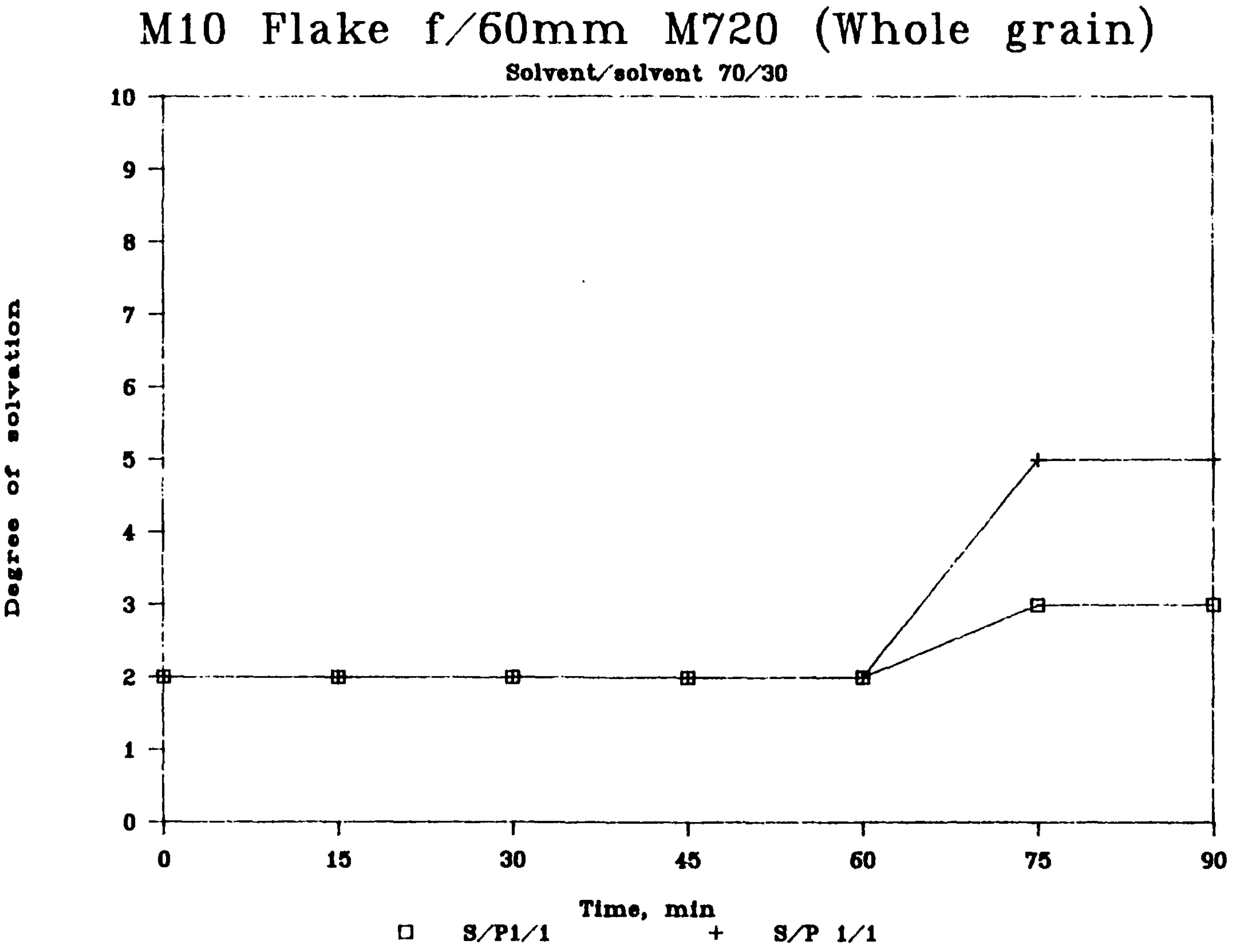

Figure 26. Degree of solvation vs time for M10 propellant (1/1 solvent/propellant ratio and 70/30 ether/ethanol ratio)

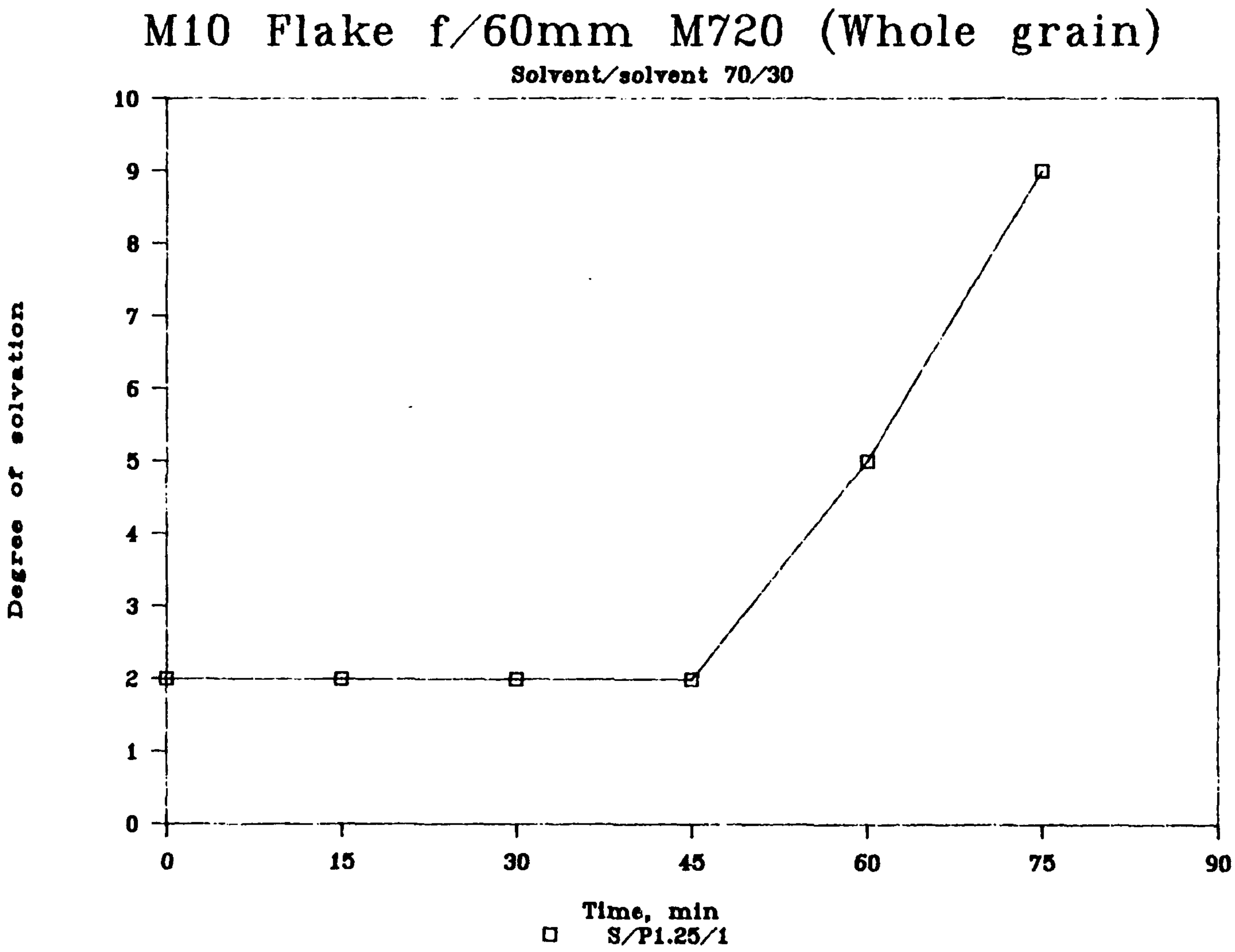

Figure 27. Degree of solvation vs time for M10 propellant (1.25/1 solvent/propellant ratio and 70/30 ether/ethanol ratio)

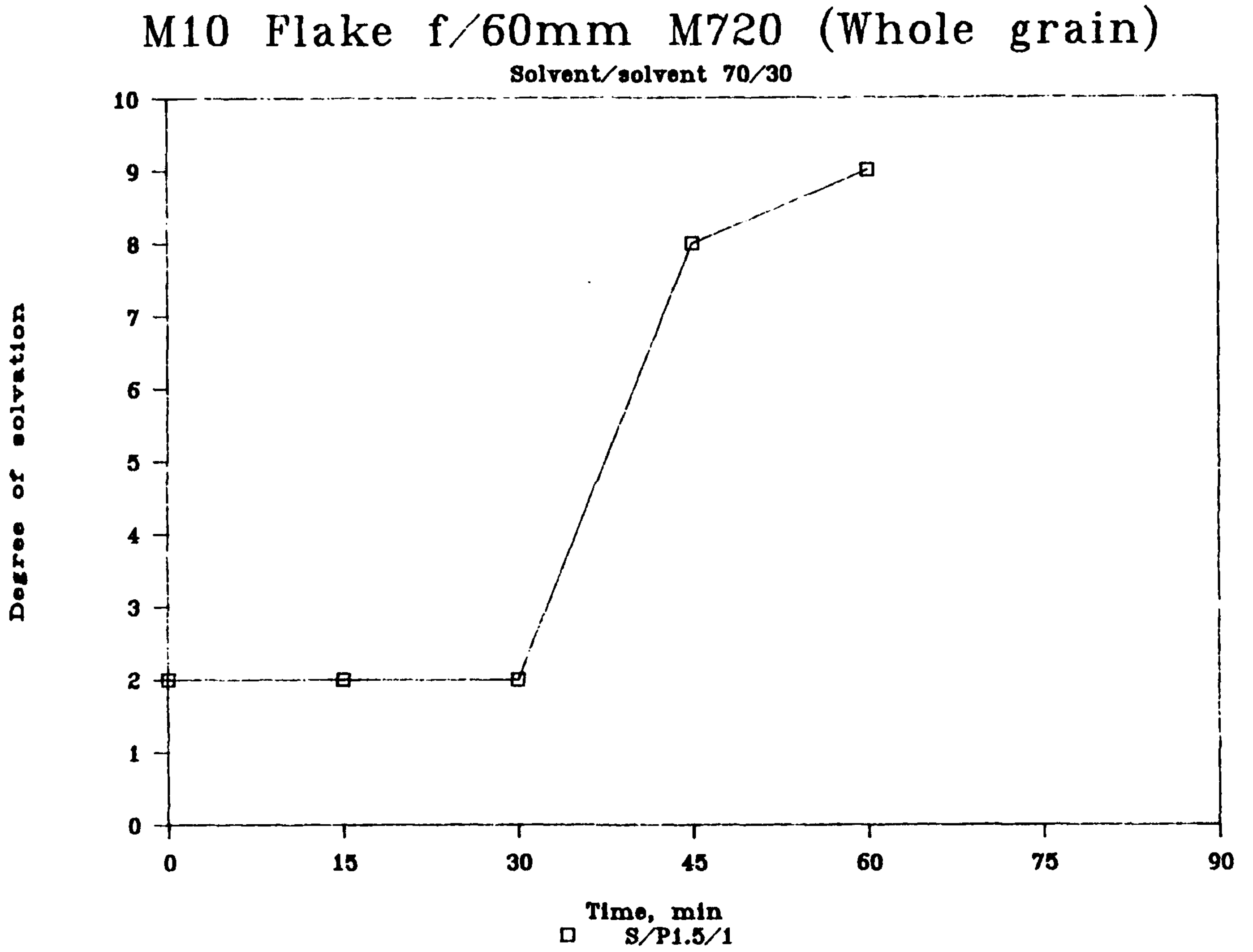

Figure 28. Degree of solvation vs time for M10 propellant (1.5/1 solvent/propellant ratio and 70/30 ether/ethanol ratio)

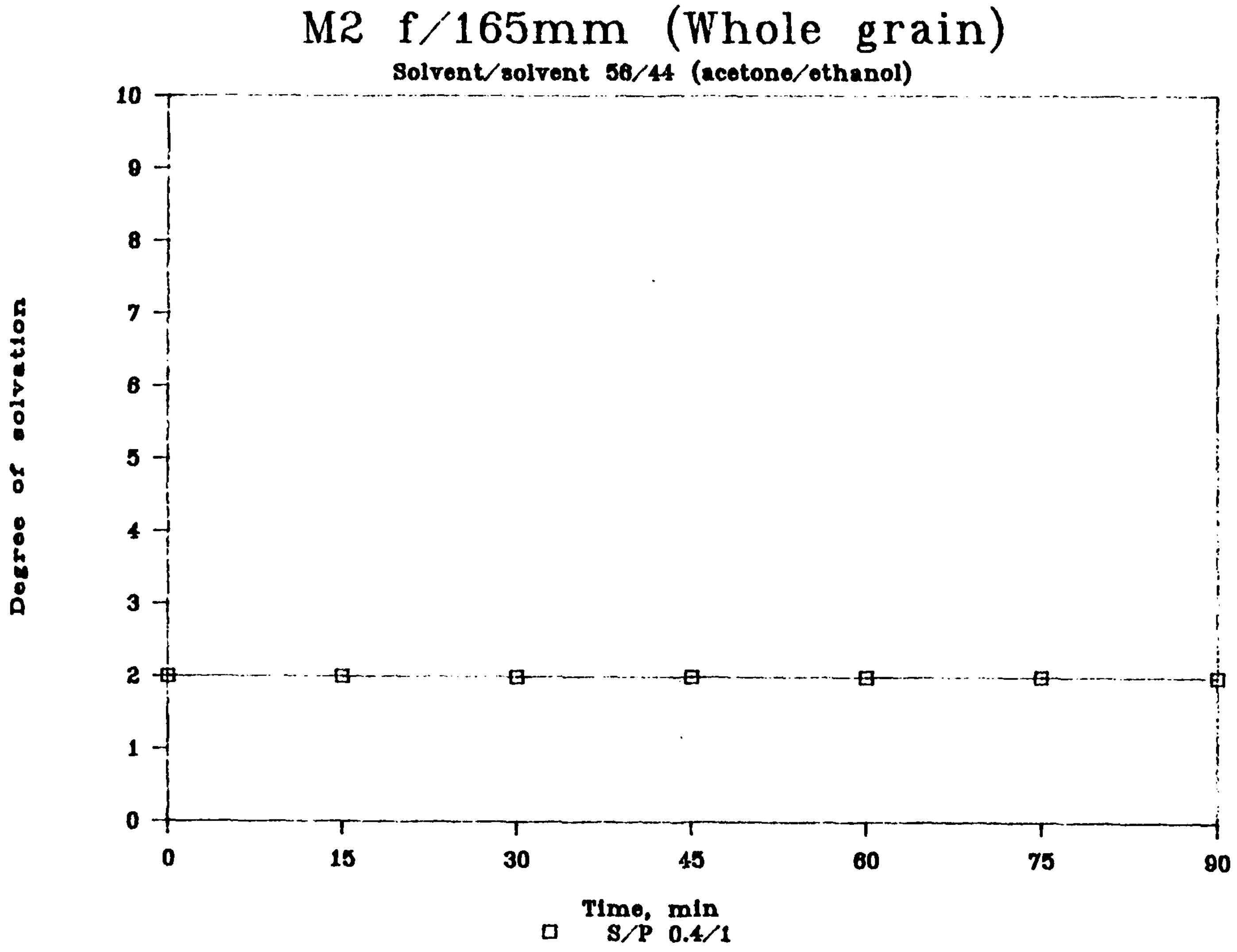

Figure 29. Degree of solvation vs time for M2 whole grain propellant (0.4/1 solvent/propellant ratio and 56/44 acetone/ethanol ratio)

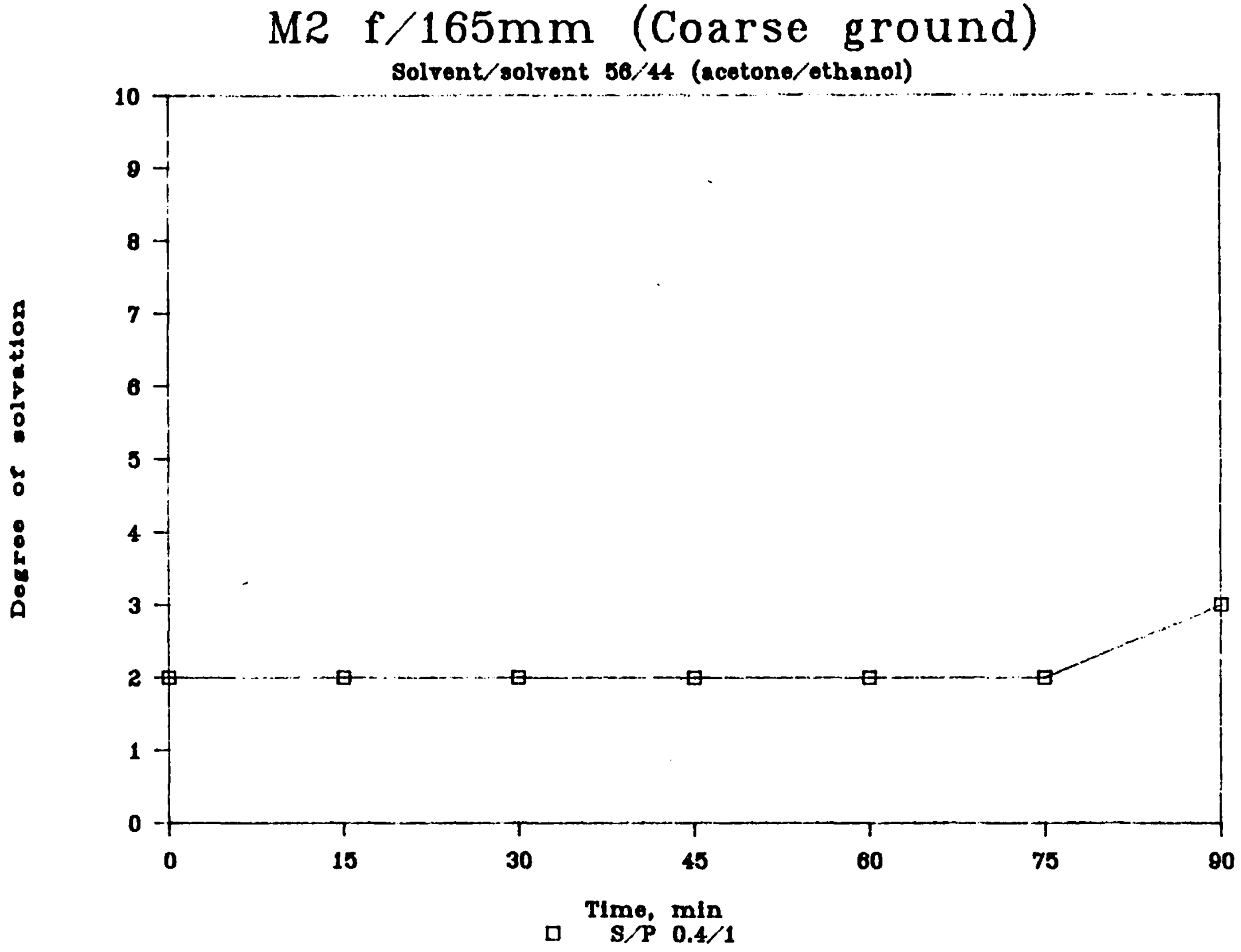

Figure 30. Degree of solvation vs time for M2 coarsely ground propellant (0.4/1 solvent/propellant ratio and 56/44 acetone/ethanol ratio)

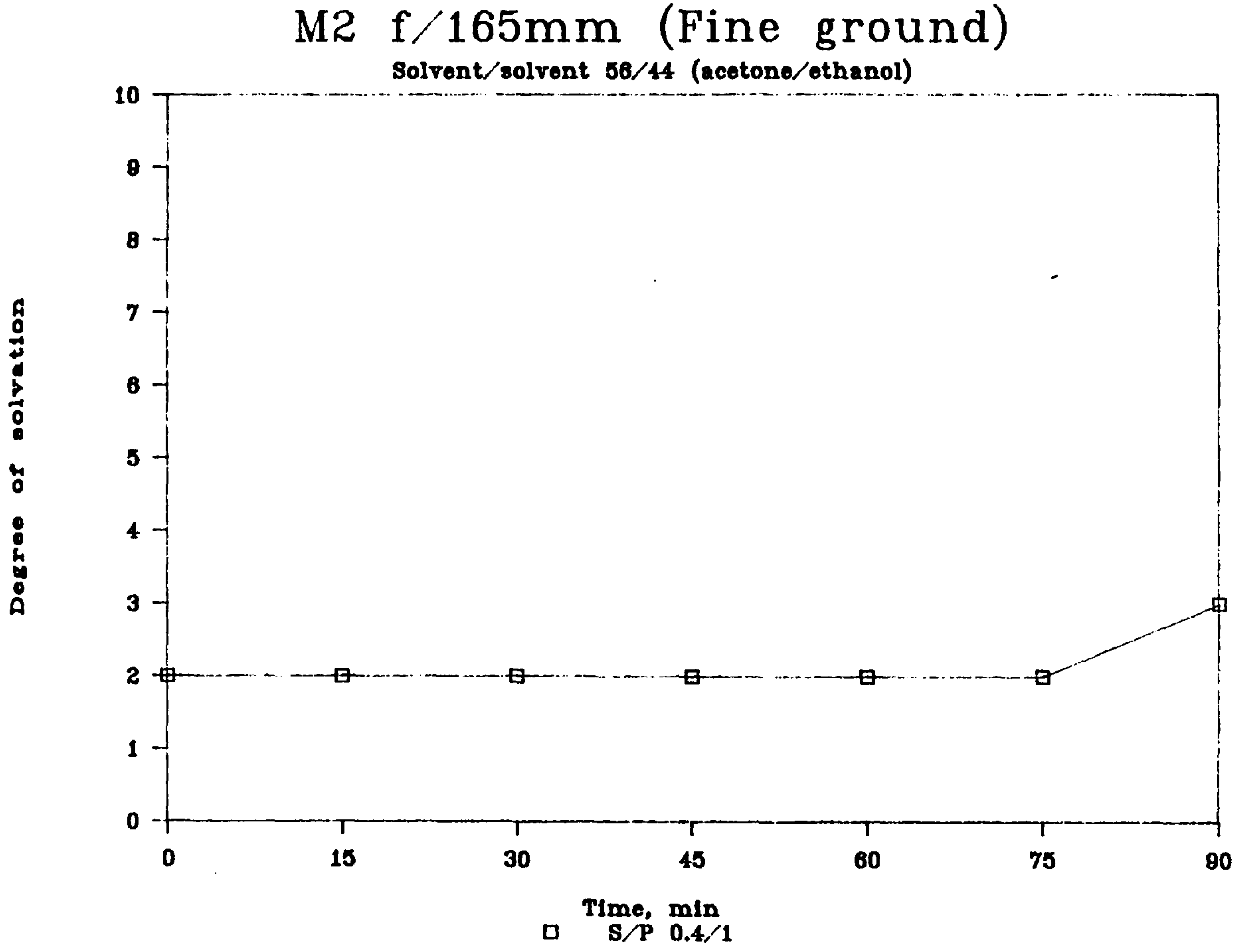

Figure 31. Degree of solvation vs time for M2 finely ground propellant (0.4/1 solvent/propellant ratio and 56/44 acetone/ethanol ratio)

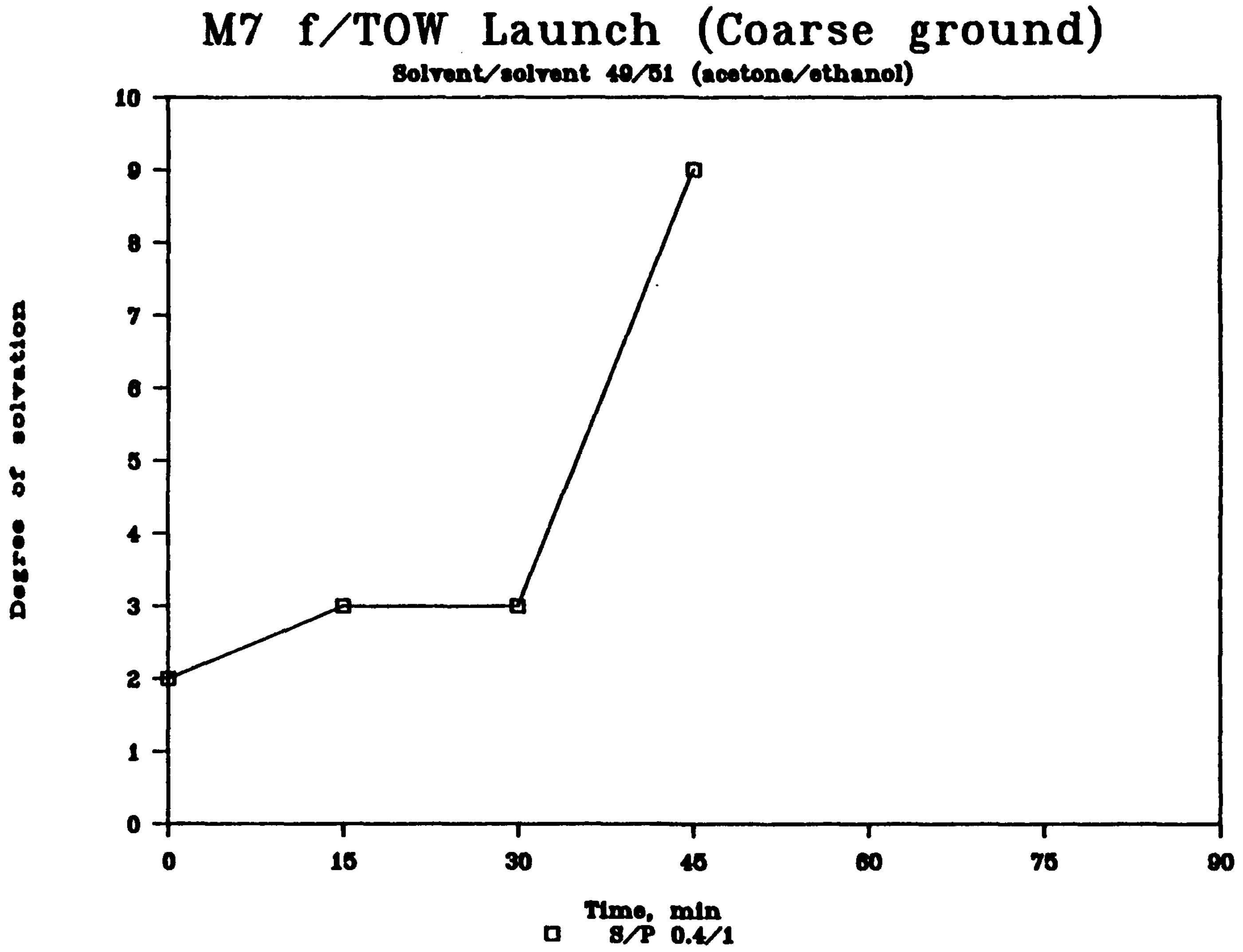

Figure 32. Degree of solvation vs time for M7 coarsely ground propellant (0.4/1 solvent/propellant ratio and 49/51 acetone/ethanol ratio)

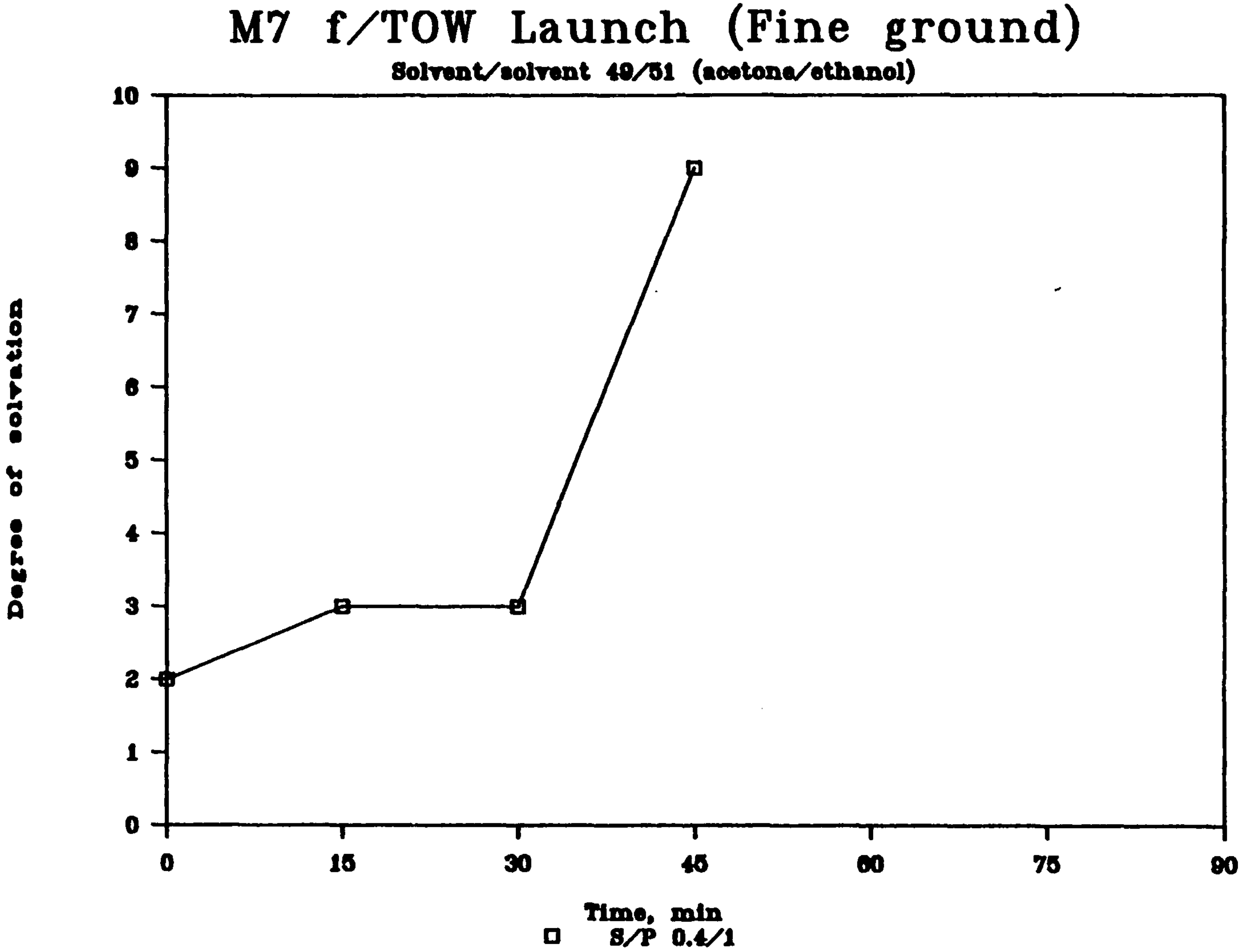

Figure 33. Degree of solvation vs time for M7 finely ground propellant (0.4/1 solvent/propellant ratio and 49/51 acetone/ethanol ratio)

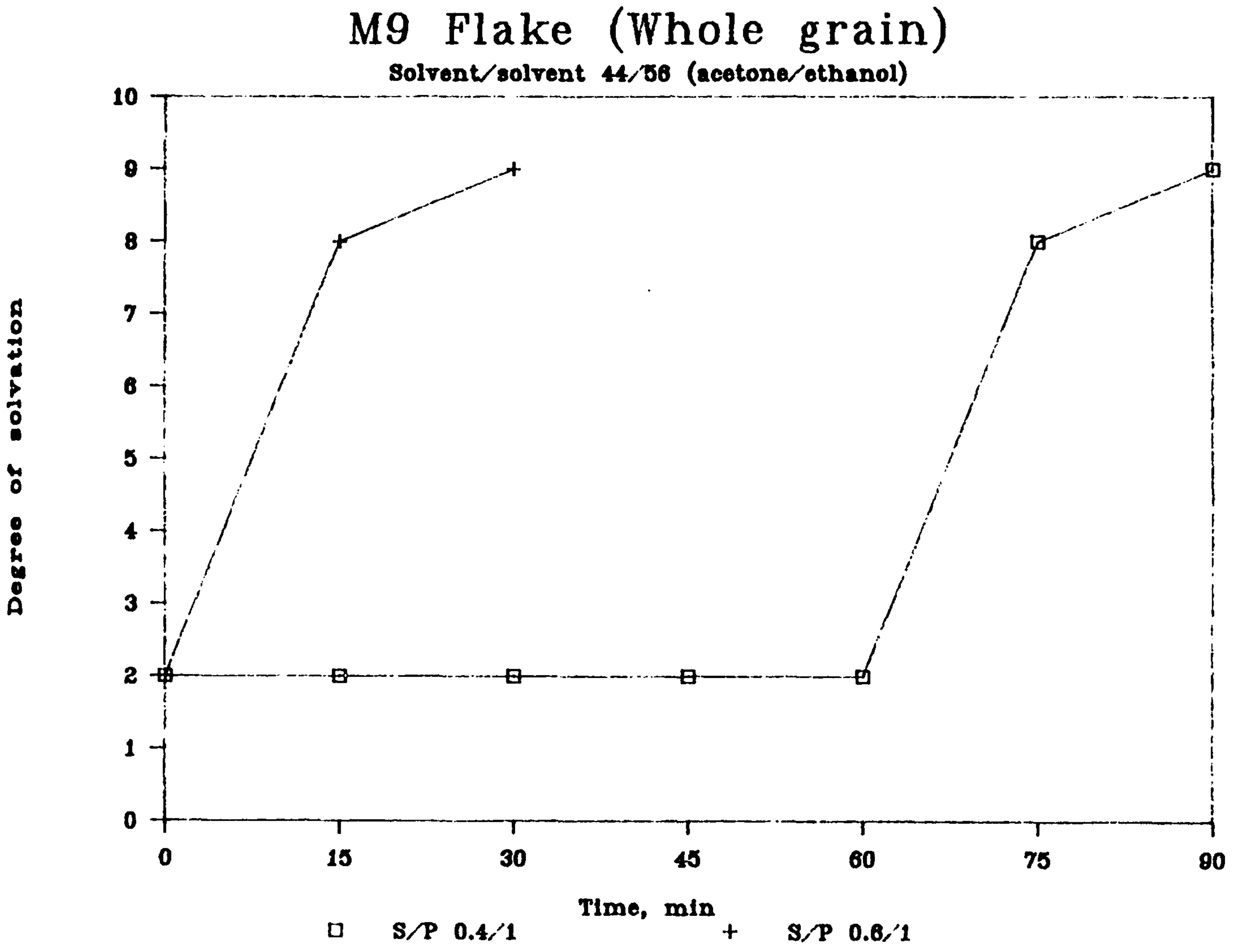

Figure 34. Degree of solvation vs time for M9 flake propellant (various solvent/propellant ratios and 44/56 acetone/ethanol ratio)

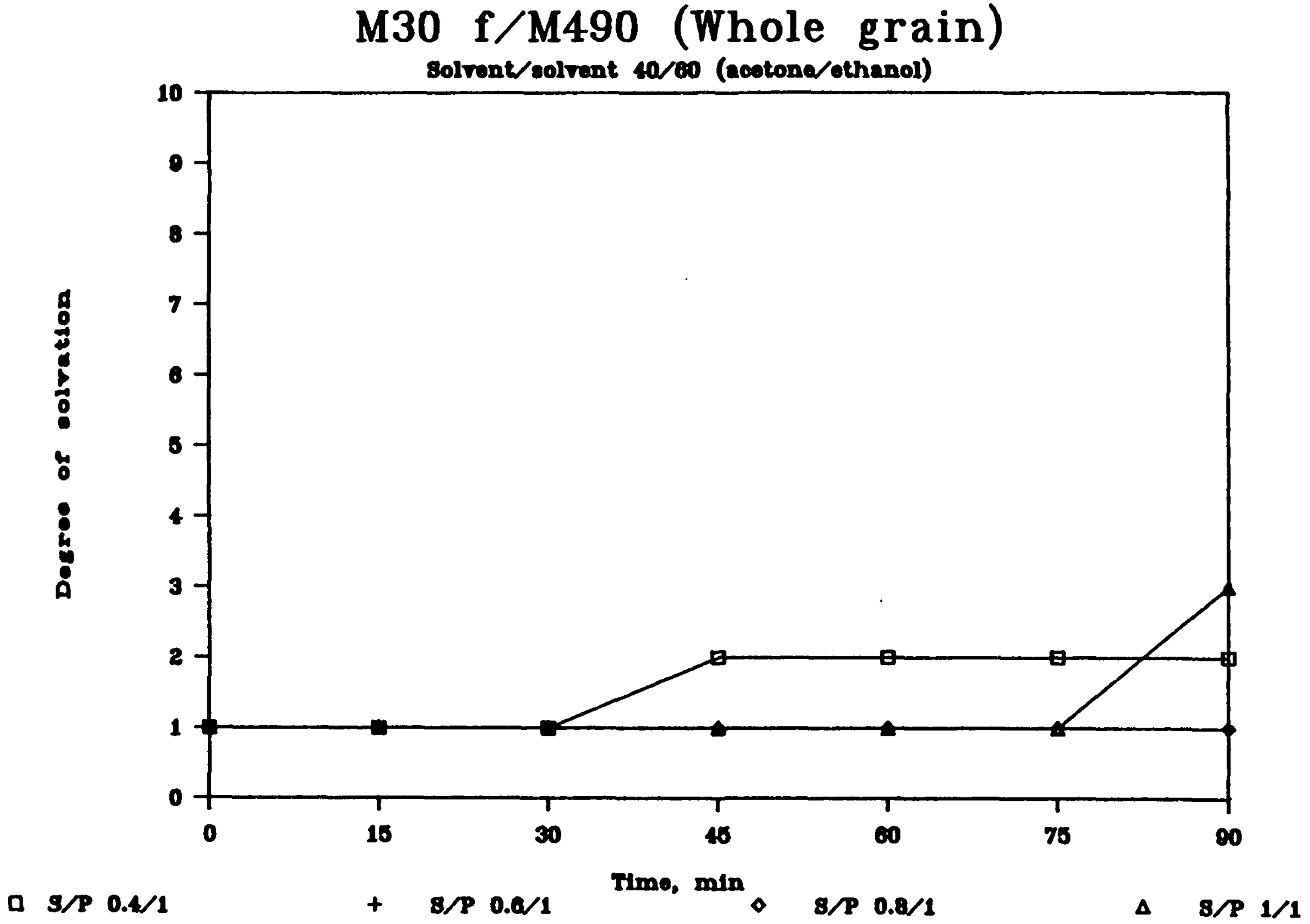

Figure 35. Degree of solvation vs time for M30 whole grain propellant (various solvent/propellant ratios and 40/60 acetone/ethanol ratio)

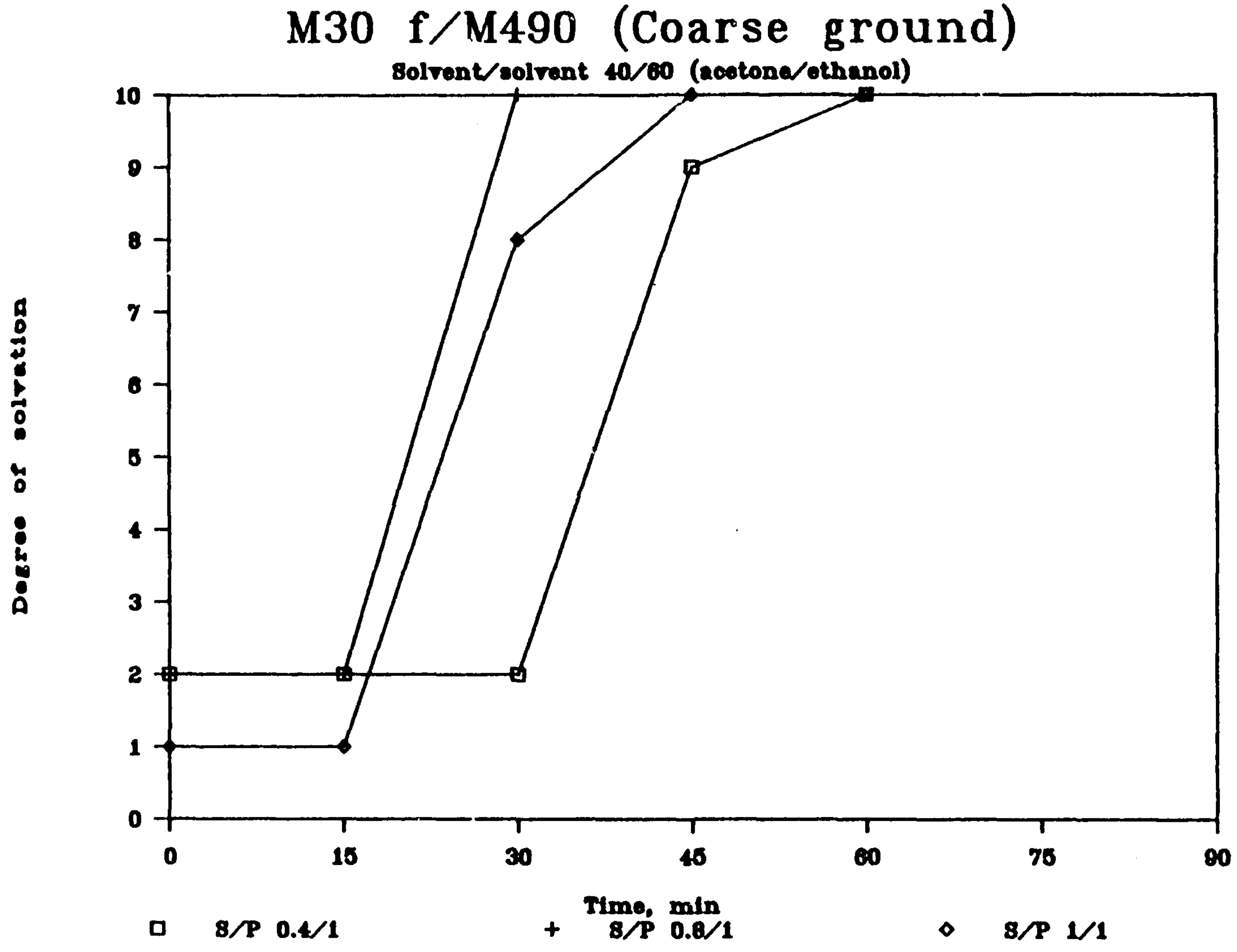

Figure 36. Degree of solvation vs time for M30 coarsely ground propellant (various solvent/propellant ratios and 40/60 acetone/ethanol ratio)

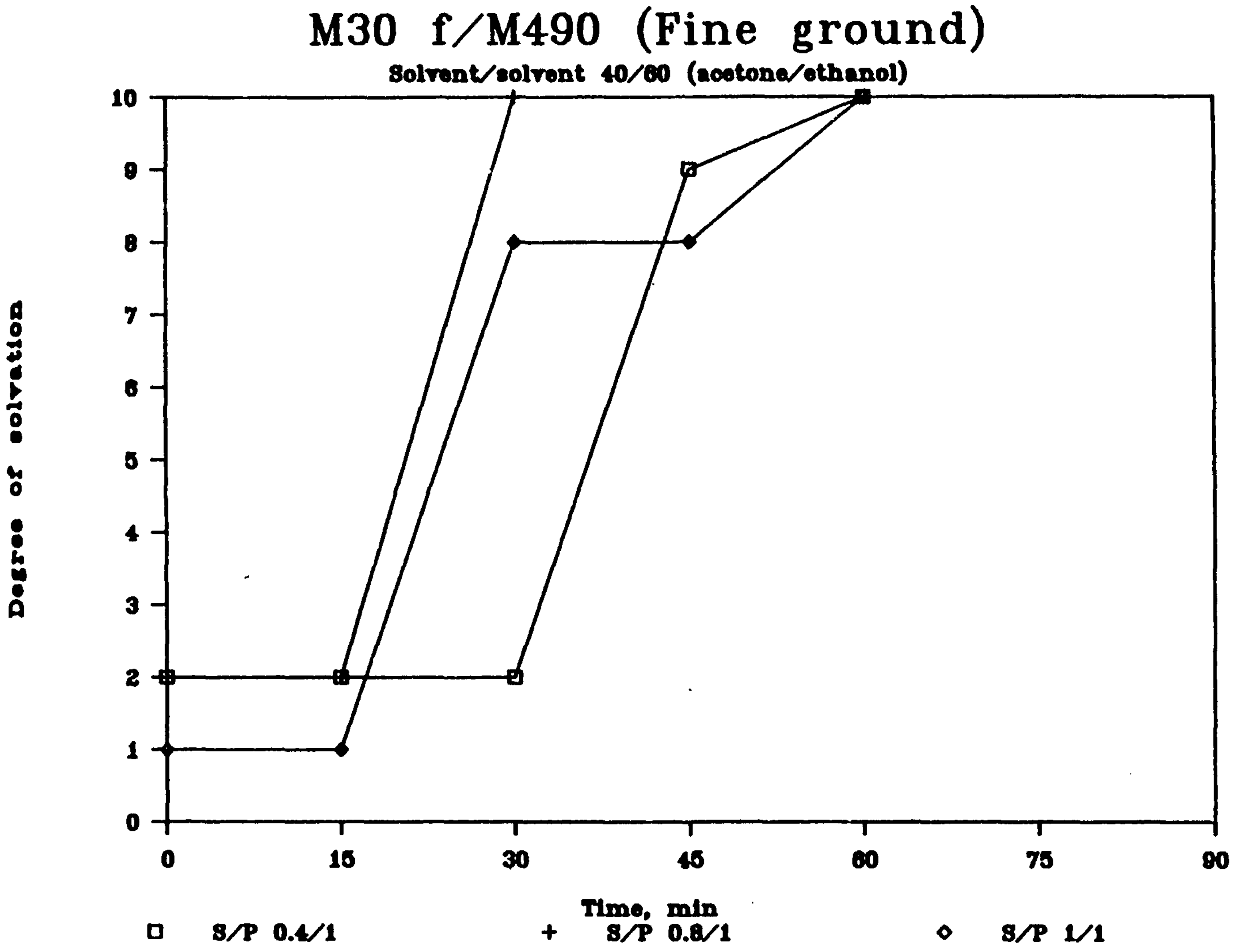

Figure 37. Degree of solvation vs time for M30 finely ground propellant (various solvent/propellant ratios and 40/60 acetone/ethanol ratio)

allotted 90-min time frame (figs. 38 through 40). Resolvation testing over a range of solvent/propellant ratios (0.4/1 to 1/1) for the whole grain samples resulted in samples having "grainy" or unsolvated propellant for solvent/propellant ratios of 0.4/1 to 0.8/1. The whole grain sample having a solvent/propellant ratio of 1/1 started to resolvate 75 min; however, at 90 min the sample was not a colloid. The coarsely and finely ground samples both resolvated in 30 min at a solvent/propellant ratio of 0.4/1, resulting in the same resolvation curve. The crushed samples showed borderline resolvation at a solvent/propellant ratio of 0.4/1; increasing the solvent/propellant ratio to 0.8/1 resulted in excess solvent over the propellant.

Ground samples of M31A1 propellant resolvated within the allotted 90-min time frame when the solvent/propellant ratio was 0.2/1 (figs. 41 and 42). At the greater solvent/propellant ratio of 0.4/1, the propellant overly solvated, resulting in a "spongy" mixture. The coarsely ground sample was below the plasticity requirement for resolvation whereas the finely ground sample was above this requirement. The whole grain and crushed samples would not resolvate due to the greater amount of surface area exposed, not allowing solvent penetration into the NG matrices.

Table 14 shows the effects of the base ingredients (NC, NG, and NQ) on propellant resolvation of ground triple-base (M31A1, M30A1, and M30), double-base (M2, M7, and M9), and single-base (M1, M6, and M10) propellants. The effects of NG and NQ on propellant resolvation appear to be minimal. As the percent of NC increases from triple-base to single-base propellants, the solvent/propellant ratio increases for propellant resolvation. The multi-base (triple- and double-base) propellant solvent systems utilize acetone and ethanol. NC is also very soluble in acetone, thereby reducing the solvent/propellant ratio required for resolvation of these propellants. NC is marginally soluble in ether as well as ethanol, both of which are used in the single-base propellant manufacturing solvent systems; however, NC will gelatinize in a 2:1 (ether:ethanol) combination of the two solvents. The increased solvent/propellant ratios for the single-base propellants are also influenced by the increasing NC content of these propellants. NQ apparently does not influence propellant resolvation since the triple- and double-base propellants require the same solvent/propellant ratio for propellant resolvation and NQ is insoluble in the individual solvents (acetone and ethanol) used in the manufacture of multi-base propellants. The presence of NG in the multi-base propellants probably influences propellant resolvation since it is very soluble in acetone, which is used in the multi-base propellant manufacturing solvent systems; NG also acts as a plasticizer that aids in resolvation. It is difficult to determine if the reduced solvent/propellant ratio required to resolvate multi-base propellants is directly influenced by the NG or NC content of the propellants.

However, as demonstrated by the resolvation of multi-base propellants, NC content apparently affects propellant resolvation. For the ground samples having the lower NC content (M31A1 propellant), the solvent/propellant ratio of 0.2/1 proved adequate for resolvation; with a solvent/propellant ratio of 0.4/1, borderline resolvation approached the

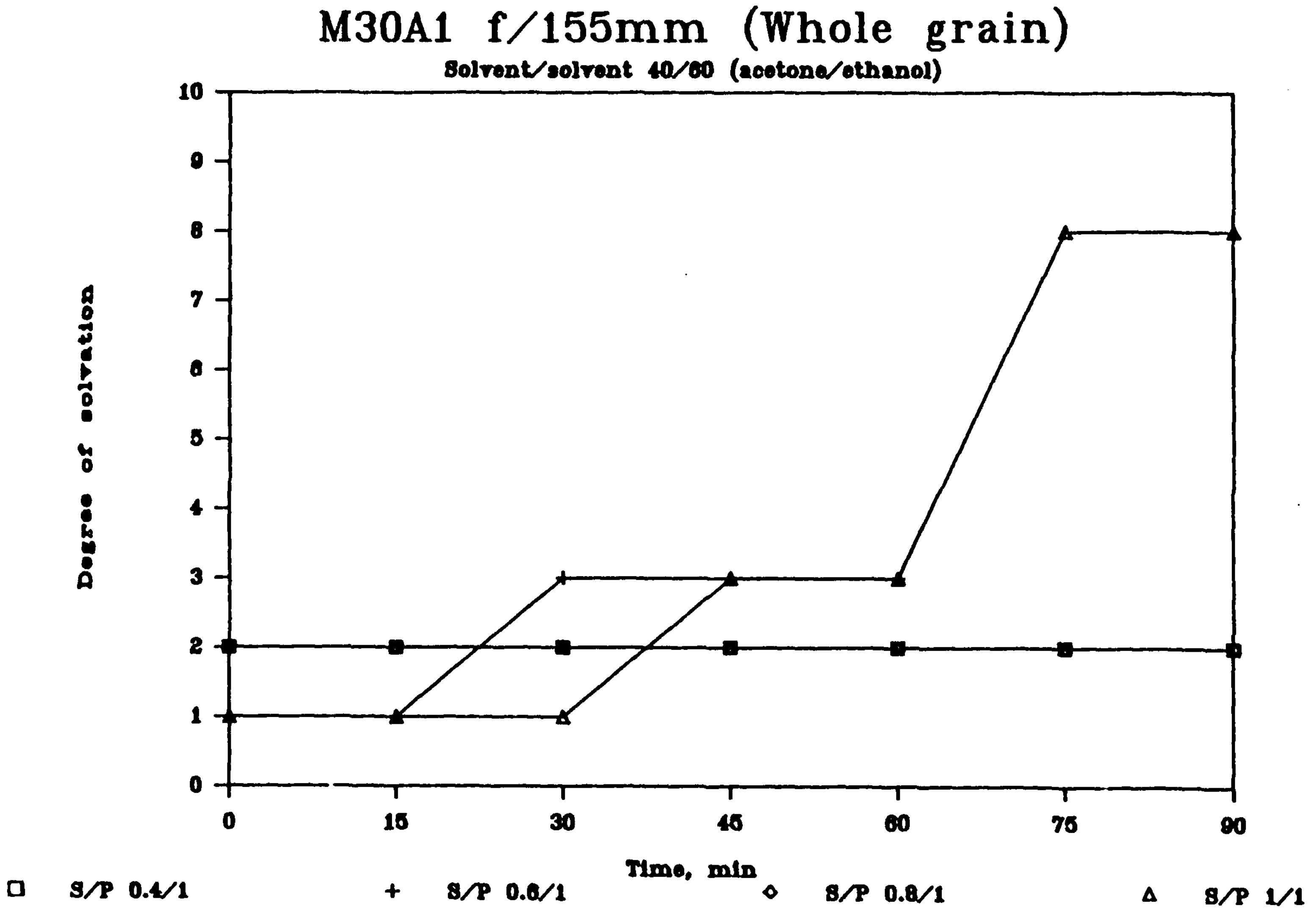

Figure 38. Degree of solvation vs time for M30A1 whole grain propellant (various solvent/propellant ratios and 40/60 acetone/ethanol ratio)

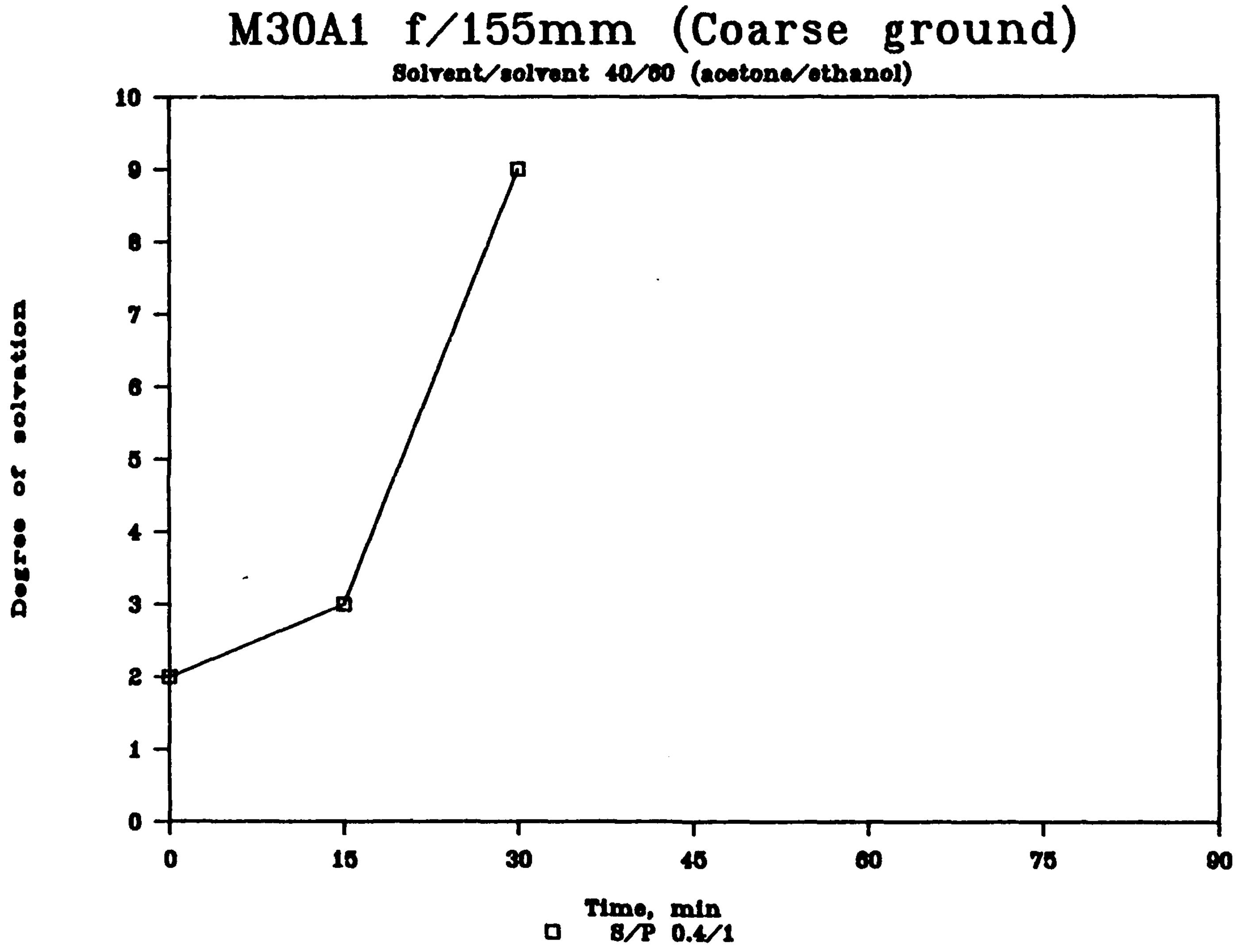

Figure 39. Degree of solvation vs time for M30A1 coarsely ground propellant (0.4/1 solvent/propellant ratio and 40/60 acetone/ethanol ratio)

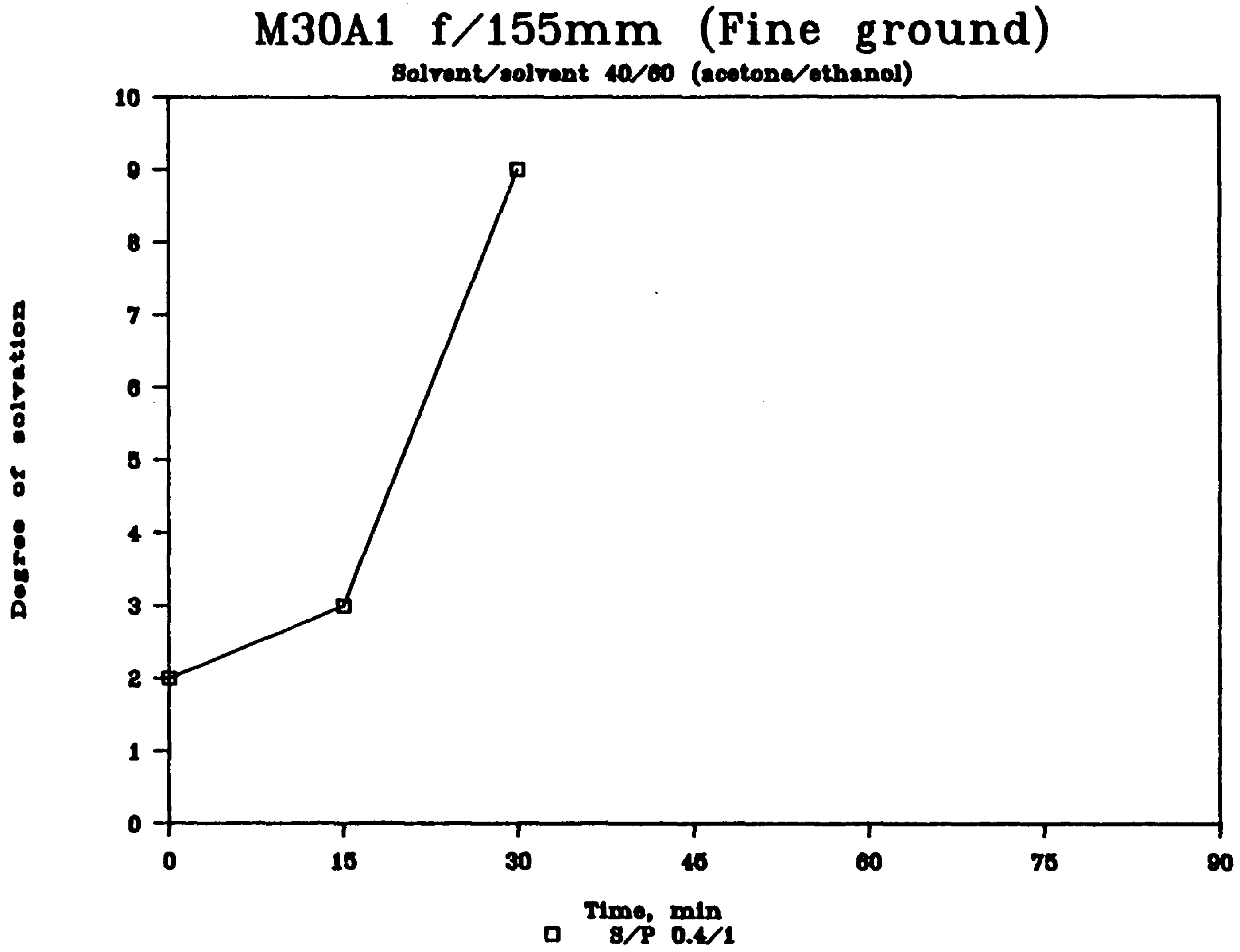

Figure 40. Degree of solvation vs time for M30A1 finely ground propellant (0.4/1 solvent/propellant ratio and 40/60 acetone/ethanol ratio)

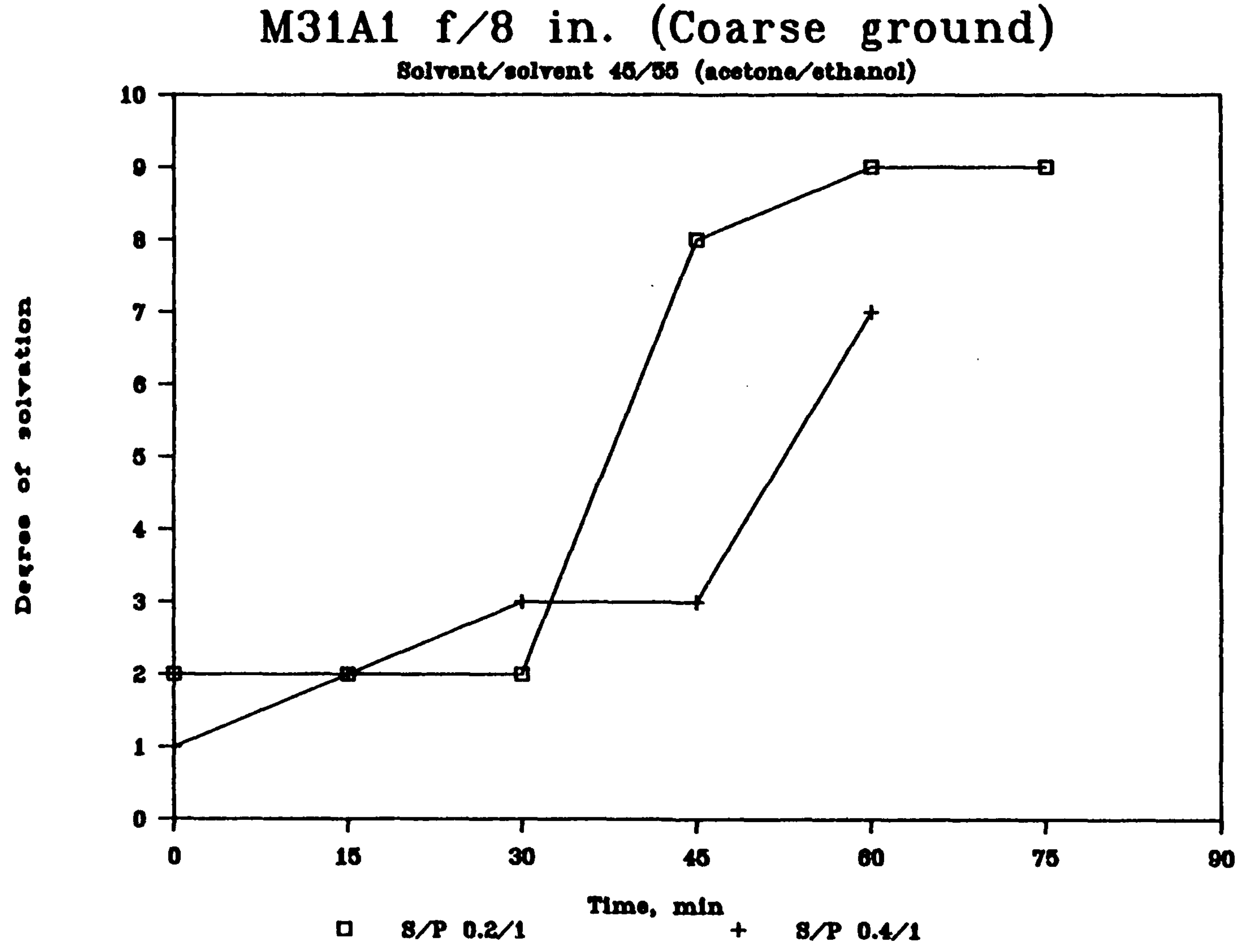

Figure 41. Degree of solvation vs time for M31A1 coarsely ground propellant (various solvent/propellant ratios and 45/55 acetone/ethanol ratio)

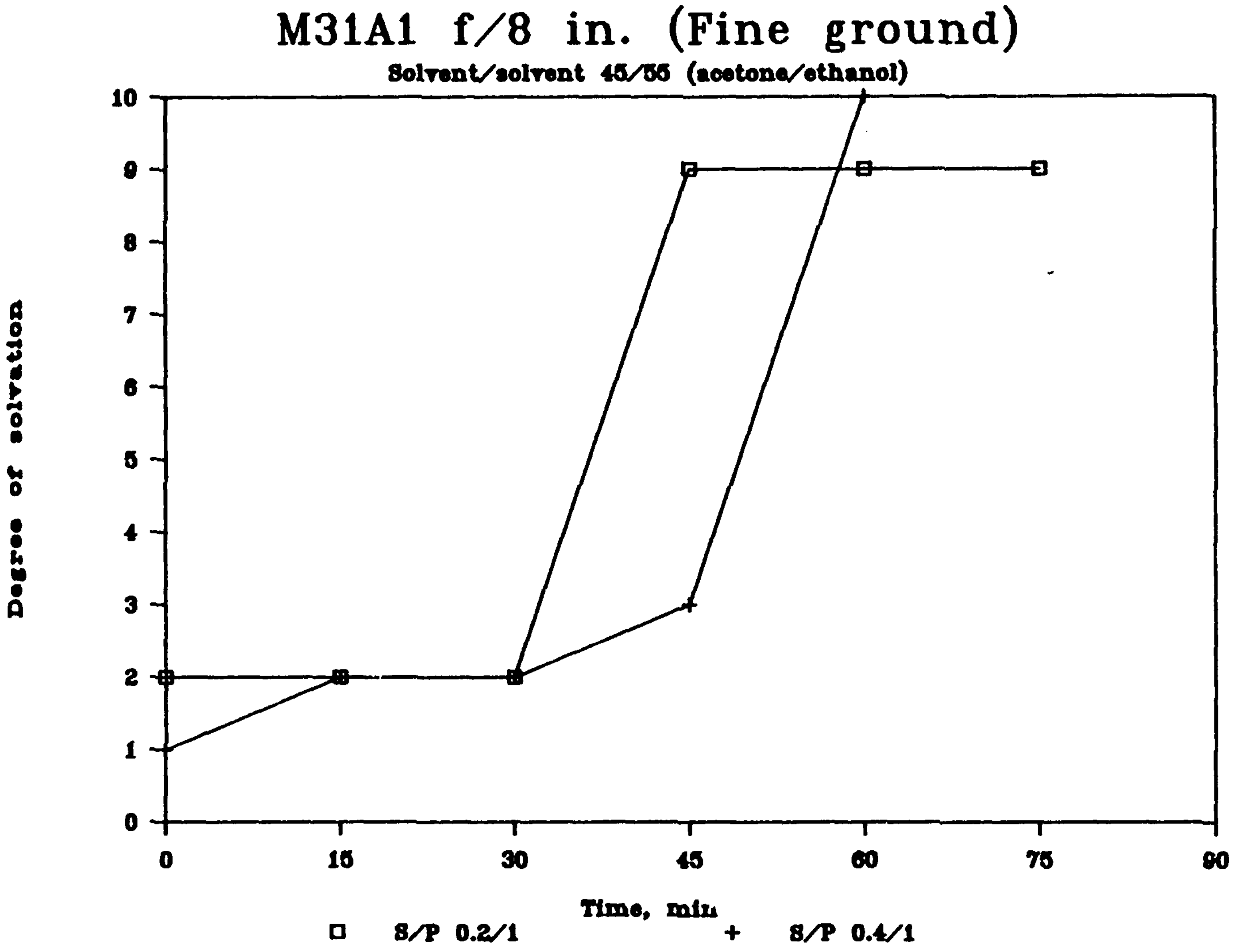

Figure 42. Degree of solvation vs time for M31A1 finely ground propellant (various solvent/propellant ratios and 45/55 acetone/ethanol ratio)

Table 14. Effects of major propellant ingredients on propellant resolvation

Ground samples	Propellant ingredient NC, %	Propellant ingredient NG, %	Propellant ingredient NQ, %	Solvent/propellant ratio
Triple-base propellant[a]				
M31A1	20.0	19.0	54.0	0.2/1 (0.4/1)[e]
M30A1	28.0	22.5	47.0	0.4/1
M30	28.0	22.5	47.7	(0.4/1)
Double-base propellant[a]				
M7	54.6	35.5	-	0.4/1
Single-base propellant[b]				
M1	85.0 ± 2.0	-	-	1/1
M6	87.0 ± 2.0	-	-	1.25/1-1.5/1 (1/1)
M10[c]	98.0 ± 1.0	-	-	1.5/1

Propellant ingredient	Solubility Acetone	Solubility Ether	Solubility Ethanol
NC	V[f]	I	I
NG[d]	V	V∞[h]	S[i]
NQ	I[g]	I	I

---

[a] Solvent system is production solvent/solvent ratio of acetone/ethanol.
[b] Solvent system is production solvent/solvent ratio of ether/ethanol.
[c] M10 is a flake propellant in which the samples were not ground.
[d] NG solubility data obtained from the literature (CRC Handbook).
[e] ( ), borderline solvent/propellant ratio for propellant resolvation.
[f] V-very soluble: >0.100 g/mL.
[g] I-insoluble: <0.010 g/mL.
[h] V ∞ - soluble in all proportions.
[i] S - soluble according to literature.

desired degree of plasticity. For the ground samples having a higher NC content than M31A1 propellant (i.e., M30A1 and M30), a solvent/propellant ratio of 0.4/1 yielded the desired degree of plasticity for M30A1 with borderline results for M30. The ground samples having the highest NC content (M7) required a solvent/propellant ratio of 0.4/1.

2.7 Discussion

In summarizing these resolvation tests, the criterion of importance is obtaining colloided propellant within a 90-min time frame to permit introduction of the resolvated propellants into the standard manufacturing processes. The parameters varied for the tests were (1) propellant particle size, (2) solvent/propellant ratios, (3) production-established solvent/solvent ratios, (4) ingredient addition, and (5) percentage of remix. The two parameters that greatly affected propellant resolvation were particle size and solvent/propellant ratios. Smaller particle sizes reduced the case-hardened area in the propellant, allowing greater solvent penetration for softening the NC matrix. This, in turn, reduced the solvent/propellant ratios for resolvation.

The production-established solvent systems used in propellant manufacturing at RAAP are ether/ethanol and acetone/ethanol systems for the single- and multi-base propellants studied, respectively. The solvent/solvent ratios of these solvent systems are determined by the %N and viscosity of the NC used in the specific propellant products. A ± 5 or ± 10% variation of these production-established solvent/solvent ratios greatly affects the mechanical disintegration of the colloid in subsequent propellant processing and final product physical characteristics (ballistics). Therefore, since production-established solvent/solvent ratios resolvated the propellant samples satisfactorily, variation of these ratios was not necessary.

The complete chemical analyses of the propellant samples (tables 4 through 12) indicated propellant ingredient addition for these tests was not necessary. Based on these results, the propellant was utilized as 100% remix; therefore, partial remix would more closely approximate the virgin mix blends in actual production processes.

Not all of the whole grain samples resolvated in the 90-min time frame as designated by the under-solvated propellant in table 15. Under-solvated propellant results from one of two conditions: (1) not enough solvents were added to the propellant sample to achieve resolvation or (2) case-hardened particles in the propellant sample precluded resolvation regardless of the amount of solvent added, resulting in excess solvents covering the dried propellant particles. The solvent/propellant ratio range tested with no propellant resolvation occurring in the 90-min time frame for each propellant type is shown in parentheses in table 15. Those that did resolvate were the smaller grains of M1 single-base (single-perforated), M9 double-base flake, and M10 single-base flake. Both the M1 single-perforated and M10 flake require a 1/1 to 1.25/1 solvent/propellant ratio for resolvation; this is in close agreement with virgin single-base propellant where 10 lb of

Table 15. Laboratory propellant resolvation results using production solvent/solvent systems

Propellant	Solvent/propellant ratios for various particle sizes			
	Whole grain	Crushed	Coarse	Fine
Single-base				
M1 single-perf	1/1 to 1.25/1	---[c]	1/1	1/1
M1 multi-perf	US[a] (1/1 to 1.5/1)[b]	---	1/1 to 1.25/1	1/1
M6	US (1/1 to 1.75/1)	US (1/1 to 1.75/1)	1/1	1/1 to 1.25/1
M10 (flake)	1.25/1	---	---	---
Double-base				
M2	US (0.4/1 to 0.8/1)	US (0.8/1 to 1/1)	0.8/1	0.6/1
M9 (flake)	0.4/1	---	---	---
M7 (stick)	---	0.4/1 to 0.6/1	0.4/1 to 0.6/1	0.4/1
Triple-base				
M30	US (0.4/1 to 1/1)	US (0.4/1 to 0.8/1)	US or OS[d] (0.2/1 to 1/1)	US or OS (0.2/1 to 1/1)
M30A1	US (0.4/1 to 1/1)	0.4/1	0.4/1	0.4/1
M31A1	US (0.6/1 to 1/1)	0.7/1	0.2/1	0.2/1

---

[a] US = under-solvated propellant.

[b] ( ) = solvent/propellant ratio range tested with no propellant resolvation occurring in the 90-min time frame.

[c] --- = not applicable.

[d] OS = over-solvated propellant.

ethanol is required to wet 38 lb NC, resulting in a production-established solvent/propellant ratio for virgin material of 0.9/1 for M10 flake and 0.62/1 for M1 single-perforated propellant. In the resolvation studies, additional solvent is required to penetrate the case-hardened propellant for softening the NC matrix. The double-base M9 flake propellant requires a 0.4/1 to 0.6/1 solvent/propellant ratio for resolvation. Again, the additional solvent was required to penetrate the case-hardened propellant.

Not all of the crushed samples resolvated in the 90-min time frame. Those that did resolvate were multi-base propellants having less NC content than the single-base propellants. M7 double-base propellant resolvated using a solvent/propellant ratio of 0.4/1 whereas M2 double-base propellant did not resolvate due to its greater NC content. M30A1 and M31A1 triple-base propellant showed borderline resolvation at solvent/propellant ratios of 0.4/1 and 0.7/1, respectively. M30 triple-base propellant is a large grain propellant and did not resolvate due to the crushed samples having a greater amount of case-hardened surface area exposed, not allowing solvent penetration into its NC matrix.

The coarsely ground propellant samples are those retained on a 20-mesh screen. With one exception, the single-base propellants resolvated using solvent/propellant ratios of 1/1 and 1.25/1, i.e., M1 single-base (single-perforated) propellant required a solvent/propellant ratio ranging from 1/1 to 1.25/1. The multi-base propellants resolvate when the solvent/propellant ratio is 0.2/1 to 0.4/1. One double-base propellant, M2, required a solvent/propellant ratio of 0.8/1 due to its greater NC content. One triple-base propellant, M30, requires a solvent/propellant ratio between 0.2/1 to 0.3/1 for resolvation. The exact solvent/propellant ratio for M30 was not established since internal mixing, i.e., shearing action (work) imparted to the propellant via mixer blades, is required to achieve resolvation.

The finely ground propellant samples are those having particles passing through a 20-mesh screen and retained on a 50-mesh screen. All of the single-base propellants resolvated using a solvent/propellant ratio of 1/1. The multi-base propellants resolvate when the solvent/propellant ratio is 0.2/1 to 0.4/1. The double-base propellant, M2, required a solvent/propellant ratio of 0.6/1 due to its greater NC content; the finely ground particle size permitted 75% of solvent usage as compared to the coarsely ground particle size. The triple-base propellants either overly solvated at a solvent/propellant ratio of 0.4/1, did not resolvate at a solvent/propellant ratio of 0.2/1, or showed borderline resolvation characteristics; again, internal mixing is required to establish the exact solvent/propellant ratios (especially for M30).

3.0 BENCH-SCALE PROPELLANT RESOLVATION STUDY

The two main parameters for the bench-scale study were that (1) the study be based on the results of the laboratory-scale study and (2) the propellant resolvated during the mixing evaluations of the bench-scale studies be properly resolvated to permit its introduction into the standard RAAP manufacturing processes. Hazards analyses were conducted before and during the bench-scale evaluations to ensure conformance to safety guidelines. Due to safety considerations of the available bench-scale mixer, e.g., the presence of NG, only single-base propellants were considered for the bench-scale study. More detailed information concerning the hazards analyses are included as appendix B.

Of the single-base propellants evaluated in the laboratory-scale study, both M1 and M6 were being produced on the RAAP production lines. M1 propellant was selected rather than M6 propellant because larger quantities of M1 were available for resolvation; furthermore, the ease of using the M1 die in the 4-in. press without modifications was a factor in selecting M1 propellant for these studies. Also, M6 propellant was not being dried in the standard drying operations but was being dried at the continuous automated single-base line (CASBL) where retaining the propellant identity would be prohibited.

Due to production constraints and availability of propellant for resolvation, sulfonated M1 multi-perforated propellant for the 155-mm gun system (designated M4A2) was produced during the bench-scale study. This propellant does not utilize the same die as the currently manufactured non-sulfonated M1 multi-perforated propellant for the 105-mm gun system (designated M724). Furthermore, the minimal sulfate content (1.0%) of the sulfonated propellant (bench-scale quantity of ~30 lb) would be diluted in the production quantities of non-sulfonated propellant (~3,000 lb) being processed and not affect final propellant specifications. (It should also be noted that the processing water itself used in normal production operations contains ~0.2% sulfate.)

Five tasks were delineated for investigation during the bench-scale study: (1) preliminary extrusion study using the 4-in. press, (2) sample preparation by grinding sulfonated M1 multi-perforated propellant at the incinerator facilities, (3) preliminary resolvation study by resolvating the ground M1 propellant in a 2-1/2 gal. Baker-Perkins mixer, (4) in-process operations of processing the resolvated, ground M1 propellant in the 4-in. press and standard propellant manufacturing operations, and (5) sample analyses and data reduction to determine final product analyses of chemical, physical, and ballistic uniformity of the propellant.

3.1 Preliminary Extrusion Studies

In order to delineate the optimum operating parameters for extruding the resolvated sulfonated propellant in the 4-in. vertical press for the bench-scale study, data was collected from both the 4-in. and 12-in. horizontal presses utilizing the 105-mm die. The data, summarized in table 16, are separated into three parts: (1) mix data, (2) 4-in. press data, and (3) 12-in. press data. These data include residual solvents (RS), total volatiles (TV), strand length, extrusion time, density, specific gravity, pressure, and temperature. These data were collected from a 12-in. press (normally used in production) during the extrusion of

Table 16. Data collected from preliminary extrusions

	Mix No. 1	Mix No. 2	Mix No. 3	Mix No. 4	Mix No. 5	Mix No. 6	Mix No. 7	Mix No. 8	Mix No. 9	Mix No. 10	Mix No. 11	Mix No. 12	Mix No. 13	Mix No. 14	Mix No. 15
Solvent Composition at Completion of Mix Cycle															
Ether, %	19.18	20.34	20.06	20.16	24.07	24.03	24.12	24.22	23.64	22.90	19.20	13.81	20.94	21.33	21.21
Ethanol, %	12.75	12.15	12.43	11.96	12.54	12.37	13.34	13.66	13.14	12.48	[illegible]1	11.94	11.73	12.20	12.15
Water, %	1.15	1.30	1.30	1.20	1.13	1.30	1.36	1.54	1.50	1.35	.51	2.53	1.47	1.40	1.61
RS, %	31.93	32.49	32.49	32.12	36.61	36.40	37.46	37.88	36.78	35.38	31.81	25.75	32.67	33.53	33.36
TV, %	33.08	33.79	33.79	33.32	37.74	37.70	38.82	39.42	38.28	36.73	33.32	28.28	34.14	34.93	34.97
Solvent Composition and 4-in. Press Data at Time of Extrusion															
Ether, %	17.19	20.15	18.78	19.06	21.66	19.50	20.03	21.02	19.81	19.17	19.27	19.13	20.49	19.23	18.75
Ethanol, %	12.44	11.59	12.24	12.32	12.09	12.60	12.70	12.45	12.88	12.29	12.28	11.84	11.38	11.94	11.46
Water, %	1.20	1.14	1.18	1.25	1.43	1.37	2.28	2.37	1.79	1.35	1.30	1.37	1.39	1.35	1.31
RS, %	29.63	31.74	31.02	31.38	33.75	32.10	32.73	33.47	32.69	31.46	31.55	30.97	31.87	31.17	30.21
TV, %	30.83	32.88	32.20	32.63	35.18	33.47	35.01	35.84	34.48	32.81	32.85	32.34	33.26	32.52	31.52
Press number	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14
Outside temp, °F	38	38	38	38	45	45	45	45	45	45–55	45–55	45–55	45–55	45–55	45–55
Bay temp, °F	70–75	70–75	70–75	70–75	70–75	70–75	70–75	70–75	70–75	80	80	70–80	70–80	70–80	70–80
Volume, mL[a]	0.44	0.43	0.42	0.44	0.43	0.42	0.41	0.42	0.43	0.42	0.43	0.42	0.41	0.42	0.43
Length, in.	760	918	681	881	805	782	892	914	845	873	860	855	843	792	832
Time, min	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Flow, in./min	380	459	340.5	440.5	402.5	391	446	457	422.5	436.5	430	427.5	421.5	396	416
Flow, mL/min	167.15	197.26	143.09	193.83	173.05	164.22	182.86	191.91	181.68	183.38	184.87	179.47	172.87	166.32	178.88
Specific gravity[b]	0.105	0.849	0.070	0.917	0.058	0.078	0.083	0.075	0.091	0.114	0.099	0.105	0.096	0.116	0.110
Weight, g/in.	0.47	0.45	0.45	0.46	0.46	0.46	0.45	0.45	0.46	0.46	0.49	0.46	0.49	0.46	0.46
Flow, g/min	176.75	207.71	154.49	204.05	185.57	179.37	201.58	203.94	193.35	202.85	212.28	197.19	205.54	183.98	191.53
Pressure, psig	2450	1900	2175	1950	2200	2355	2113	1950	2130	1980	2065	2130	2000	2125	2030
Density, g/mL	1.06	1.05	1.08	1.05	1.07	1.09	1.10	1.06	1.06	1.11	1.15	1.10	1.19	1.11	1.07
Ram rate, in./min	0.77	1.05	0.64	0.74	0.88	0.87	0.97	1.07	0.81	1.03	0.81	0.81	0.51	1.00	0.73

Table 16. (cont)

	Mix No. 1	Mix No. 2	Mix No. 3	Mix No. 4	Mix No. 5	Mix No. 6	Mix No. 7	Mix No. 8	Mix No. 9	Mix No. 10	Mix No. 11	Mix No. 12	Mix No. 13	Mix No. 14	Mix No. 15
Solvent Composition and 12-in. Press Data at Time of Extrusion															
Ether, %	15.82	17.99	18.24	18.47	23.06	22.38	22.04	21.32	21.03	19.04	19.39	18.19	19.62	19.91	19.22
Ethanol, %	12.95	11.74	12.11	12.53	14.04	12.56	13.29	13.11	13.36	12.44	12.23	11.70	11.86	11.90	11.80
Water, %	1.32	1.25	1.29	1.33	1.67	1.36	2.58	1.77	1.60	1.44	1.50	1.49	1.47	1.38	1.35
RS, %	28.77	29.73	30.35	31.00	37.10	34.94	35.33	34.43	34.39	31.48	31.62	29.89	31.48	31.81	31.02
TV, %	30.09	30.98	31.64	32.33	38.77	36.30	37.91	36.20	35.99	32.92	33.12	31.38	32.95	33.19	32.37
Press number	2	1	1	2	4	1	2	1	4	3	3	4	4	4	3
Outside temp, °F	38	38	38	38	45	45	45	45	45	45-55	45-55	45-55	45-55	45-55	45-55
Bay temp, °F	70-75	70-75	70-75	70-75	70-75	70-75	70-75	70-75	70-75	70-75	70-75	70-75	70-75	70-75	70-75
Volume, mL[a]	0.44	0.45	0.48	0.40	0.43	0.44	0.42	0.43	0.41	0.41	0.44	0.41	0.45	0.44	0.44
Length, in.	426	419	424	546	384	475	510	548	499	535	588	634	797	438	765
Time, min	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Flow, in./min	1704	1676	1696	2184	1536	1900	2040	2192	1996	2140	2352	2536	3188	1752	3060
Flow, mL/min	745.50	754.20	805.60	873.60	652.80	831.25	849.15	931.60	823.35	882.75	1029.00	1046.10	1434.60	766.50	1338.75
Specific gravity[b]	0.104	0.083	0.085	0.985	0.066	0.059	0.075	0.074	0.083	0.091	0.107	0.095	0.109	0.104	0.112
Weight, g/in.	0.52	0.47	0.43	0.49	0.45	0.45	0.46	0.46	0.46	0.46	0.48	0.47	0.47	0.46	0.47
Flow, g/min	884.00	779.81	730.22	1070.77	696.32	857.64	931.03	1005.28	918.71	982.02	1127.65	1183.47	1496.59	803.97	1432.25
Pressure, psig	2400	2200	2400	1900	2600	2600	2200	2200	2200	2100	2150	2300	2200	2150	2500
Density, g/mL	1.19	1.03	0.91	1.23	1.07	1.03	1.10	1.08	1.12	1.11	1.10	1.13	1.04	1.05	1.07
Ram rate, in./min	7.25	8.50	7.60	7.00	7.00	9.25	9.50	11.00	7.75	10.50	9.50	10.00	9.00	9.75	11.50

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[a] Calculated as the volume of a 1-in. length of the propellant extrudate.

[b] Calculated on the basis of a 2-in. length of the propellant extrudate.

non-sulfonated M1 multi-perforated propellant. To obtain data on the 4-in. press (not normally used in the production of single-base propellants), 10 lb of the non-sulfonated M1 propellant was removed from the production mixes and extruded through the 4-in. press using the same die and screen size as the 12-in. press.

The mix data shown in table 16 represents propellant samples from the production line mixes at the completion of the mix cycle. The RS and TV data were collected to obtain initial conditions prior to extrusion in the 4-in. vertical press and the 12-in. horizontal press. The 4-in. press data includes mix RS and TV after extrusion, test press number, temperatures (outside and bay), volume displacement of the extruded strand (for flow rate calculations), length of the strand over a timed cycle, specific gravity (SpG), weight and density of the strand, and pressure. The ram rate (X_4) was calculated for the 4-in. press using the flow rates from the 4- and 12-in. presses, the cross sectional area and number of dies, and the measured ram rate (X_{12}) of the 12-in. press. Similar data was collected for the 12-in. press.

The critical information required to extrude bench-scale mixes in the 4-in. vertical press is pressure vs ram-rate ratio (X_{12}/X_4) at known TV. This data shown in figure 43 would be comparable to the 155-mm die since the pressure must remain in the 12-in. press control limits to ensure proper processing of the propellant throughout the remaining operations of cutting and drying (solvent recovery, water dry, and air dry). The upper control limit (UCL) is 2,600 psig whereas the lower control limit (LCL) is 1,800 psig. The 4-in. press tracked extremely well with the 12-in. press, i.e., only 19% maximal variation (30% variation is allowable). The range in ram-rate ratio of 7.96 to 17.52 is due to the TV of the extruded propellant. The lesser ratio of 7.96 had a maximum TV difference between the extruded strands (3.59%) whereas the greater ratio of 17.52 had a minimum TV difference (0.31%) for the same test presses. In order to extrude bench-scale mixes in the 4-in. press, a TV range of 28 to 40% is allowable with an ether/ethanol ratio of 1.9 for both dies (105-mm and 155-mm).

3.2 Sample Preparation

The granular M1 propellant selected for the bench-scale study is cylindrical with the following dimensions: 0.18-in. diameter and 0.40-in. length (fig. 44). The size of the propellant granules was reduced with the Mitts and Merrill grinder (Model Number 14-CSF) located at the RAAP incinerator facilities. A schematic diagram of this process unit is shown in figure 45. This unit is a knife grinder (or granulator) with a cutting chamber containing rotating and stationary knives. A 30 x 40-in. screen containing nine thousand 3/16-in. diameter holes in the bottom of the cutting chamber limits output particle size through the bottom discharge. The propellant is introduced into the grinder as a separate feed along with a water feed to eliminate the potential of fire. The reduced propellant is then discharged as a slurry of ground propellant and water.

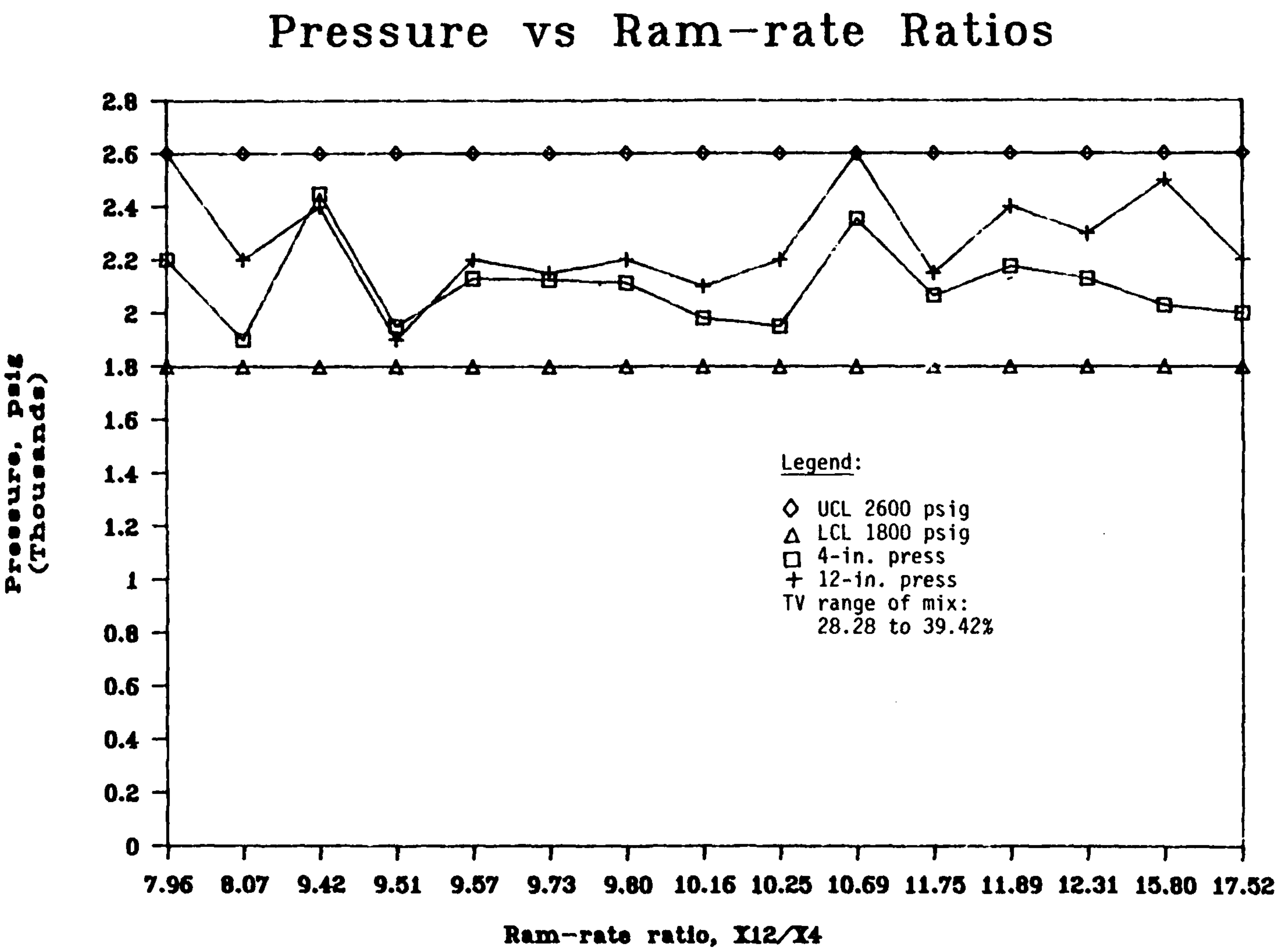


Figure 43. Summary of pressure vs ram-rate ratios of 12-in. horizontal and 4-in. vertical presses

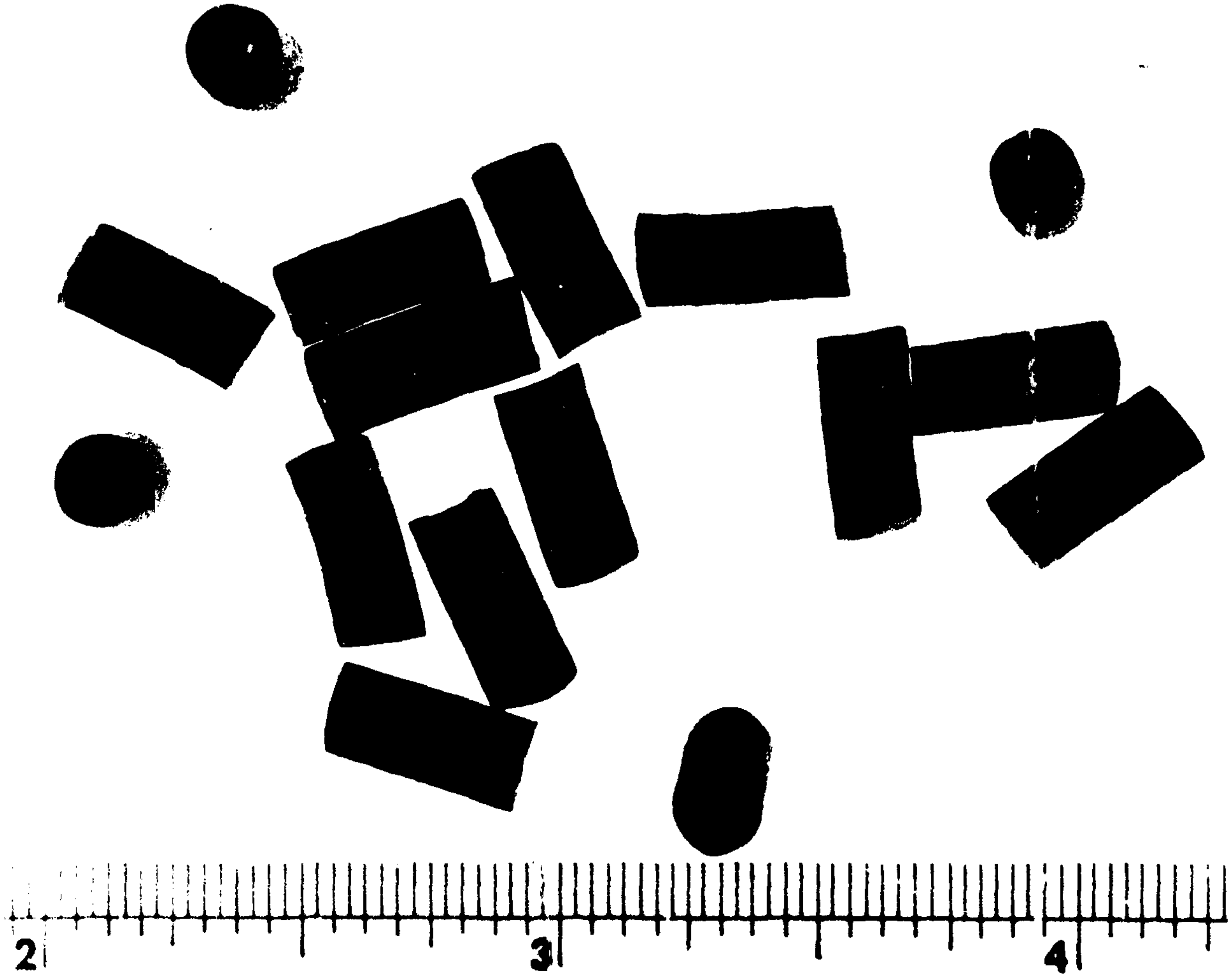


Figure 44. Sulfonated whole grain M1 multi-perforated propellant

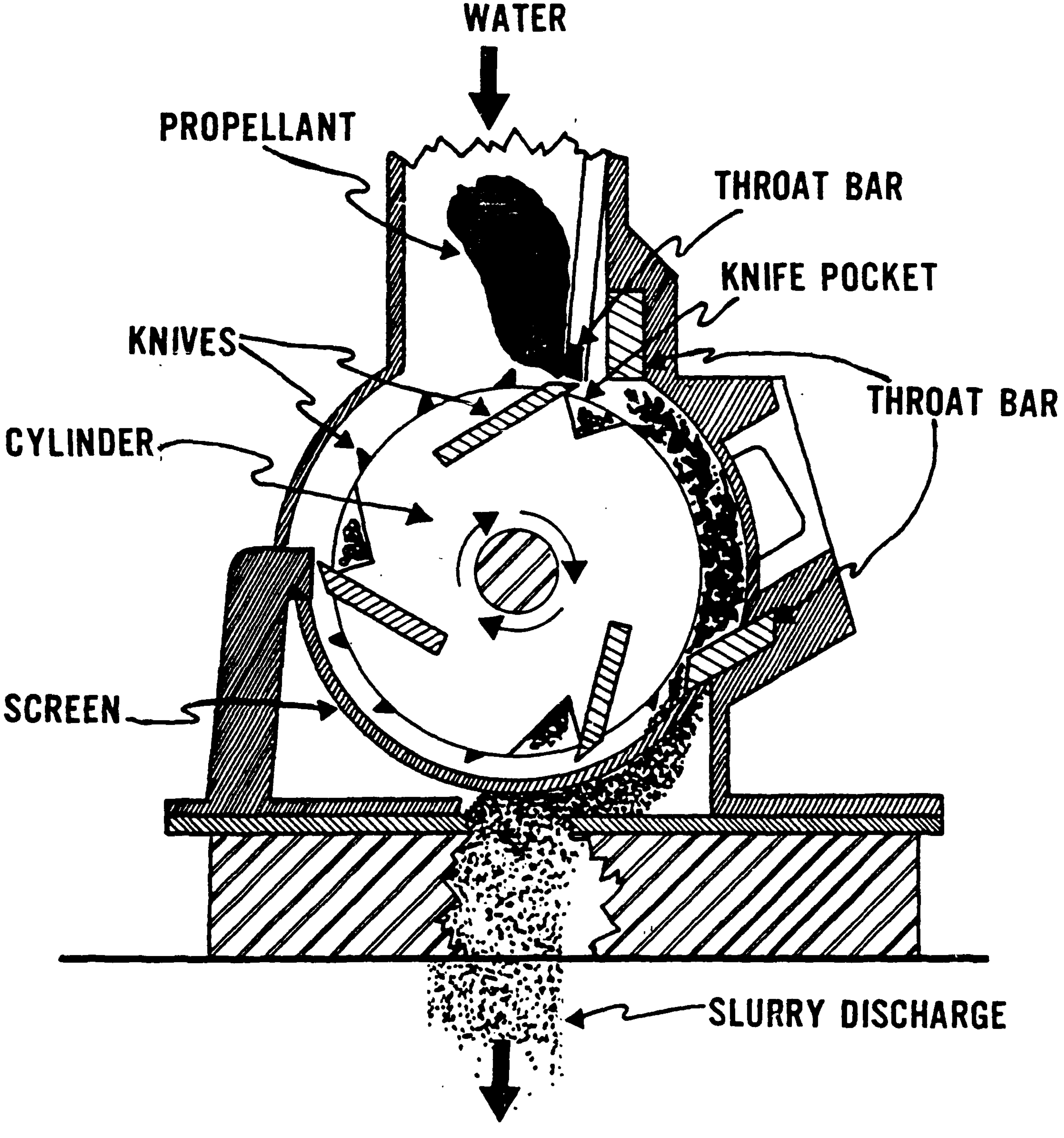


Figure 45. Mitts and Merrill knife grinder

The slurry was transferred to the separation facility to be dewatered by gravity filtering on a Sweco® Vibro-Energy separator (fig. 46). Separation was accomplished by continually feeding the slurry to the center of the 48-in. screen (150 mesh, 0.0041-in. wire diameter, 0.0026-in. wire opening) in which the dewatered solid propellant moved by vibration across the screen cloth to a discharge spout. The water passed through the screen to a lower discharge spout. The propellant was collected from the separator in 20-lb (wet weight) increments and placed on trays which were loaded into drying cabinets. A total of seventeen trays were filled, with the top tray remaining empty so that the propellant fines on the lower trays would not contaminate the FAD bay during drying. Six cabinets were filled, resulting in 2,040 lb (wet weight) of ground propellant.

The propellant was dried at 140°F for 24 h in a FAD to reduce moisture content to <1%. Propellant containing >3% moisture will not process properly. Chemical analyses were conducted according to MIL-STD-286B on the propellant prior to grinding and after drying; no ingredient loss occurred during sample preparation according to these chemical analyses (refer to table 4 for the M1 propellant specifications). However, the MIL-STD-286B analysis for total stabilizer uses DPA as the reference measure; HPLC analysis revealed that two by-products of DPA (N-NDPA and 2-NDPA) were present in the propellant, thus distorting the actual DPA content. Because of these by-products, 0.14% of DPA was added to the solvent mixture for the resolvation studies to compensate for the actual DPA loss. The TV analysis indicated 0.15% water, 0% ethanol, and 0.02% ether. Photographs of the various propellant particle sizes, together with particle size distribution, are shown in figure 47. The propellant was then remotely dumped and packed out in ten drums, each weighing 135 lb.

3.3 Preliminary Resolvation Study

A remotely controlled 2.5-gal. Baker Perkins mixer was used to perform the bench-scale resolvation studies. The mixer, fabricated of stainless steel, is jacketed for water cooling or steam heating. The sigma-configured mixer blades (fig. 48) are rotated in a front-to-back speed ratio of approximately 1.88 to 1.0. Nominal clearances for this mixer are summarized as follows: 0.035 in. between blade and bottom of bowl, 0.125 in. between blade hub and bowl ends, and 0.180 in. between blade tips and bowl ends. A Reeves Vari-Speed motor drive unit provides for manual variation from 57.5 to 230 rpm; this unit was originally driven by a 2-hp motor with explosive classification of Class I, Group D, and Class II, Groups E, F, and G.

The Hazards Analysis conducted prior to the bench-scale studies indicated that this motor did not meet proper electrical classification, i.e., Division I, Class I, Groups C and D and Division I, Class II, Groups E and G. Therefore, a modified air-purge to the motor meeting this classification was installed and safety approved. Mixer evaluations were initiated using the ground, dried M1 propellant. Blade speeds of 15 and 30 rpm were used to approximate the blade speeds of the standard

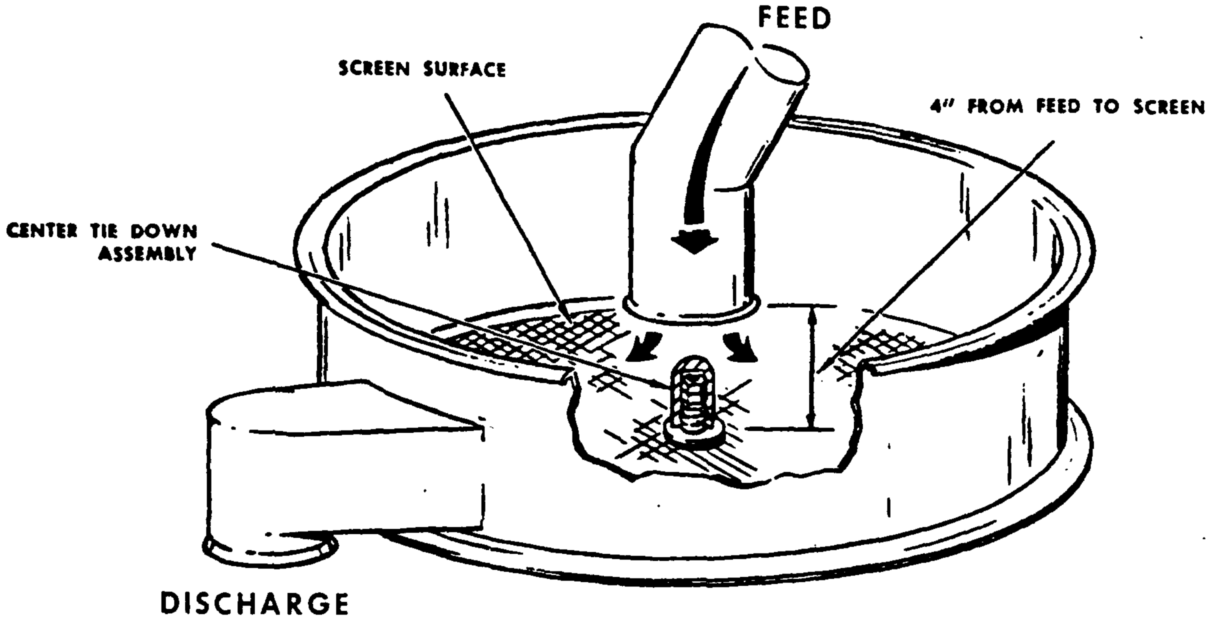


Figure 46. Sweco® Vibro-Energy separator

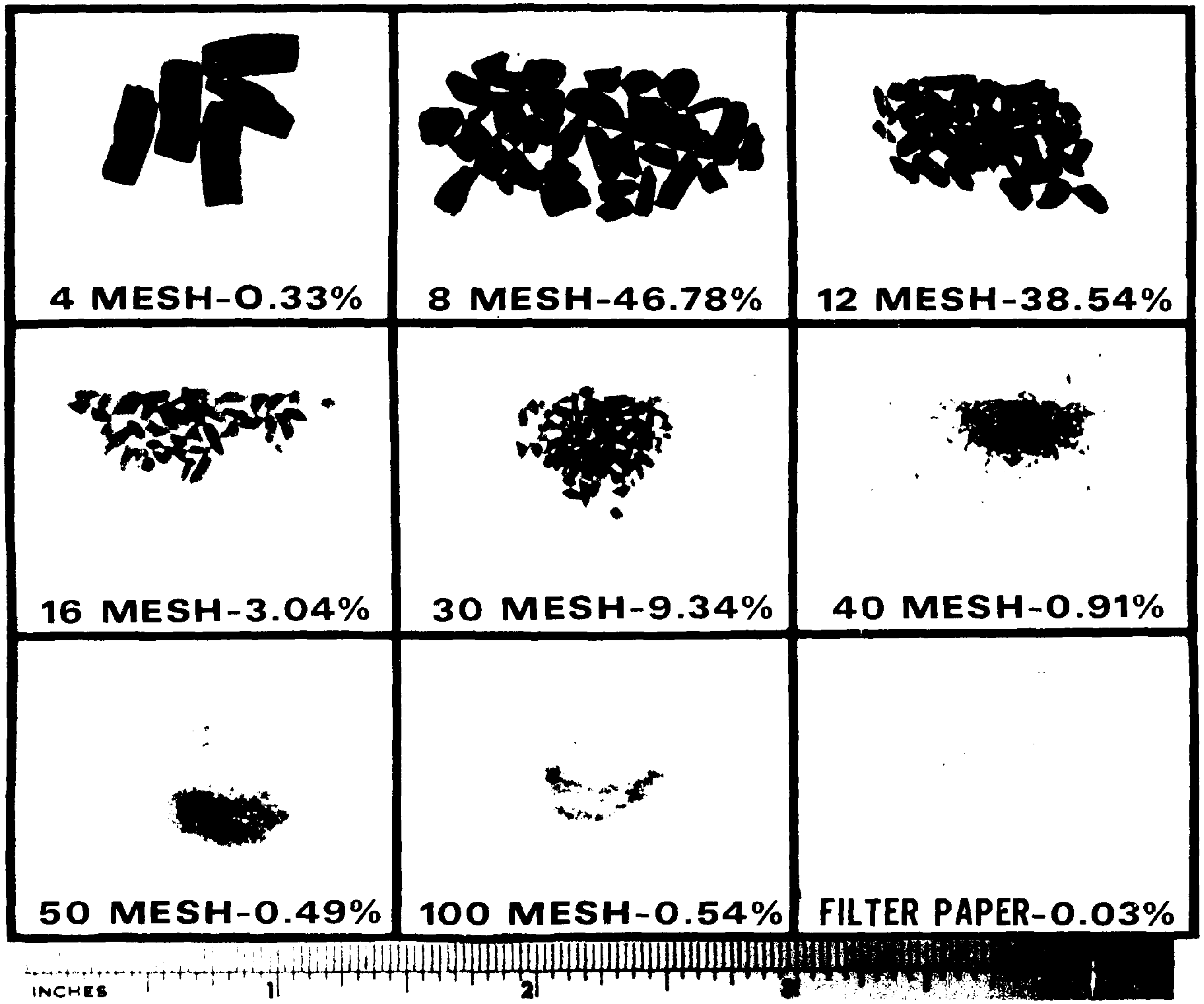


Figure 47. Particle size distribution of ground, sulfonated M1 multi-perforated propellant (wt% retained on standard Tyler screens)

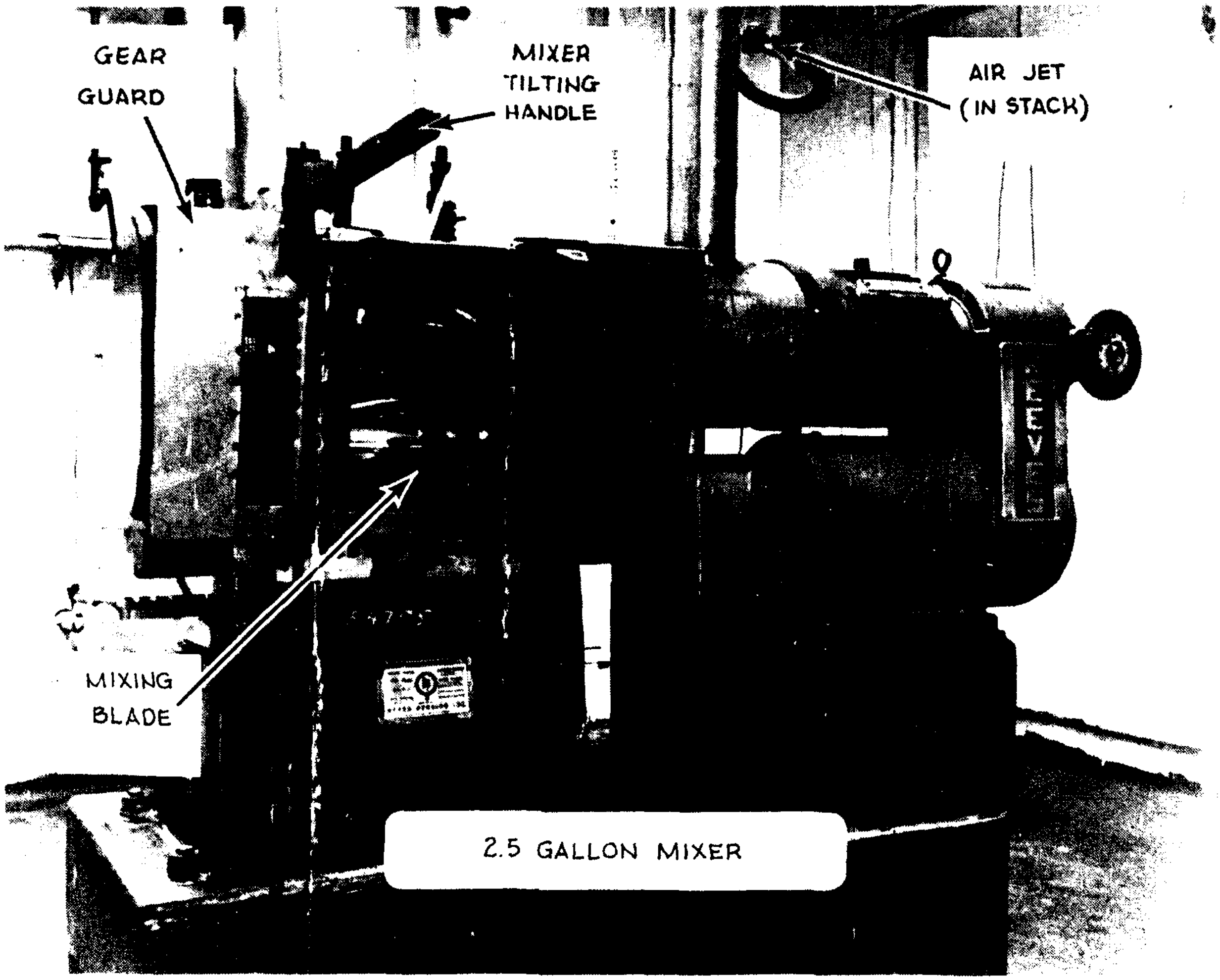


Figure 48. Remotely controlled 2.5-gal. Baker Perkins sigma-blade mixer

production sigma-blade mixers. A total of thirty iterative mixing trials using 4 lb of ground propellant per trial were conducted in order to optimize the operating parameters, with the last nine trials being processed in the standard production operations of extruding, cutting, and drying for sample analyses. The results of the iterative trials for the bench-scale resolvation studies are summarized in table 17.

Based on the results of the laboratory-scale resolvation studies, the following operating parameters were established for Trial 1: a solvent/propellant ratio of 1/1, a sorption cycle of 15 min (required to allow the solvent ample time to permeate the dry propellant), and a mix cycle of 20 min. The mixing operation was stopped at 5-min intervals for examination. The data (TV and approximation of the degree of solvation attained) indicated that maximum solvation was attained at 15-min mix time; however, the mix was over-solvated and a 24-min drying cycle was required to remove the excess solvent. A plasticity degree of ~90% was attained.

To reduce the drying time, a solvent/propellant ratio of 0.8/1 was evaluated in Trial 2 in order to more closely approximate standard production ratios. A 25-min mix cycle in conjunction with a 15-min sorption cycle was selected in order to compensate for the lowered solvent/propellant ratio; however, propellant resolvation was attained in 15 min, thus negating further evaluations of mix cycle times. Only a 5-min drying cycle was necessary to attain the required TV level for extrusion. As in Trial 1, ~90% plasticity was achieved.

In Trial 3, using the same conditions for Trial 2, the procedure for charging the mixer was reversed. In the first two trials, the solvent was added to the propellant in the mixer (to simulate actual production procedures); apparently, when the solvent is added to the propellant in the mixer, a gelatinous layer forms, thus limiting solvent sorption throughout the contents of the mixer. In this trial the solvent was placed in the mixer and the propellant evenly distributed in it. This procedure did not improve final plasticization (~70%) since the mix was over-solvated and a 15-min drying cycle was required to remove the excess solvents.

In order to further enhance plasticization, Trials 4 and 5 were performed using a solvent/propellant ratio of 0.8/1 and a 30-min sorption cycle. The solvents were added to the propellant to simulate actual production procedures. The additional time for the sorption cycle did not change the drying cycle (table 17); however, plasticization greatly improved, i.e., ~95% and ~80-85% for Trials 4 and 5, respectively.

Trial 6 was also conducted with a solvent/propellant ratio of 0.8/1. Since indications of a gelatinous layer were observed in Trials 4 and 5, the solvent was placed in the mixer and the propellant evenly distributed in it. The sorption cycle was increased to 45 min, followed by a 15-min mix cycle and a 4-min drying cycle to achieve ~98% plasticity.

In Trial 7, an actual standard production solvent/propellant ratio of 0.7/1 was evaluated with the solvent added to the propellant (standard production procedure) using a 15-min mix cycle. Visual observation of

Table 17. Results of iterative trials for bench-scale resolvation studies

Trial	Solvent/propellant ratio	Particle size	Sorption cycle, min	Mixing cycle, min	Drying cycle, min	TV after mixing, %	TV after drying, %	TV after extrusion, %	Degree of plasticity, %
1	1/1	Unscreened	15	20	24	42.88	36.57	---	90
2	0.8/1	Unscreened	15	25	5	37.07	36.23	---	90
3	0.8/1	Unscreened	15	15	15	39.54	39.26	---	70
4	0.8/1	Unscreened	30	15	6	38.71	34.17	---	95
5	0.8/1	Unscreened	30	15	7	36.40	38.48	---	80-85
6	0.8/1	Unscreened	45	15	4	36.81	36.47	---	98+
7	0.7/1	Unscreened	15	15	11	32.57	31.08	---	70
8	0.7/1	Unscreened	30	15	3	37.14	33.86	---	80-85
9	0.8/1	Unscreened	45	75	0	13.48	---	13.29	95+
10	0.8/1	Passed 8-mesh	45	30	15	41.61	40.82	40.70	95+
11	0.8/1	Passed 10-mesh	45	15	0	44.72	---	43.65	95+
12	0.7/1	Passed 10-mesh	45	15	0	41.72	---	38.05	95+
13	0.8/1	Passed 12-mesh	45	15	0	42.65	---	40.74	95+
14	0.7/1	Passed 12-mesh	45	20	0	45.11	---	32.98	95+
15	0.7/1	Passed 12-mesh	60	15	0	39.26	---	38.71	95+
16	0.75/1	Passed 12-mesh	60	15	0	38.91	---	---	95+
17	0.75/1	Passed 12-mesh	60	15	0	39.42	---	42.49	95+
18	0.75/1	Passed 12-mesh	60	15	0	46.00	---	---	95+
19	0.75/1	Passed 12-mesh	60	15	0	38.74	---	35.98	95+
20	0.75/1	Passed 12-mesh	60	15	0	39.58	---	35.72	95+
21	0.75/1	Passed 12-mesh	60	15	0	39.66	---	39.16	95+
22	0.75/1	Passed 12-mesh	60	15	0	47.73	---	35.51	95+
23	0.75/1	Passed 12-mesh	60	15	0	36.66	---	35.90	95+
24	0.75/1	Passed 12-mesh	60	15	0	35.65	---	34.72	95+
25	0.75/1	Passed 12-mesh	60	15	0	38.28	---	33.26	95+
26	0.75/1	Passed 12-mesh	60	15	0	34.54	---	33.73	95+
27	0.75/1	Passed 12-mesh	60	15	0	36.84	---	31.88	95+
28	0.75/1	Passed 12-mesh	60	15	0	37.06	---	34.08	95+
29	0.75/1	Passed 12-mesh	60	15	0	35.47	---	33.28	95+
30	0.75/1	Passed 12-mesh	60	15	0	36.55	---	34.53	95+

the mix following the 15-min mix cycle indicated that all propellant particulates had not been plasticized, i.e., ~70% plasticity. However, the under-solvated particles were evenly distributed throughout the coalesced over-solvated propellant, indicating that additional mixing for further distribution of the under-solvated particles would not result in additional plasticization. An 11-min drying cycle was required to remove the excess solvent from the over-solvated propellant.

To improve plasticization using solvent/propellant ratios approximating standard production ratios, the procedure for charging the mixer was again reversed in Trial 8, i.e., the solvent was placed in the mixer and the propellant evenly distributed in it; furthermore, the sorption cycle was increased to 30 min to achieve greater plasticity. A plasticity of ~80-85% was attained with a 3-min drying cycle.

Resolvation of the propellant for Trial 9 was conducted using the following parameters which were optimized in Trials 1 through 8: (1) solvent/propellant ratio of 0.8/1, (2) 45-min sorption cycle, (3) propellant addition to the solvent, and (4) 15-min mix cycle. To eliminate the drying cycle and determine that a 15-min mix cycle will resolvate the propellant, an additional 1 h of mixing was performed to verify that the 15-min cycle was adequate. A 95% degree of plasticity was attained. Even though the TV level was low (19.48%), this mix was tested in the 4-in. vertical press. Excessive extrusion pressure (3,000 psig) was observed due to the mix fouling the 16- and 40-mesh press screens. The particles on the screen, which were solvated on the outside, contained dry pieces of propellant on the inside. This indicated that the method of determining plasticity did not consider the incomplete resolvation of the larger particles

Trial 10 utilized propellant particles that passed an 8-mesh screen to assure more complete solvation of the propellant to reduce fouling of the 16- and 40-mesh press screens. After a 45-min sorption cycle in which the propellant was added to the solvent, followed by a 30-min mix cycle to assure thorough mixing, a 15-min drying cycle was required to remove excess solvent from the plasticized (95+%) mix. Extrusion of this mix also resulted in high pressure (3,000 psig) and fouling of the press screens.

In Trials 11 and 12, propellant particles that passed a 10-mesh screen were evaluated using solvent/propellant ratios of 0.8/1 and 0.7/1, respectively. The propellant was added to the solvent for a 45-min sorption cycle, followed by a 15-min mix cycle. No drying cycle was conducted in either trial in order to ensure solvent-wet propellant (95+% plasticity) for extrusion. Both mixes, which were extruded in the 4-in. press, resulted in high extrusion pressures (~3,000 psig) with fouling of the press screens; however, propellant strands were obtained. Visual inspection of the strand from trial 11 (0.8/1 solvent/propellant ratio) indicated that the strand was too soft for further processing, i.e., cutting, whereas the strand from trial 12 (0.7/1 solvent/propellant ratio) was processible. The high pressures and the fouling of the press screens prohibited complete extrusion of both mixes. Since propellant strands were obtained from both of these trials, the drying cycle following mixing was unnecessary; therefore, the drying cycle was eliminated in subsequent trials.

Trials 13 and 14 were performed similarly to trials 11 and 12, respectively, with an additional 5-min mixing time in trial 14 to assure even distribution of the solvents. The same degree of plasticity (95+%) was obtained for both mixes. The extrusion of trial 13 resulted in low pressure (~1,000 psig) with the resulting strand being too soft to cut. In trial 14, high pressure (~3,000 psig) during the extrusion resulted from fouling of the press screens; however, a short strand of propellant was extruded before the extrusion was discontinued. Visual inspection indicated that this strand was processable for cutting.

To determine if additional sorption time would have improved the extrusion in trial 14, i.e., reduce fouling of the press screens, trial 15 was conducted using a 60-min sorption cycle and a 20-min mix cycle. The results were similar to those of trial 14; however, the additional sorption time produced an improved quality strand for cutting, i.e., the surfaces of the strands were smoother than in the previous trials.

Trials 16 through 20 were conducted similarly to trial 15 with one exception. A 0.75/1 solvent/propellant ratio was chosen for two reasons:

(1) The 0.8/1 solvent/propellant ratio (trial 13) resulted in low extrusion pressure (~1,000 psig) and a propellant strand that was too soft to cut whereas a 0.7/1 solvent/propellant ratio (trials 14 and 15) resulted in fouling of the press screens (prohibiting complete extrusion of the mix) even though the strands were processable for cutting.

(2) Consideration was also given to further processing with respect to granule shrinkage that occurs during solvent removal in the drying operations.

The propellant mix in Trial 16 was not extruded due to the unavailability of the 4-in. press. The addition of solvents to prevent the propellant mix from drying until it could be extruded would have negated the results of the trial, i.e., an unknown solvent/propellant ratio. The extrusion pressures during Trials 17 through 20 were high (~3,000 psig), due to slight fouling of the press screens. The majority of the propellant mix in each trial was extruded before fouling of the press screens occurred, yielding acceptable strand lengths with varying surface qualities ranging from rough to smooth. These factors, i.e., high pressure, screen fouling, and varying surface qualities of the strands, indicated that the ram rate of the press was inconsistent and the press required additional hydraulic fluid to increase the ram rate.

Trial 21 was conducted similarly to trials 16 through 20. When this mix was extruded, additional hydraulic fluid was added to press head to increase the ram rate, resulting in complete extrusion of acceptable propellant strands and clean press screens. The addition of excess hydraulic fluid to the press head is not a normal operating procedure for the production of M1 propellant in the 12-in. horizontal press.

Trials 22 through 30 were conducted as trial 21. The propellant strands were processed through the cutting and drying operations as described below. Chemical, physical, and ballistic analyses were performed on the finished M1 product for comparison to the specifications in MIL-STD-286B (table 18).

3.4 Processing

As noted earlier, the propellant from the last nine of the thirty iterative mixing trials was further processed in the standard production operations, i.e., extruding, cutting, and drying, to produce a finished product. The extrudate from the 4-in. press was collected on cones for transport to the cutting operation. During this operation, the strands are fed into the cutting machine through holes in a feed bar. Knurled rollers grip the strands and draw them inward through a middle and rear feed plate, or cutting die, to the blades. The speed of the rollers is synchronized with the speed of the blades so that a length of strand equal to the desired length of grain will be drawn into the machine each time a blade passes the cutting die. A reservoir, positioned on top of the cutting machine, contains a coolant solution (water) which drops on the die to keep the surface moist. This solution helps prevent excessive friction and keeps particles of propellant from sticking to the cutting blades.

The grains of propellant are severed from the incoming strand and fall in stainless steel containers. After cutting, the propellant contains ~30-33% solvent which must be removed. The propellant grains were placed in sausage bags (muslin bags equipped with drawstrings) to retain propellant identity throughout the remaining manufacturing processes, i.e., solvent recovery, water dry, and air dry. The sausage bags of propellant were placed in heated solvent recovery tanks which are purged with inert gas to lower the oxygen content of the tank to a safe operating limit (~0.8%). Heated inert gas is forced through the propellant to vaporize solvent which is then condensed and sent to activated carbon tanks for purification; the solvent remaining in the propellant (~7.0%) is then removed to an acceptable level via the water dry operation. The resolvated propellant remained in the solvent recovery tank for 36 h.

The water dry operation is accomplished in a large wooden tank in which heated water is circulated throughout the propellant. The retained solvent in the propellant has a high affinity for water; surrounding the grains with water causes a condensation and diffusion of solvent at or near the surface of the propellant into the water. The resultant voids are filled by solvent from the interior of the grain. The water dry process is continued until the RS level meets specification requirements, i.e., 0.70% maximum. Following 90 h in the water dry tank, the resolvated propellant was sampled for RS analysis, resulting in 0.69% RS. The propellant remained in the water dry tank for an additional 27 h prior to transfer to the air dry tank.

Table 18. Results of chemical, physical, and ballistic analyses for resolvated M1 propellant

Chemical composition

Propellant ingredient/ characteristic	Specification requirement	M1 f/155mm M4A1 Composite
Nitrocellulose (NC), %	85.00 ± 2.00	85.05
Dinitrotoluene (DNT), %	10.00 ± 2.00	9.75
Dibutylphthalate (DBP), %	5.00 ± 1.00	5.20
Diphenylamine (DPA), %	1.00 + 0.20, -0.10	1.08
Potassium sulfate (K_2SO_4), %	1.00 ± 0.30	0.65
Total volatiles (TV), %	-	1.13
Moisture (H_2O), %	0.60 ± 0.20	0.62
Residual solvent (RS), %	0.80 maximum	0.51
Stability		
Color change	No color change in 40 min (minimum)	>60 min
Explosivity	Shall not explode in <5 h	>5 h

Physical dimensions

				Std dev, % of mean	
	Specification	Die	Finished	Spec (max)	Actual
Length (L), in.	-----	0.447	0.4161	6.25	1.22
Diameter (D), in.	-----	0.266	0.1882	6.25	1.39
Perf dia (d), in.	-----	0.022	0.0160	----	----
Web diff., s	-----	-----	------	----	----
% of web avg	15 max	-----	-5.36	----	----
L:D	2.10-2.50	-----	2.21	----	----
D:d	5.0-15	-----	11.8	----	----
Web avg, in.	-----	-----	0.0354	----	----

Closed bomb (200 cm^3, +90F)

Relative quickness (RQ)	99.44
Relative force (RF)	99.74

The air dry operation removes surface moisture from the propellant grains by forcing heated air through the propellant grains and exhausting it to the atmosphere. In the air dry process, the propellant is loaded into tanks through which the circulating air is maintained at ~130-150°F. After drying for 6 h (based on production operating procedures for M1 propellant), the propellant was sampled for moisture analysis. The results of this analysis indicated 3.1% moisture, well above the defined specification requirements of 0.6 ± 0.2%. However, additional drying of 18 h resulted in 0.62% moisture; this additional time was required since the propellant was contained in sausage bags which may have hampered drying. During packout of the final propellant product, samples were taken for various physical, chemical, and ballistics testing. The results of these analyses are presented in table 18.

3.5 Sample Analyses

Chemical, physical, and ballistic testing was performed to determine compliance of the reclaimed M1 propellant to the applicable propellant specifications. The military specifications pertaining to each ingredient in M1 single-base propellant are summarized as follows:

Nitrocellulose (NC)	MIL-STD-244
Dinitrotoluene (DNT)	MIL-STD-204, Rev. A
Diphenylamine (DPA)	MIL-D-98
Potassium sulfate (K_2SO_4)	MIL-P-193
Dibutylphthalate (DBP)	MIL-D-218

Chemical analysis is defined as the determination of the percentages of all ingredients present. The chemical analyses were performed in compliance with the test methods delineated in the item specifications for final lot acceptance testing or in MIL-STD-652D, "Propellants, Solid, for Cannons, Requirements and Packing." The standard procedures for conducting these tests are contained in MIL-STD-286B, "Propellant Solid, Sampling, Examination and Testing."

Physical dimensions play an important role in propellant performance in that ballistic effects are controlled to some degree by the physical form of the propellant, e.g., grain diameter and web distance. Physical testing consists of visual measurement, using a toolmaker's microscope, of propellant grain configuration and physical characteristics. The following parameters were monitored: grain diameter, grain length, perforation diameter, and web thickness.

Ballistic testing was conducted in the RAAP closed bomb, a heavy-walled cylinder capable of withstanding pressures up to 100,000 psi. The closed bomb is equipped with a piezo-electric gage which responds to pressure changes; the testing was conducted under two constants: a volume of 200 ± 10 cc and a temperature of 90 ± 2°F. The purpose of the test is to determine the quickness voltage, i.e., the time rate of pressure rise (dp/dt) for a sample using a firing sequence of three shots of standard (M1 production-grade propellant) and three shots of sample (reclaimed M1 propellant) alternately. The results of the testing, i.e., relative force (RF) and relative quickness (RQ), are used to determine sample compliance to specification. RF is the ratio of the maximum pressure of the sample to the maximum pressure of the standard; RQ is the average rate of change in pressure with respect to time (psi/s).

The propellant met all the specification requirements for physical, chemical, and ballistic testing except the K_2SO_4 content, which was slightly low. This was due to excess leaching during the drying cycle; the sausage bags also retained excess moisture which continued to leach the K_2SO_4 following removal from the water dry tank.

4.0 SOLVENT EXTRACTION OF SELECTED PROPELLANT INGREDIENTS

Laboratory-scale solvent extraction studies were performed to determine extraction efficiencies and affinities of selected solvents for specific propellant ingredients in single-, double-, and triple-base propellants. A preliminary hazards analysis was performed to review the development, sampling, storage, and process procedures to be used in this study (appendix A). Appropriate solvents were selected based on solubility and distribution coefficient determinations and ingredient extraction procedures were developed for the three types of propellant. Two testing procedures were prepared for the solvent extraction studies: high-performance liquid chromatography (HPLC) and atomic absorption spectrometry. A statistical study was conducted to verify that the HPLC methods developed for these evaluations were comparable to the analytical methods delineated in MIL-STD-286B.

The solvents to be evaluated were chosen on the basis of safety and toxicity hazards as well as a literature review conducted during the preparation of the test plan for this project.[5] These solvents included water (acidic, basic, and neutral), alcohols, and ketones, among others. Solubility determinations for each solvent on sixteen propellant ingredients were conducted. Distribution coefficient testing was performed on the non-miscible solvent pairs to determine separation characteristics of these solvents for ingredient reclamation. Those solvents that optimally concentrated propellant ingredients were then selected for use in the extraction procedures.

Solubility testing for the solvents listed in table 19 was performed. The solubility data for propellant ingredients have been divided into three general categories: very soluble (>0.100 g/mL), slightly soluble (0.010 to 0.100 g/mL), and insoluble (<0.010 g/mL). Solubility determinations for the solvents listed in the test plan were completed, with the exception of chloroform. Since it is expected that no significant difference would be noted between the use of chloroform and methylene chloride, and because minimal use of chloroform is mandated in the RAAP laboratory policy, chloroform was not tested. It must be noted that these results represent relatively crude determinations of solubility and may or may not agree with literature values; however, because all testing was conducted in the same manner, the results are valid. The propellant ingredients were then separated into four groups: hydrophilic, organophilic, insoluble, and others as shown in table 20.

Table 19. Solubility data for propellant ingredients

Propellant ingredient	Neutral water	(HNO_3) Acidic water	(NaOH) Basic water	Methylene Chloride	Acetone	Tetrahydrofuran	Methanol	Toluene	Ether	Hexane	Dimethylsulfoxide	Isopropanol	Ethanol (2T)*	n-Butyl alcohol
Potassium nitrate	V	V	V	I	I	I	I	I	I	I	I	I	I	I
Barium nitrate	V	V	V	I	I	I	I	I	I	I	I	I	S	I
Potassium perchlorate	S	I	I	I	I	I	I	I	I	I	I	I	I	I
Lead carbonate	I	S	I	I	I	I	I	I	I	I	I	I	I	I
Potassium sulfate	V	V	V	I	I	I	I	I	I	I	I	I	I	I
Graphite	I	I	I	I	I	I	I	I	I	I	I	I	I	I
Carbon black	I	I	I	I	I	I	I	I	I	I	I	I	I	I
Cryolite	I	I	I	I	I	I	I	I	I	I	I	I	I	I
Dinitrotoluene	I	I	I	V	V	V	S	V	V	V	V	V	V	S
Dibutylphthalate	I	I	I	V	V	V	V	V	V	V	V	V	V	V
Diphenylamine	I	I	I	V	V	V	V	V	V	S	V	V	V	V
2-nitrodiphenylamine	I	I	I	V	V	V	S	V	V	S	V	S	S	S
Ethyl centralite	I	I	I	V	V	V	V	V	V	V	V	V	V	V
12.6% N nitrocellulose	I	S	I	I	V	S	S	S	I	I	I	S	I	I
13.15% N nitrocellulose	I	S	I	I	V	S	S	S	I	I	I	S	I	I
Nitroguanidine	I	I	I	I	I	I	I	I	I	I	I	I	I	I

V - very soluble : >0.100 g/mL.
S - slightly soluble: 0.010 - 0.100 g/mL.
I - insoluble : <0.010 g/mL.
* - 2T = 2% toluene.

Table 20. Separation of propellant ingredients into groups

Hydrophilic	Organophilic
Potassium nitrate	Dinitrotoluene
Barium nitrate	Dibutylphthalate
Potassium perchlorate	Diphenylamine
Lead carbonate	2-nitrodiphenylamine
Potassium sulfate	Ethyl centralite
Insolubles	**Others**
Graphite	Nitrocellulose (12.6%N)
Carbon black	Nitrocellulose (13.15%N)
Cryolite	Nitroguanidine

Based on the solubility data, distribution coefficient (K_d) testing of propellant ingredients in four non-miscible solvent pairs was performed: methylene chloride/water, hexane/water, toluene/water, and ether/water. Only neutral water (distilled tap water, pH ~5.9) was used for this testing. The K_d results are presented in table 21; these results follow the trends that could be predicted from the solubility data. Determination of K_d was not performed on any insolubles, NC, or NQ.

As evidenced in table 21, there are no appreciable differences among the four non-miscible solvent pairs which were evaluated. Therefore, the ether/water solvent pair was chosen since ether is an established production solvent at RAAP. However, during testing on M10 single-base propellant, the consistency of the propellant matrix appeared to change after the addition of the ether, hampering completion of the extraction. All subsequent extractions were performed using methylene chloride to yield concise phases for separation; because of safety and toxicity considerations, hexane and toluene were not evaluated.

4.1 Testing Procedures

The analytical standards for use in the liquid chromatographic analysis of the extracts generated in the solvent extractions are shown in table 22. A stock solution, prepared in HPLC-grade methanol, was volumetrically diluted yielding the standards for the single-base propellants and double-base propellants; a stock solution, prepared in 75/25 acetonitrile/water (HPLC grades), was volumetrically diluted to yield the standards for triple-base propellants. Because of the limited solubility of NQ, it was necessary to modify the amount of NQ included in the triple-base standard. A chromatographic standard containing the 1,3 and 1,2 isomers of dinitroglycerin (DNG) was prepared in order to analyze for the possible breakdown products of NG in double- and triple-base propellants. A stock solution, prepared in HPLC-grade water, was volumetrically diluted to give the standards also listed in table 22. These standards were injected separately.

Testing was performed to determine the linearity of the calibration curves resulting from the injection of propellant ingredients and degradation products in the single-base standard. For the series of curves (figs. 49 through 53), correlation coefficients are >0.999 for all components except N-nitrosodiphenylamine (N-NDPA), which has a coefficient of 0.998. A representative chromatogram for a single-base standard is shown in figure 54 which also lists the chromatographic conditions.

The linearity of the generated calibration curves for double-base propellants was investigated; the results are presented graphically in figures 55 through 58. As with the single-base propellant calibration curves, correlation coefficients were very high, ranging from >0.999 for 1,2-DNG to 0.998 for NG. A representative chromatogram for a double-base standard is shown in figure 59; the chromatographic conditions are listed on the figure.

Table 21. Distribution coefficients for propellant ingredients

	Organic phase			
Propellant ingredient	Methylene chloride	Hexane	Toluene	Ether
Potassium nitrate	<1	<1	<1	<1
Barium nitrate	<1	<1	<1	<1
Potassium perchlorate	<1	<1	<1	<1
Lead carbonate	<1	<1	<1	<1
Potassium sulfate	<1	<1	<1	<1
Graphite	-*	-	-	-
Carbon black	-	-	-	-
Cryolite	-	-	-	-
Dinitrotoluene	983	1217	1590	1260
Dibutylphthalate	614	890	700	1083
Diphenylamine	1290	971	1031	1173
2-nitrodiphenylamine	584	674	512	685
Ethyl centralite	810	915	714	815
12.6%N nitrocellulose	-	-	-	-
13.15%N nitrocellulose	-	-	-	-
Nitroguanidine	-	-	-	-

---

* K_d was not performed on the insolubles, cellulose nitrate, or nitroguanidine:

$$K_d = \frac{[X]\ \text{organic phase}}{[X]\ \text{aqueous phase}}$$

Table 22. Liquid chromatographic standards for single-, double-, and triple-base propellants

Ingredient, ppm	Std 1 (2x)[a]	Std 2 (1x)	Std 3 (3/4x)	Std 4 (1/2x)
Single-base:				
Dinitrotoluene	2088	1044	783	522
N-nitrosodiphenylamine	132	66	50	33
Diphenylamine	200	100	75	50
2-nitrodiphenylamine	200	100	75	50
Dibutylphthalate	1172	586	440	293

	Std 1 (2x)	Std 2 (1x)	Std 3 (4/5x)	Std 4 (1/2x)
Double-base:				
Nitroglycerin	2062	1031	825	516
Ethyl centralite	162	81	65	40

	Std 1 (2x)	Std 2 (1x)	Std 3 (4/5x)	Std 4 (1/2x)
Triple-base:				
Nitroguanidine[b]	2039	2039	1631	1020
Ethyl centralite	254	127	102	64
2-nitrodiphenylamine	142	71	57	36
Dibutylphthalate	430	215	172	108
Nitroglycerin	3600	1800	1440	900

	Std 1	Std 2	Std 3	Std 4
Isomers:				
1,3-dinitroglycerin	634	317	254	159
1,2-dinitroglycerin	160	80	64	40

---

[a] Std 1 is the stock solution.

[b] NQ is in excess in Std 1.

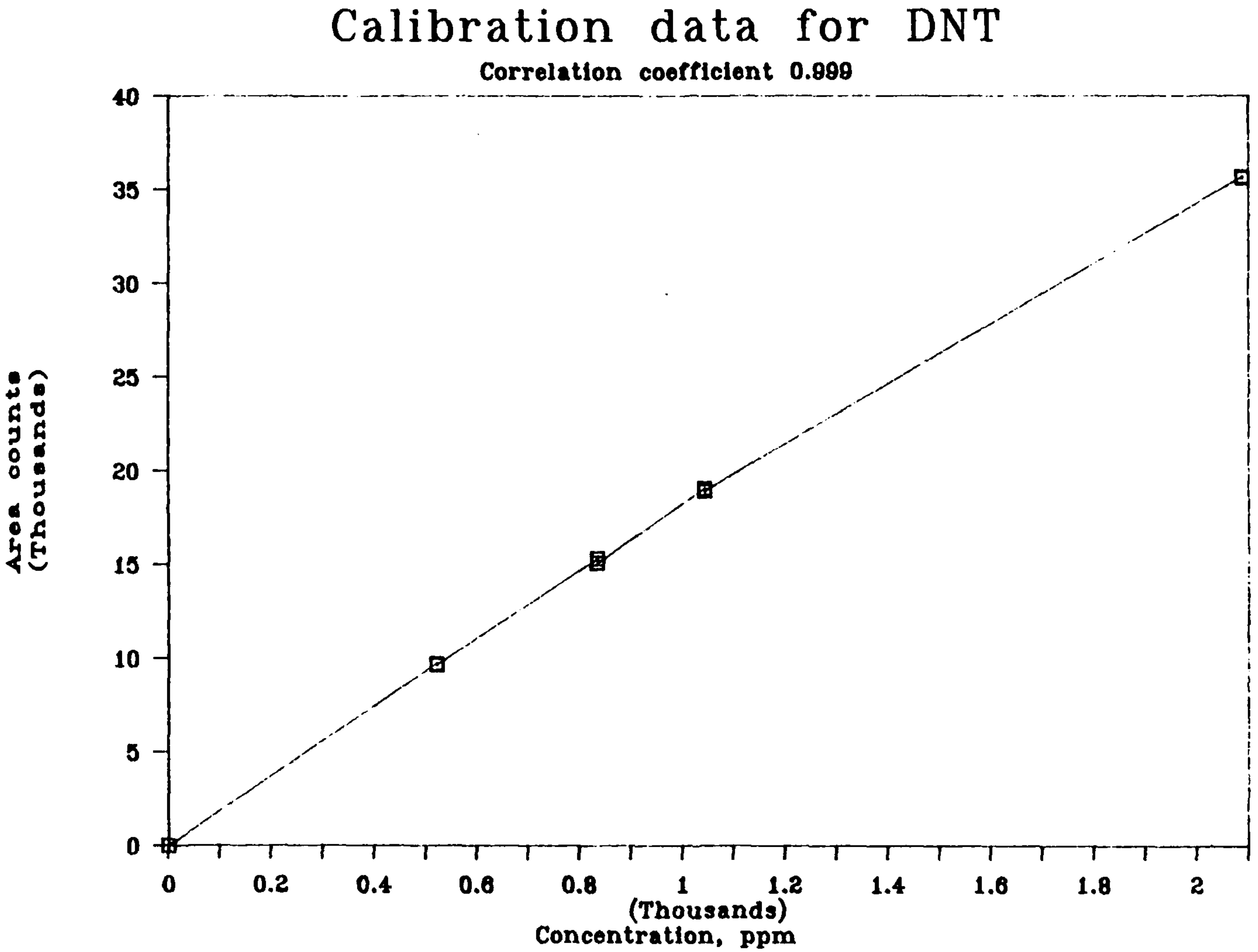


Figure 49. Single-base standard calibration data of area counts vs concentration for dinitrotoluene (DNT)

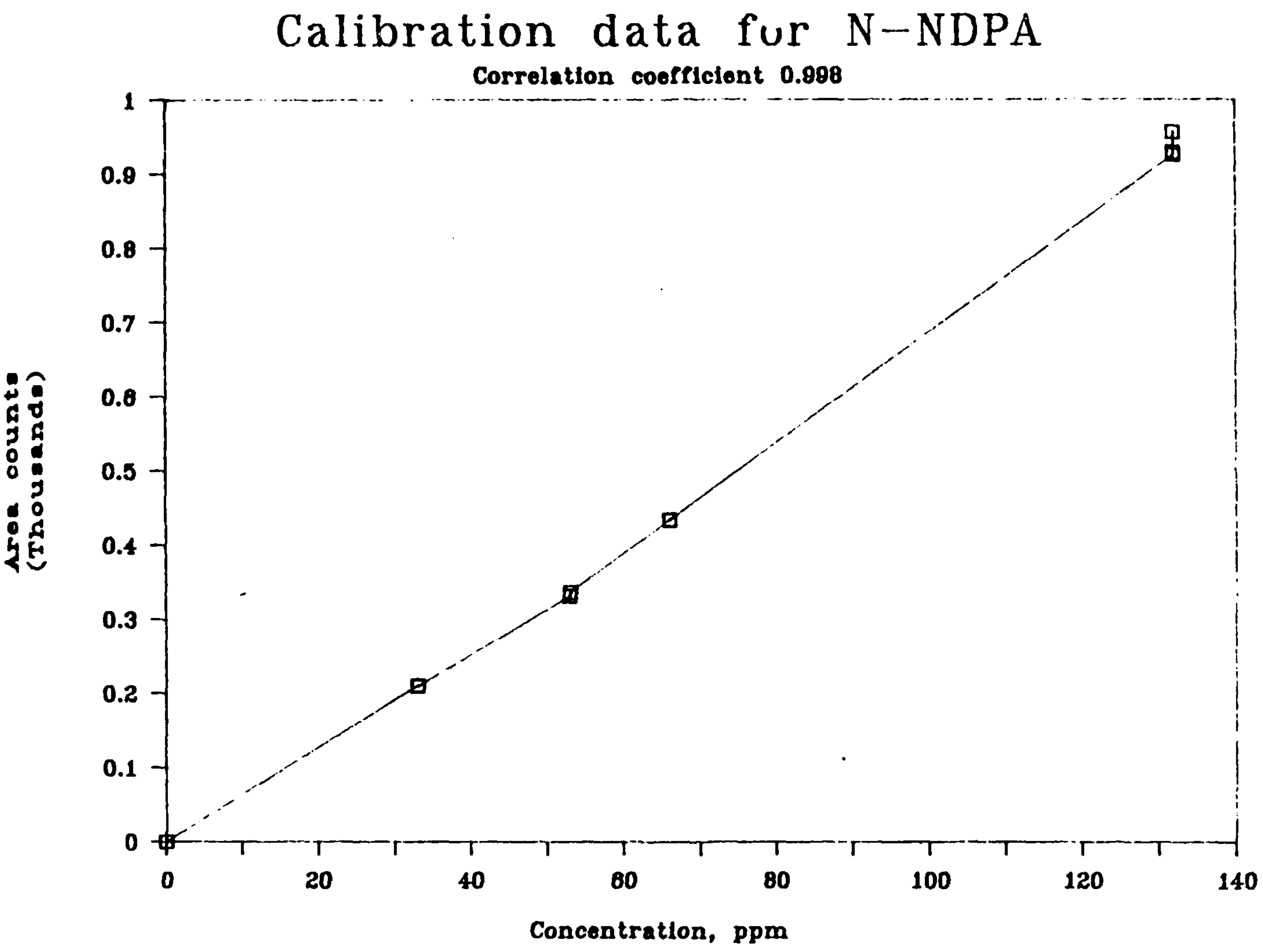


Figure 50. Single-base standard calibration data of area counts vs concentration for N-nitrodiphenylamine (N-NDPA)

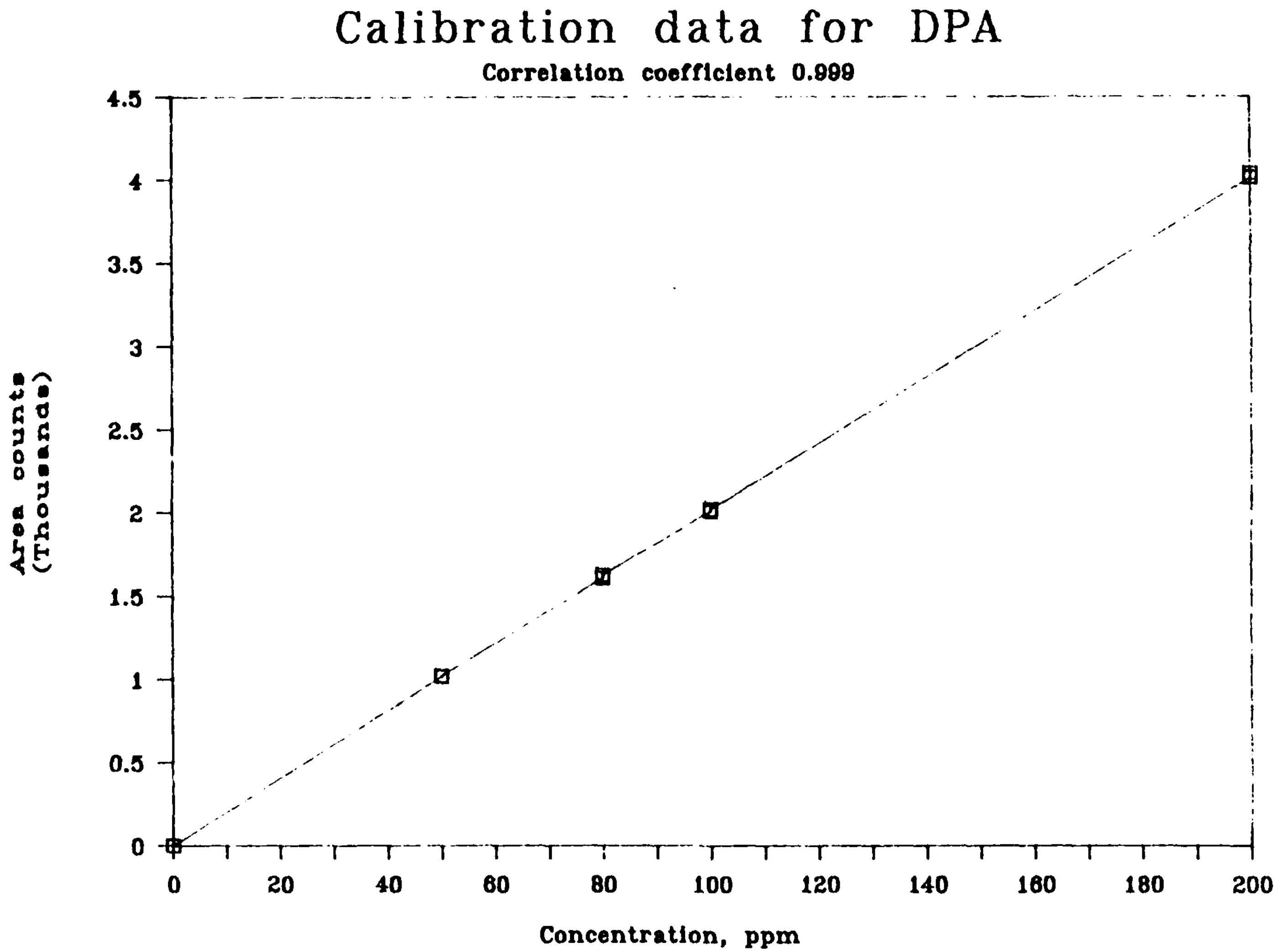


Figure 51. Single-base standard calibration data of area counts vs concentration for diphenylamine (DPA)

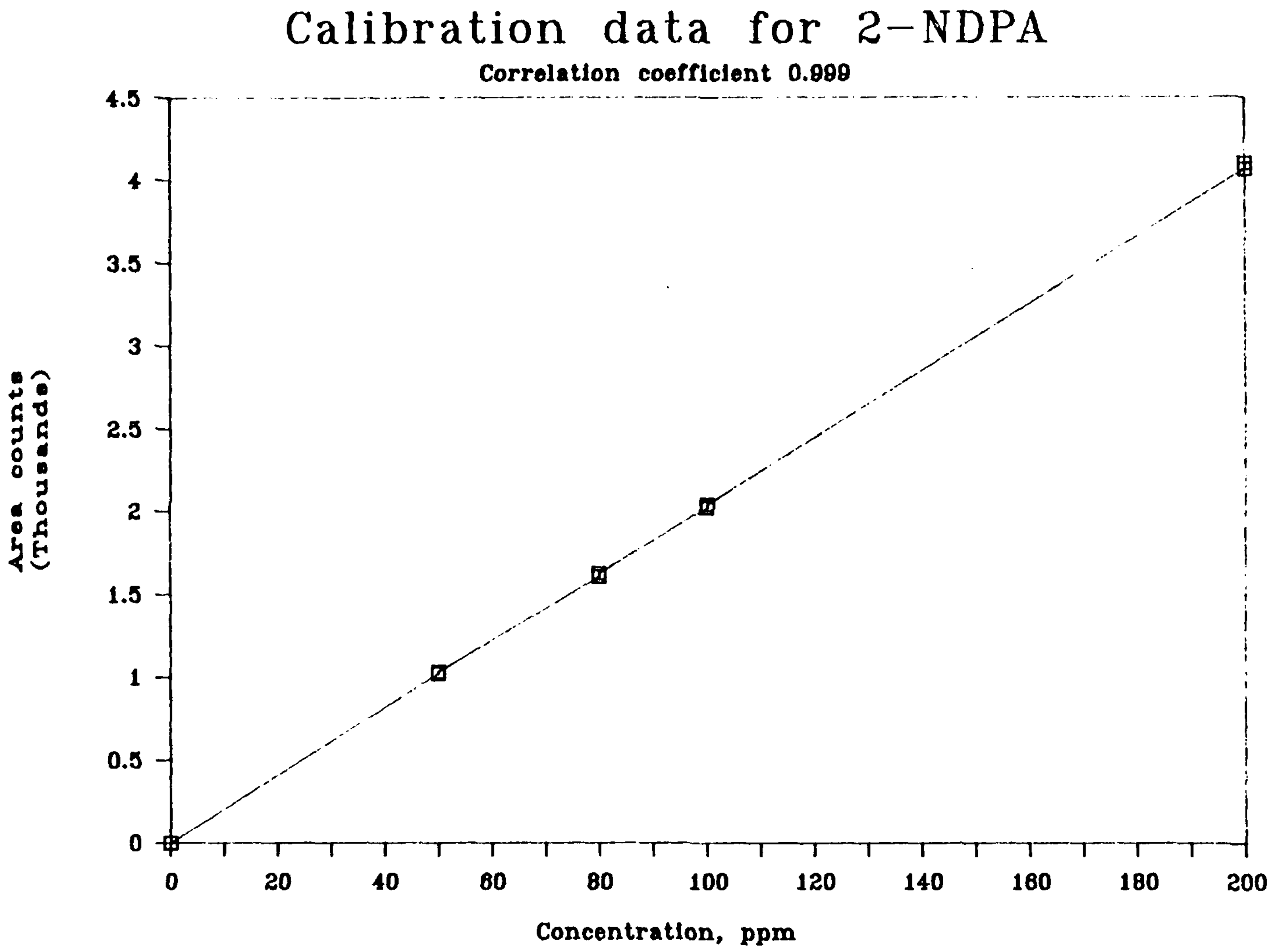


Figure 52. Single-base standard calibration data of area counts vs concentration for 2-nitrosodiphenylamine (2-NDPA)

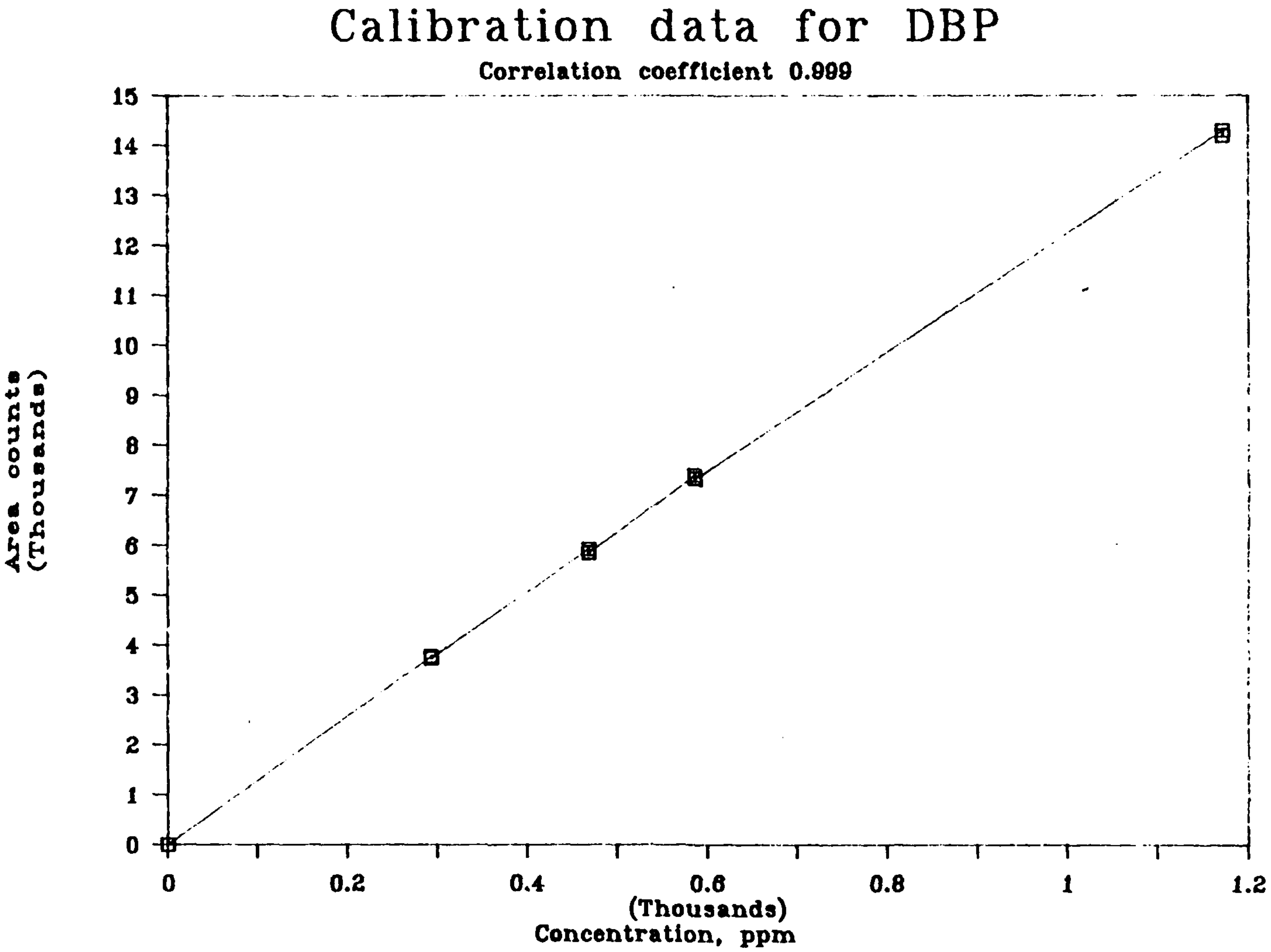
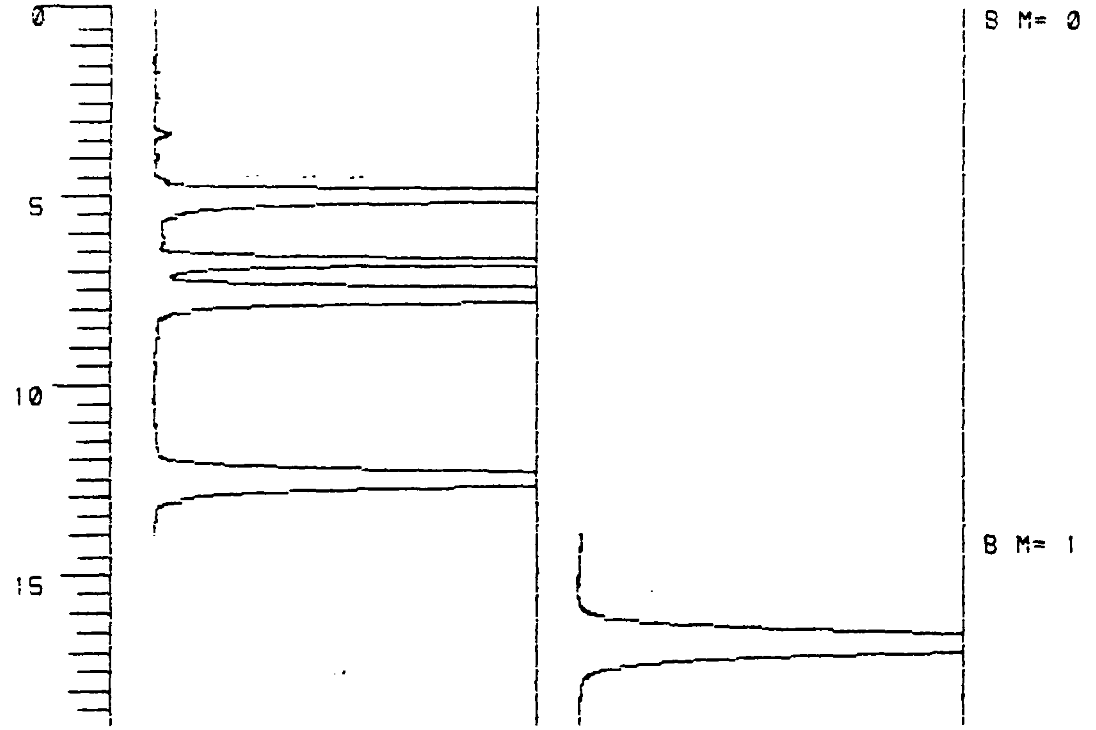


Figure 53. Single-base standard calibration data of area counts vs concentration for dibutylphthalate (DBP)

```
Integration & online plot from DPU memory
Signal              A                             B                            Annotation
S wl,bw             265,20                        214,20
Range               100                           100
Zero %              10                            10
```



```
ESTD

 #  NAME              GR SI    TIME   TYPE REF          AMOUNT  WIDTH  dTIME      QUOTIENT
                               [min]               [      ppm]  [min]  [min]      [amount]

  3 2,4DNT               A    4.936    VB           562.901  0.174
  4 NNDPA                A    6.731    BV           227.525  0.231
  5 DPA                  A    7.589    VB           369.156  0.259
  6 2NDPA                A   12.502    BB           243.119  0.401
  7 DBP                  B   16.773    BB           445.703  0.510
```

Chromatographic conditions:

25 cm Resolvex C18 4.6 ID 5 µm particles
Flow rate = 1.0 mL/min
Mobile phase = 75/25 methanol/water
Temperature = 40°C
Injection volume = 10 µL
Diode Array detection at 265 and 214 nm

Figure 54. Representative HPLC chromatogram for single-base propellant ingredients

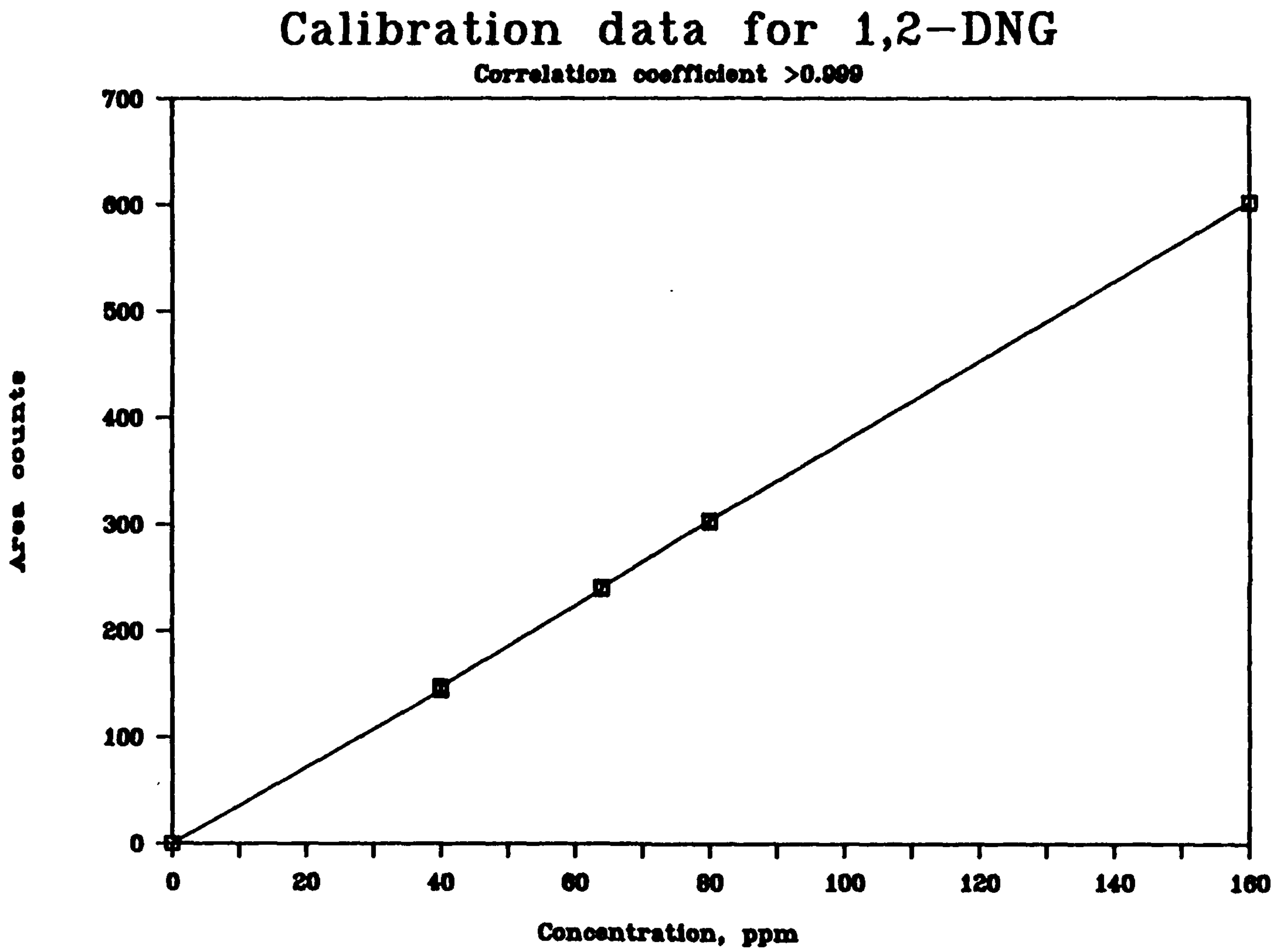


Figure 55. Double-base standard calibration data of area counts vs concentration for 1,2-dinitroglycerin (1,2-DNG)

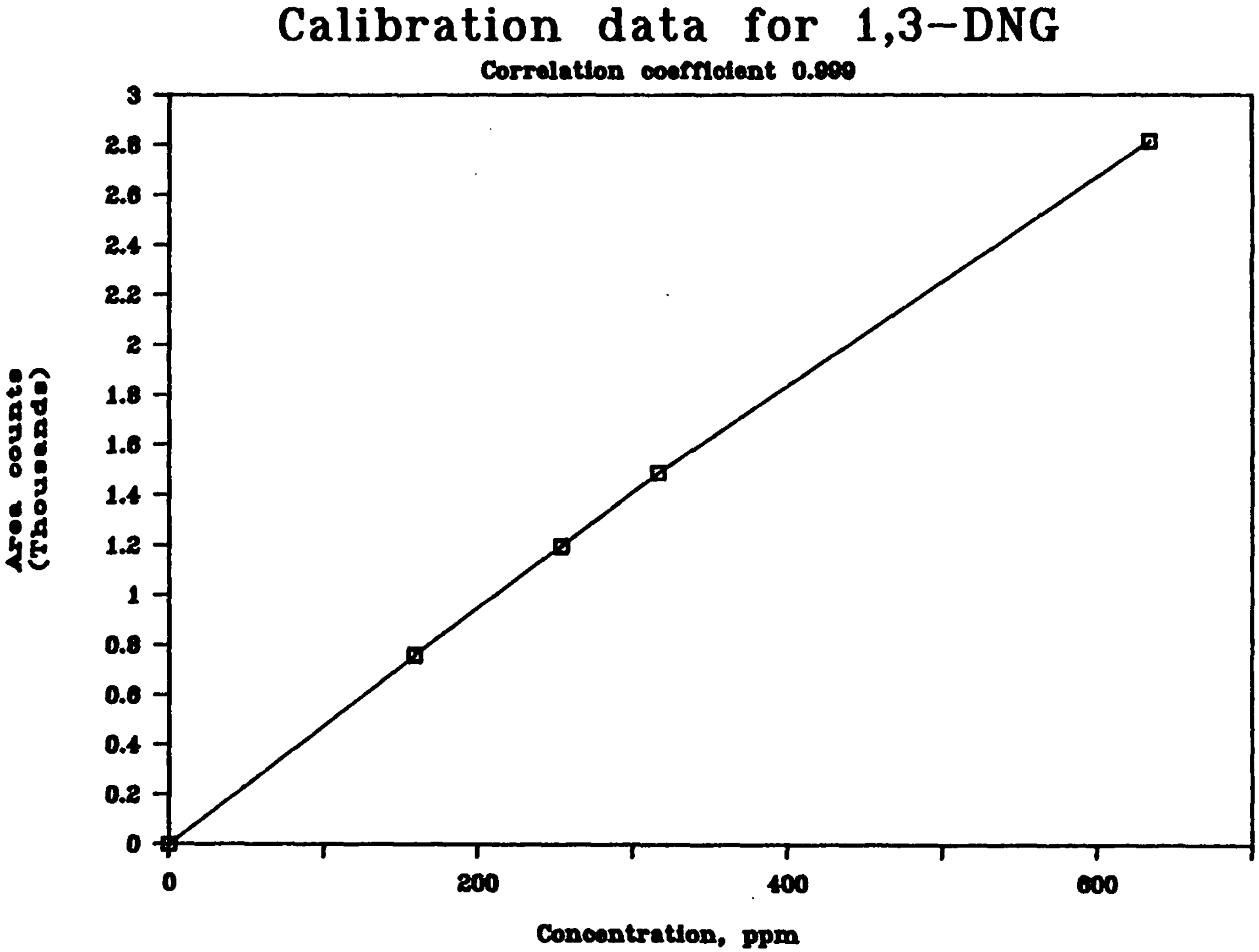


Figure 56. Double-base standard calibration data of area counts vs concentration for 1,3-dinitroglycerin (1,3-DNG)

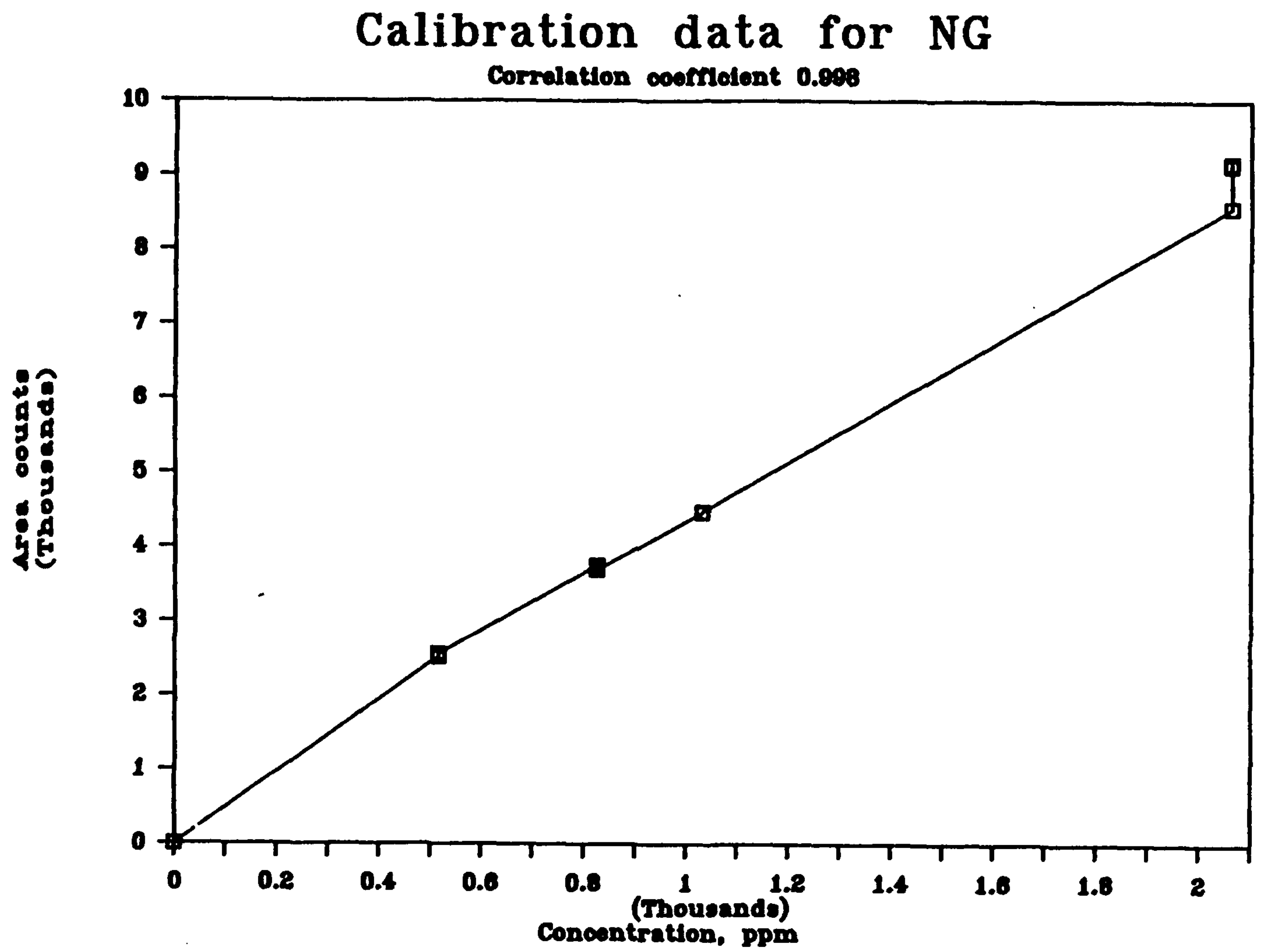


Figure 57. Double-base standard calibration data of area counts vs concentration for nitroglycerin (NG)

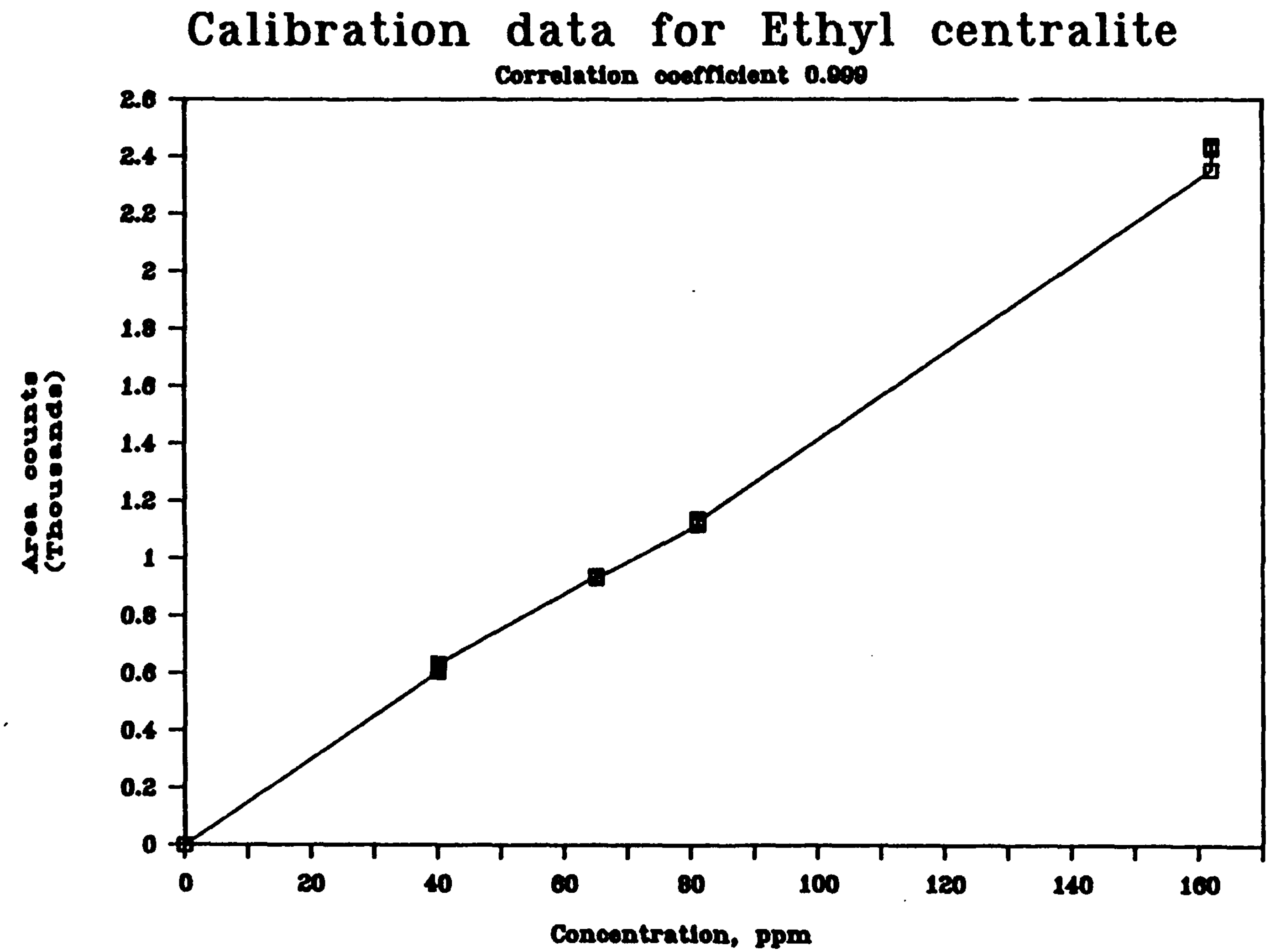
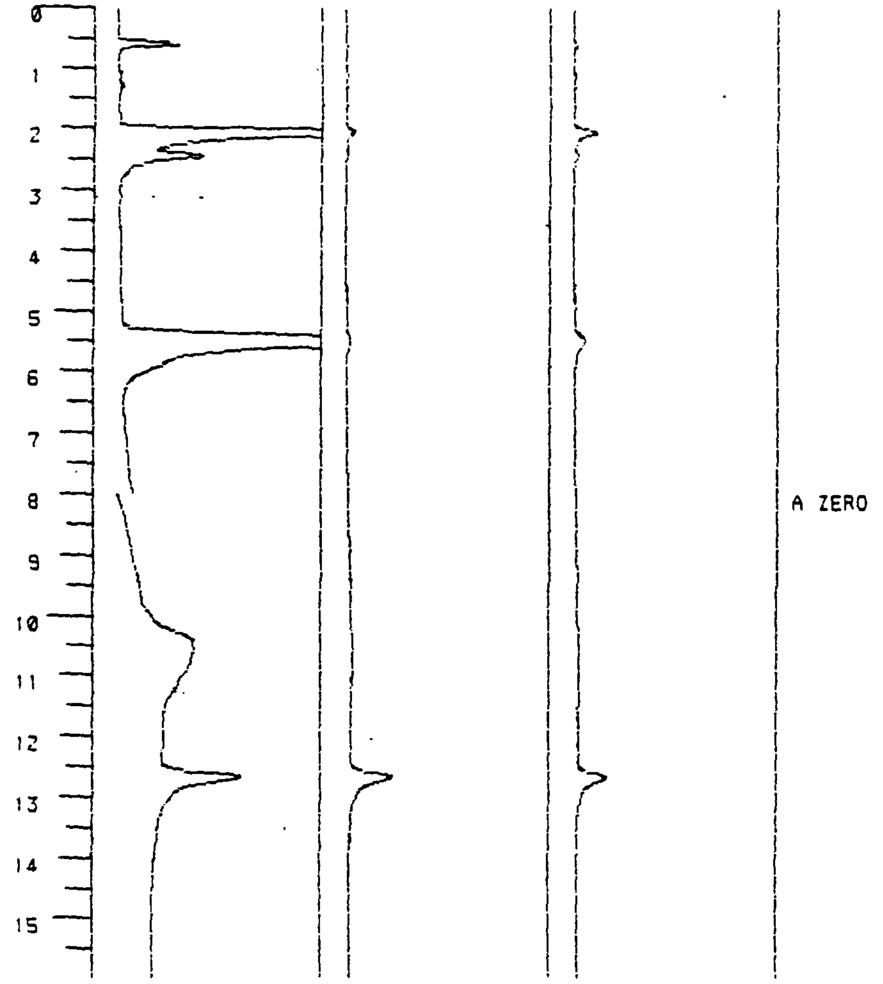


Figure 58. Double-base standard calibration data of area counts vs concentration for ethyl centralite (EC)

```
Integration & online plot from DPU memory
Signal         A                   B                   C                   Annotation
S wl,bw        214,20              254,20              260,80
Range          100                 100                 100
Zero %         10                  10                  10
```



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ESTD

 #  NAME           GR SI    TIME  TYPE REF          AMOUNT  WIDTH  dTIME     QUOTIENT
                           [min]               [      ppm] [min]  [min]     [amount]

 2 1,3DNG             A    2.080   BV             379.950  0.130
 3 1,2DNG             A    2.448   VB             98.9820  0.150
 4 NG                 A    5.501   BB             541.747  0.268
 5 EC                 A   12.679   BB             39.4348  0.226
```

<u>Chromatographic Conditions</u>:

20 cm Hewlett Packard RP-8 4.6 mm ID 5 μm particles
Flow rate: 0 to 6.0 min = 2.5 mL/min
6.0 to 8.5 min = linear ramp from 2.5 to 3.0 mL/min
8.5 to 12 min = 3.0 mL/min
Mobile Phase: 0 to 5.4 min = linear gradient from 25 to 35% methanol/water
5.4 to 8.6 min = linear gradient from 35 to 55% methanol/water
8.6 to 12.0 min = linear gradient from 55 to 65% methanol/water
Temperature = 40°C
Injection volume - 20 μL
Diode Array detection at 214, 254, and 260 nm

Figure 59. Representative HPLC chromatogram for double-base propellant ingredients

The linearity of calibration curves generated by the analysis of triple-base propellant ingredients (and final degradation products) was established. Figures 60 through 66 represent the calibration curves for NQ, 1,3-DNG, 1,2-DNG, NG, 2-nitrodiphenylamine (2-NDPA), EC, and DBP, respectively. Correlation coefficients ranged from 0.9998 for DBP to 0.9212 for 1,2-DNG. The calibration curves for NQ and the isomers of DNG show a slight curvature at the upper end of the concentration range. This area of the curve should not be used due to the predictable (specification value or less) nature of the propellant samples. Together with the acceptable correlation coefficients, use of the calibration curves is justified. Figure 67 is a representative chromatogram of a triple-base standard.

Detection limits were determined for the various propellant ingredients analyzed by the single-base propellant method. Determination of the detection limit was performed by injecting lesser amounts of the compound onto the chromatographic column. The lowest amount which was recognized as a peak by the integrator at its most sensitive setting was considered the detection limit. It must be noted that at this level a peak was clearly visible, and the signal-to-noise ratio was much higher than 3. The detection limits for single-, double-, and triple-base propellants are listed in table 23. Detection limits of double-base propellant are considerably higher (>100 ng injected) than for single-base propellants; this can be attributed to the much lower signal-to-noise ratio present in the 214-nm region of the ultraviolet (UV) detector.

Detection limits for the triple-base propellant ingredients and degradation products were determined (table 23). Nitrate esters show a higher detection limit due to the decreased signal-to-noise ratio in the wavelength band of interest. The detection limit presented for NQ is high because of the wavelength (340 nm) from which it is taken. Though NQ can be detected more easily at 214 nm, it was determined that with such a small capacity factor (k' value of 1.27), a selective determination of NQ would be accomplished at 340 nm. This detection limit represents a minimum NQ concentration of 6.5 ppm.

A statistical study was initiated to determine if the HPLC methods were comparable to the analytical methods delineated in MIL-STD-286B. Ten samples of each for a representative single-, double-, and triple-base propellant were analyzed by both methods. The means were compared by a Student's t-test to assure that both methods were comparable (table 24).

Results for DNT and DPA in single-base propellants indicate no difference at the 95% confidence level as determined by the Student's t test to establish the difference between means. The t values of DNT and DPA were 1.3701 and 0.7032, respectively. The critical t value is 2.110 for seven degrees of freedom. Results for DBP also indicate no difference at the 95% confidence level as determined by the Student's t test to determine the difference between means. The t value for DBP was 1.397, with the critical t value of 2.110 for seventeen degrees of freedom. Results for EC in double-base propellant indicate no difference at the 95% level while NG shows no difference at the 90% level for either

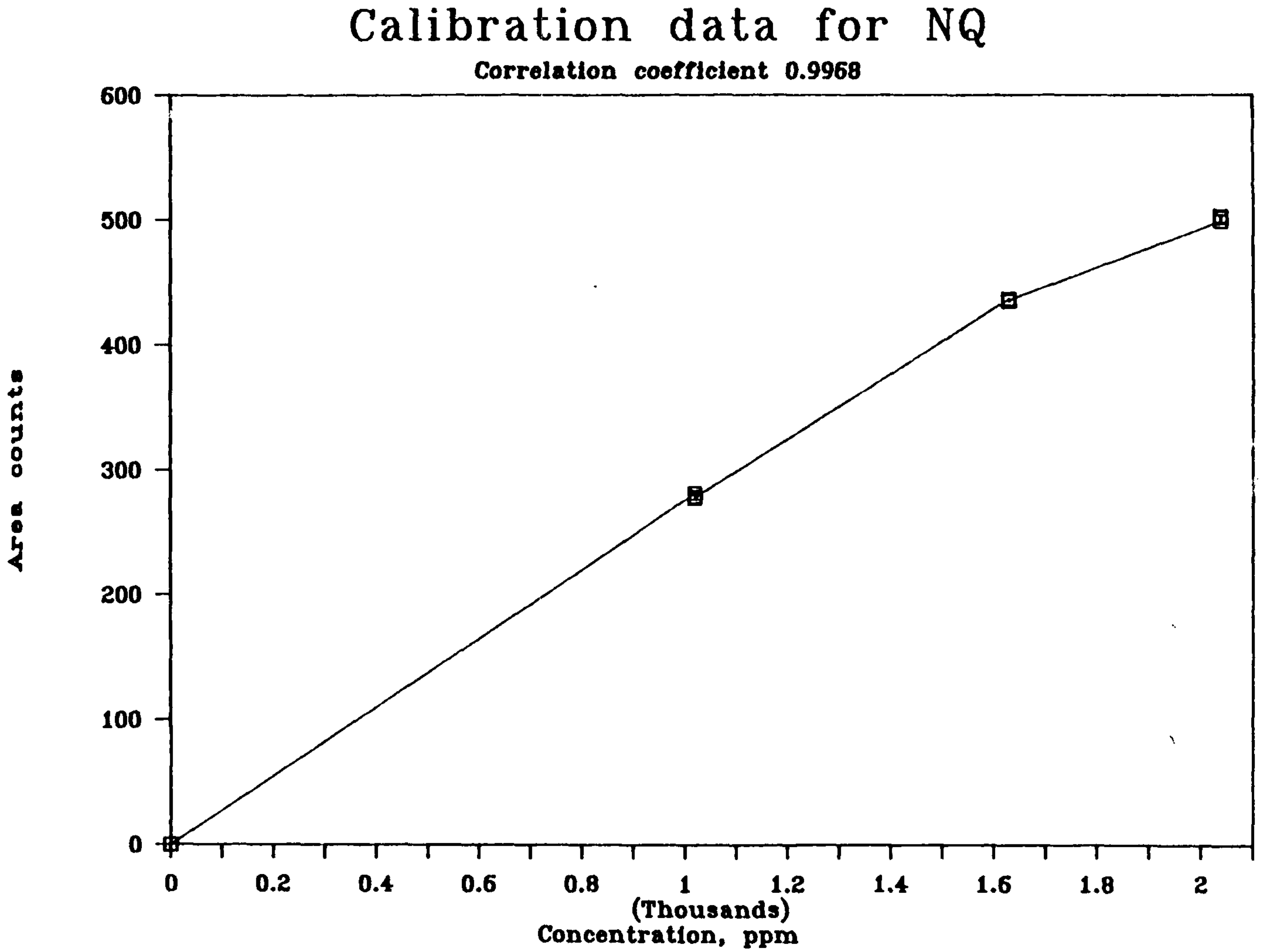


Figure 60. Triple-base standard calibration data of area counts vs concentration for nitoguanidine (NQ)

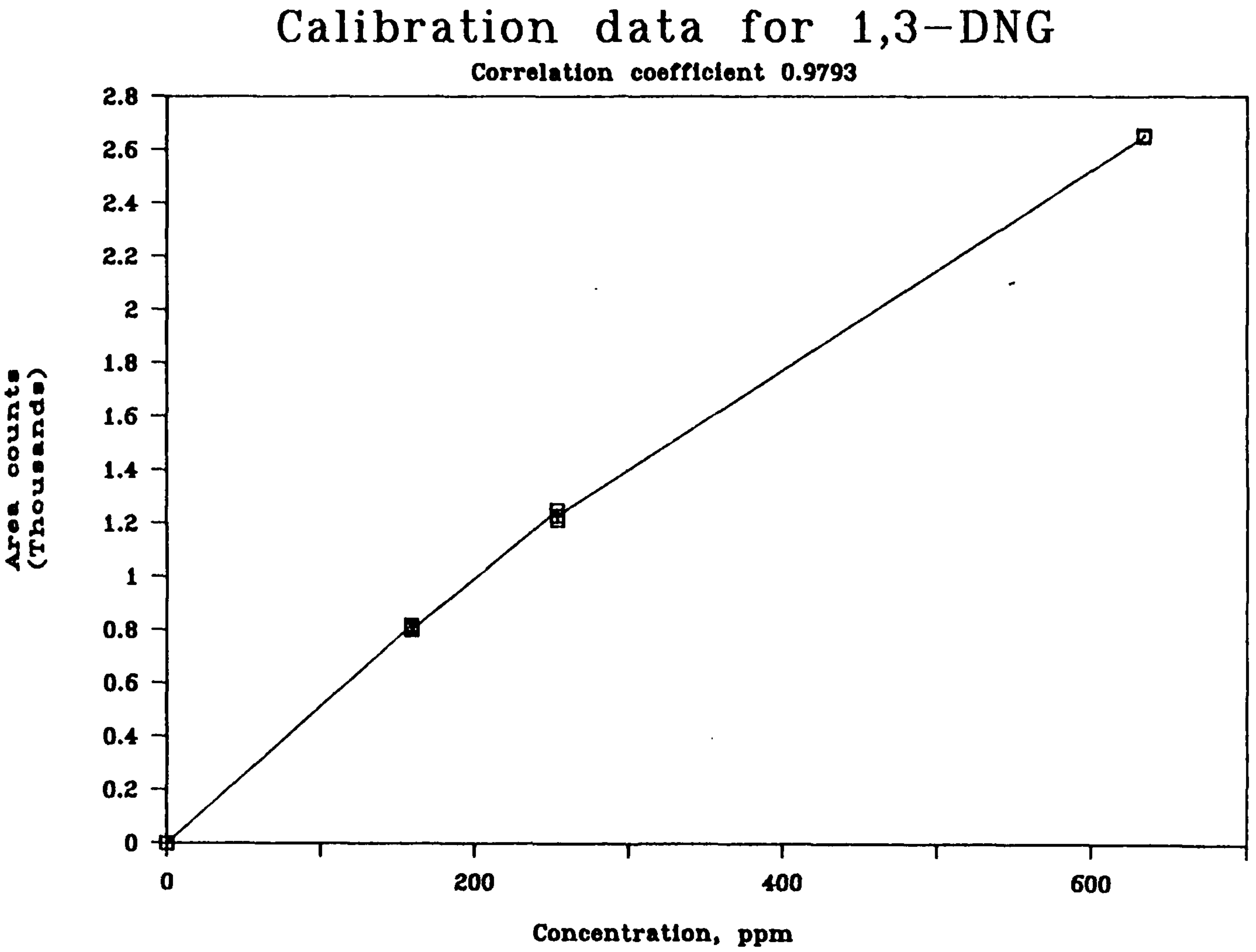


Figure 61. Triple-base standard calibration data of area counts vs concentration for 1,3-dinitroglycerin (1,3-DNG)

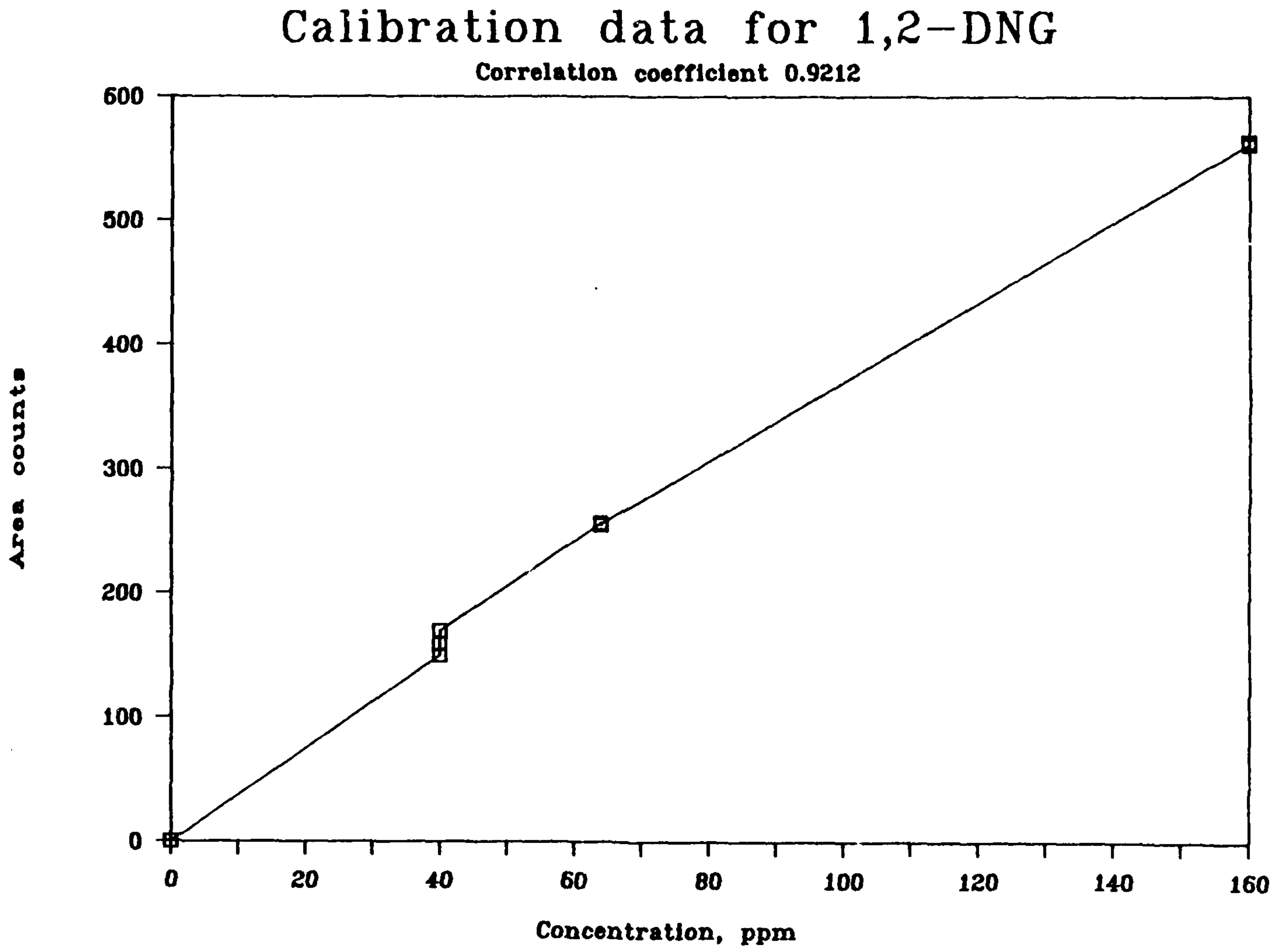


Figure 62. Triple-base standard calibration data of area counts vs concentration for 1,2-dinitroglycerin (1,2-DNG)

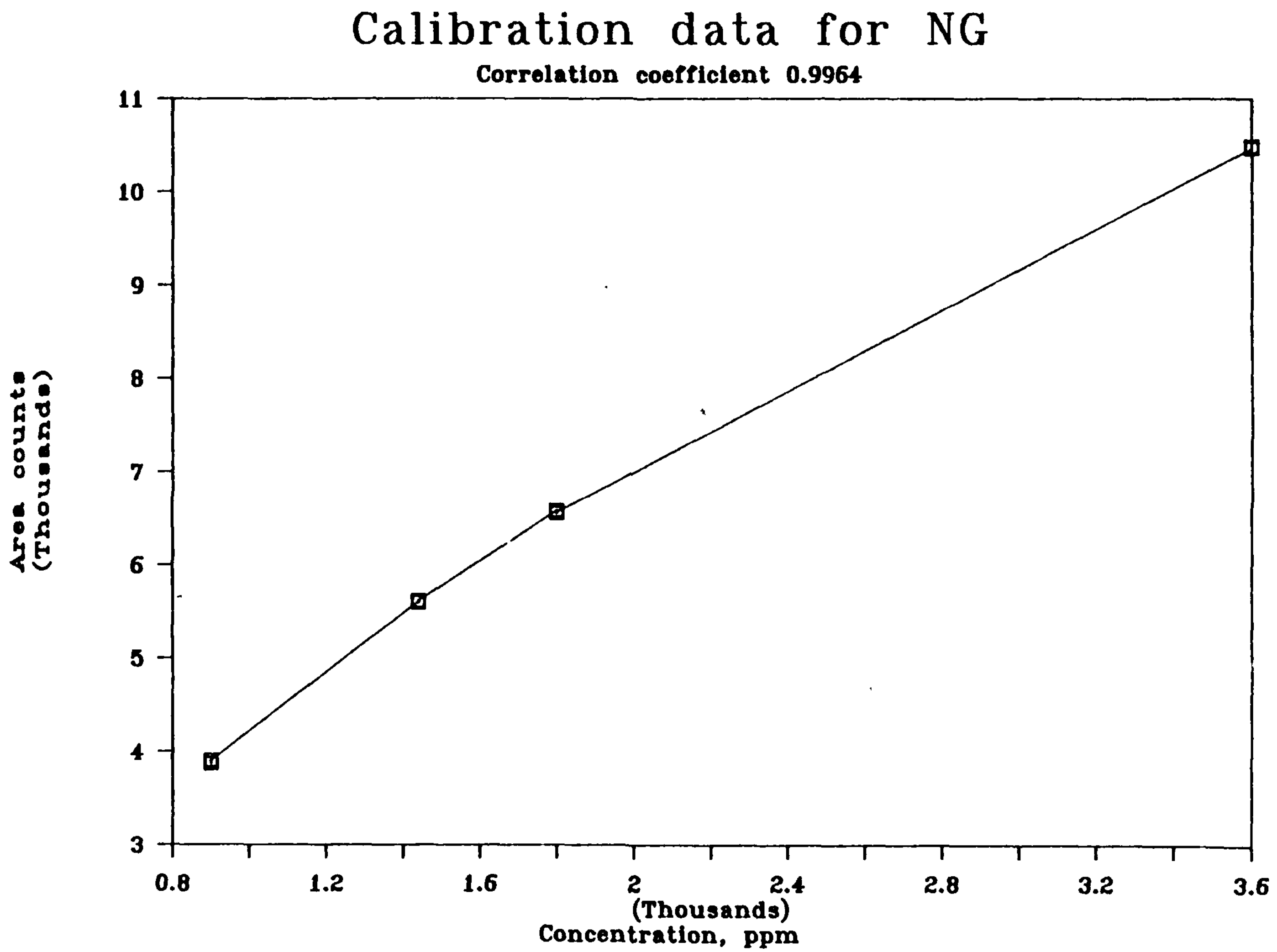


Figure 63. Triple-base standard calibration data of area counts vs concentration for nitroglycerin (NG)

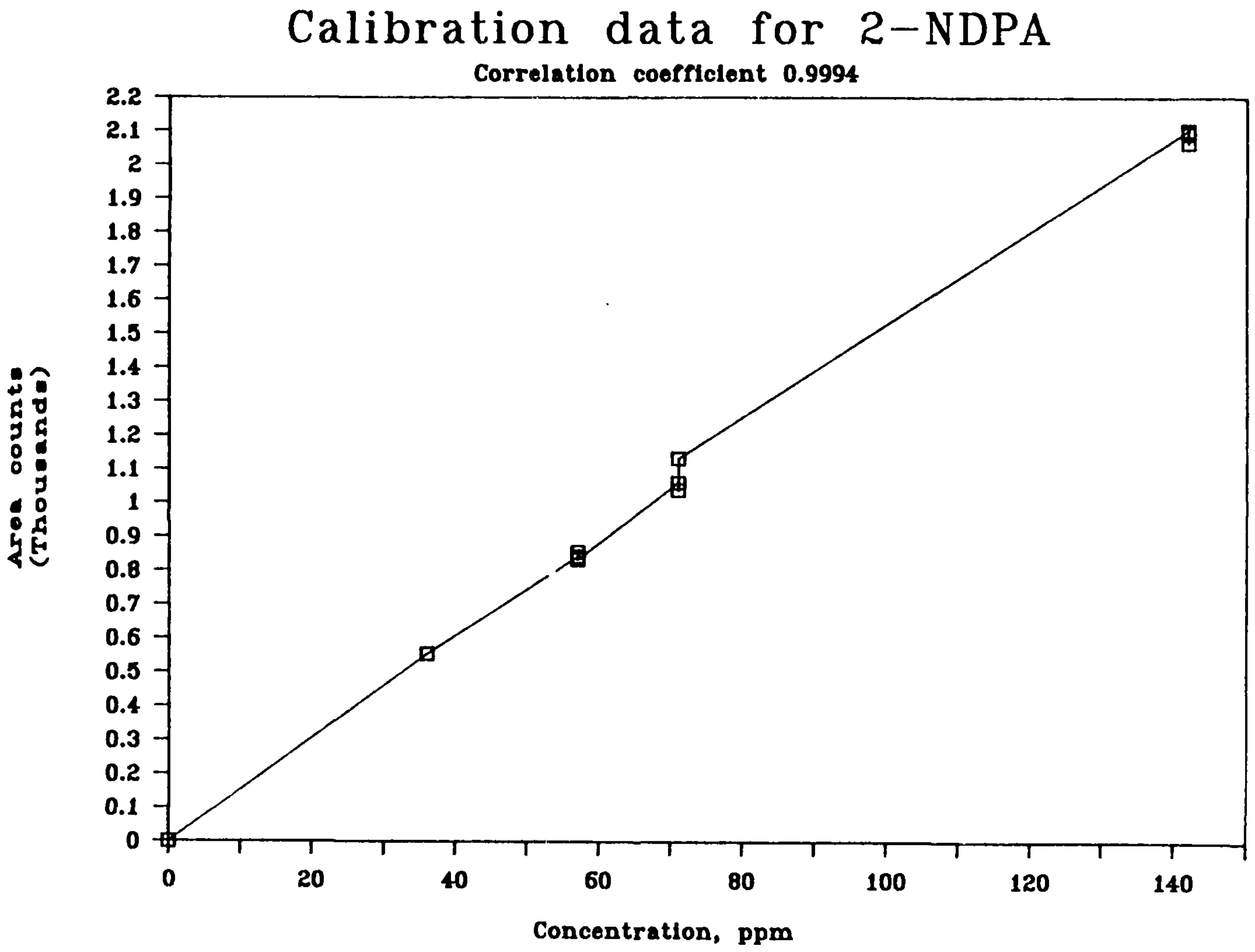


Figure 64. Triple-base standard calibration data of area counts vs concentration for 2-nitrosodiphenylamine (2-NDPA)

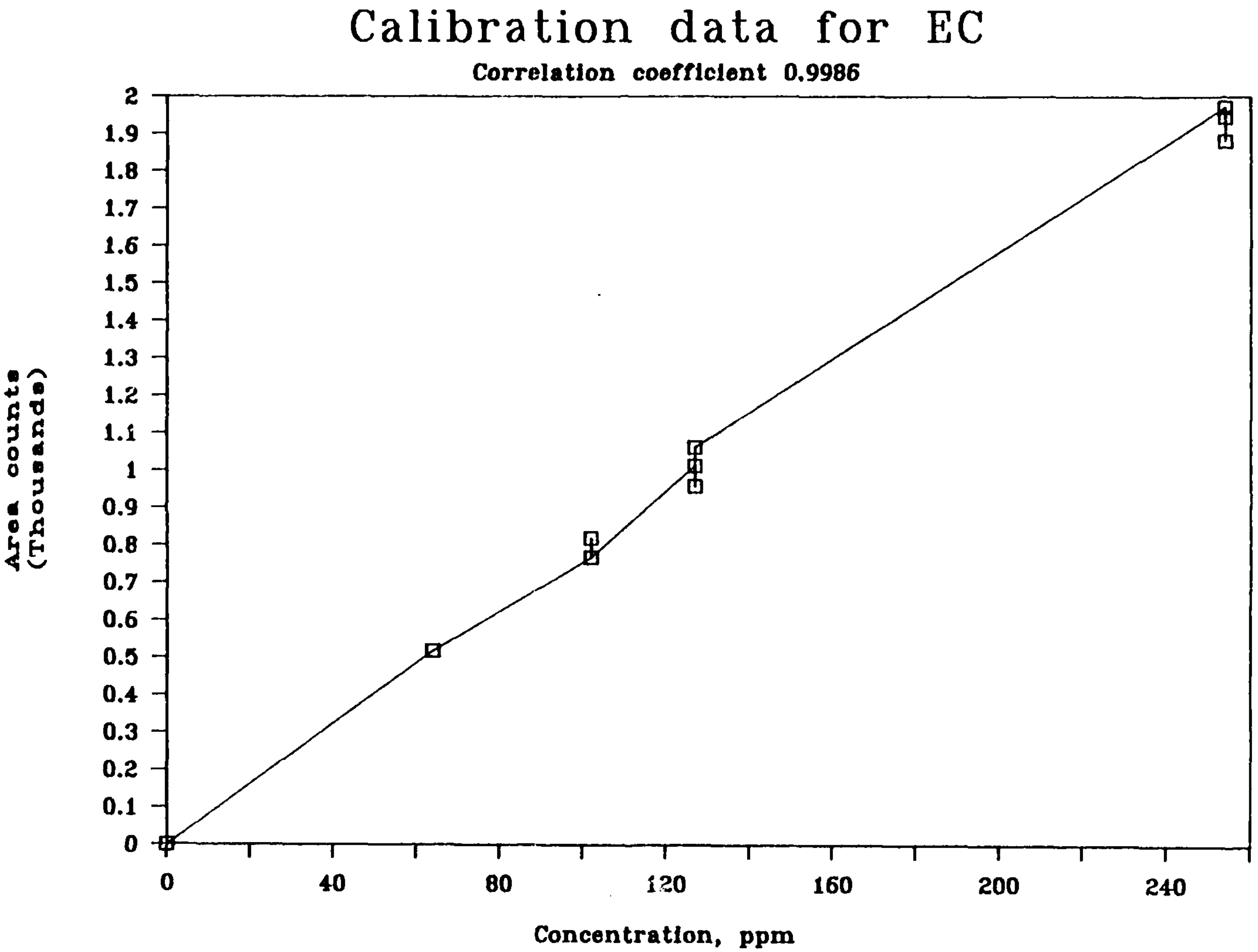


Figure 65. Triple-base standard calibration data of area counts vs concentration for ethyl centralite (EC)

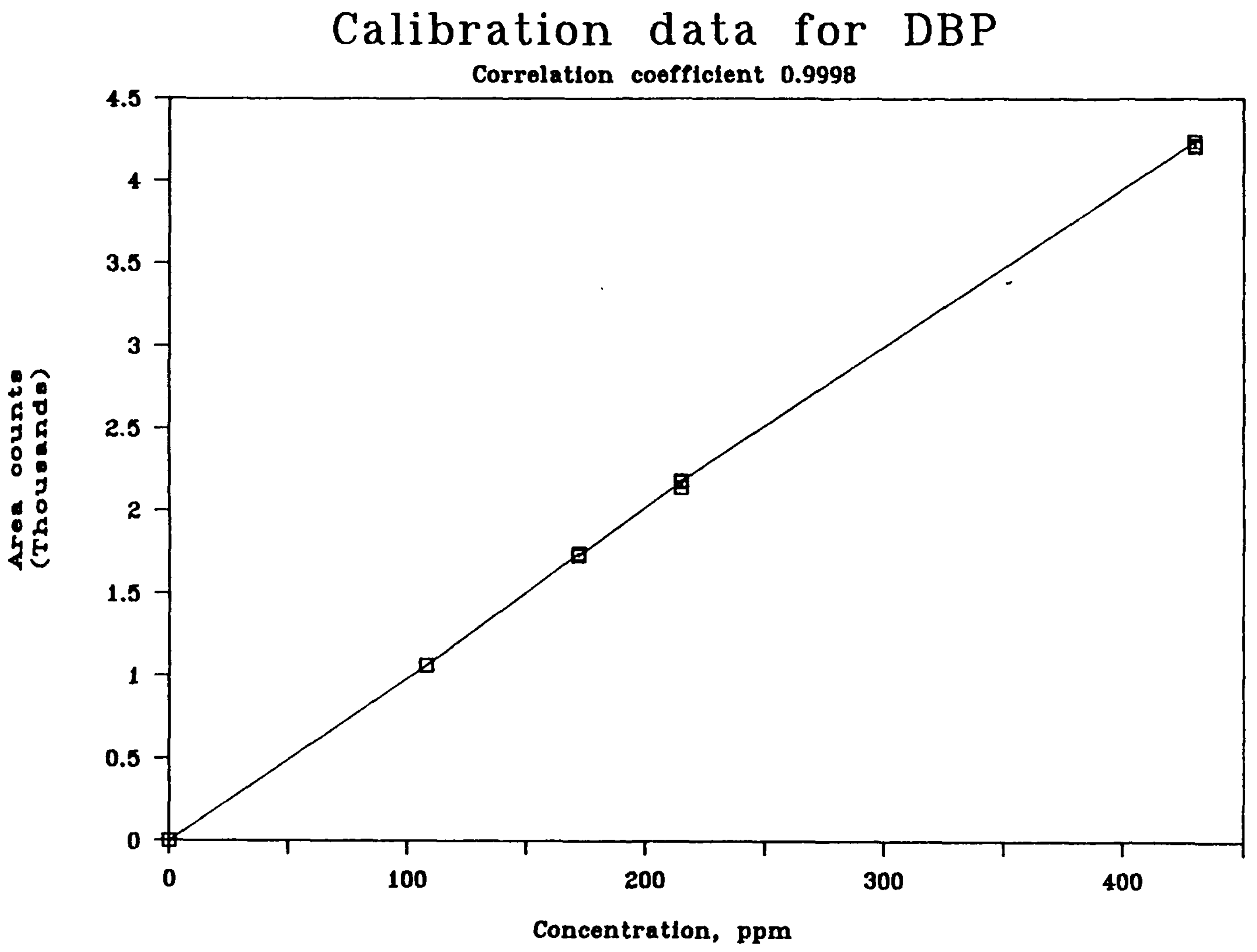
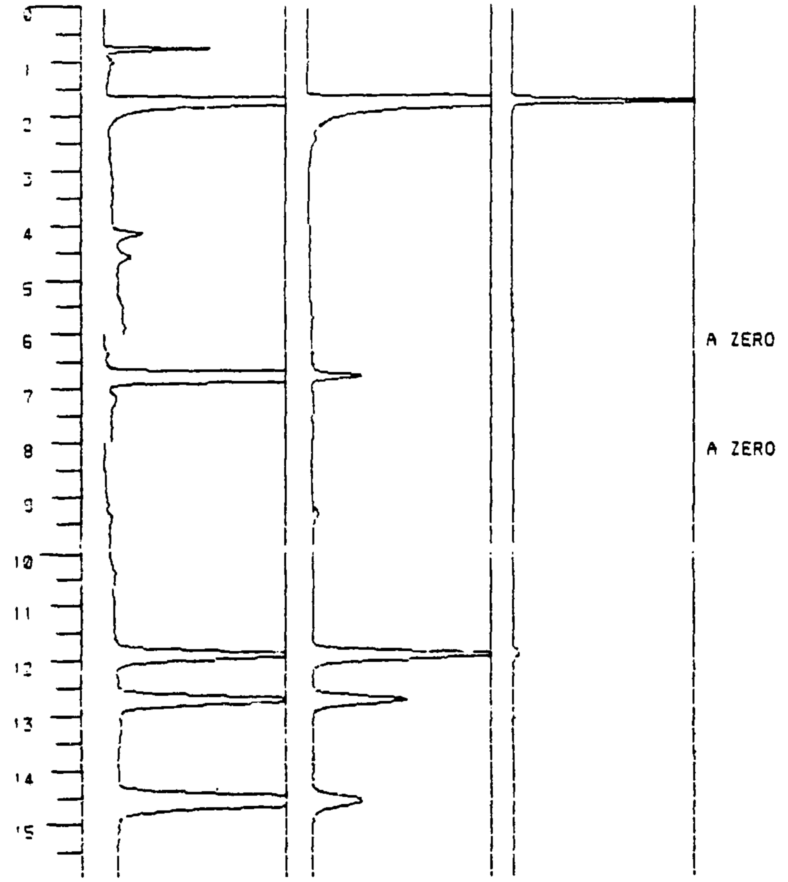


Figure 66. Triple-base standard calibration data of area counts vs concentration for dibutylphthalate (DBP)

```
Integration & online plot of new analysis
          VIAL 100  INJ 1                                   [illegible]      11:37

Signal      A              B              C              Annotation
S wl,bw     214,20         254,20         340,20
Range       100            100            100
Zero %      10             10             10
```



```
ESTD

 # NAME           GR SI   TIME   TYPE REF         AMOUNT  WIDTH  dTIME       QUOTIENT
                         [min]               [       ppm] [min]  [min]       [amount]

 4 NGU               B   1.701   OPU      ------------  0.049
 7 1,3-DNG           A   4.155    PB      ------------  0.092
 1 1,2-DNG           A   4.595    BP      ------------  0.130
 8 NG                A   6.758    VV       [illegible]  0.115  0.000  A/B   1.042
 9 2-NDPA            A  11.309    PP       [illegible]  0.156  0.000  A/B   0.995
10 EC                A  [illegible] BP     [illegible]  0.158  0.000  A/B   1.003
11 DBP               A  14.551    BP       [illegible]  0.[illegible] 0.000  A/B   0.990
```

<u>Chromatographic Conditions:</u>

20 cm Hewlett Packard RP-8 4.5 mm ID 5 µm particles
Flow rate: 0 to 6 min = linear ramp from 2.5 to 3.0 mL/min
6 to 16 min = 3.0 mL/min
Mobile phase: 0 to 5.4 min = linear ramp from 0 to 45% methanol/water
5.4 to 8.6 min = linear ramp from 45 to 55% methanol/water
8.6 to 12 min = linear ramp from 55 to 65% methanol/water
Temperature = 40°C
Injection volume: 20 µL
Diode Array detection at 214,254,340 nm

Figure 67. Representative HPLC chromatogram for triple-base propellant ingredients

Table 23. Detection limits for propellant ingredients in single-, double-, and triple-base propellants

Propellant ingredient	Detection limit, ng*
Single-base:	
Dinitrotoluene	33
N-nitrosodiphenylamine	41
Diphenylamine	16
2-nitrodiphenylamine	16
Dibutylphthalate	55
Double-base:	
1,3-dinitroglycerin	79
1,2-dinitroglycerin	80
Nitroglycerin	120
Ethyl centralite	40
Triple-base:	
Nitroguanidine	1631
1,3-dinitroglycerin	159
1,2-dinitroglycerin	120
Nitroglycerin	144
2-nitrodiphenylamine	17
Ethyl centralite	30
Dibutylphthalate	52

---

* The detection limit represents the amount injected onto the column and analyzed by the method listed in the test plan.

Table 24. Summary of Student's t-test for single-, double-, and triple-base propellants

Single-base propellants:

	DNT		DPA		DBP	
	MIL-STD-286B	HPLC	MIL-STD-286B	HPLC	MIL-STD 286B	HPLC
$\bar{X}$	9.98	10.12	1.00	1.06	4.99	5.01
s	0.14	0.29	0.03	0.06	0.01	0.04
n	10	9	10	9	10	9
t	1.367		0.703		1.397	
df	17		17		17	

Double-base propellants:

	NG		EC	
	MIL-STD 286B	HPLC	MIL-STD 286B	HPLC
$\bar{X}$	19.76	20.11	0.43	0.45
s	0.45	0.51	0.02	0.03
n	10	10	10	10
t	1.713		1.985	
df	18		18	

Triple-base propellants:

	NG		2-NDPA		DBP	
	MIL-STD 286B	HPLC	MIL-STD 286B	HPLC	MIL-STD 286B	HPLC
$\bar{X}$	19.86	19.40	1.32	1.40	4.54	4.53
s	0.39	0.36	0.03	0.08	0.08	0.13
n	10	10	10	10	10	10
t	1.740		0.993		1.495	
df	18		18		18	

$\bar{X}$ = mean
s = standard deviation
n = number of determinations
t = Student's t value
df = degrees of freedom: $n_1 + n_2 - 2$

the double- or the triple-base propellant. Results for DBP and 2-NDPA in triple-base propellants indicate no statistical difference between analytical methods at the 95% confidence level as established by the Student's t-test to determine the difference between means.

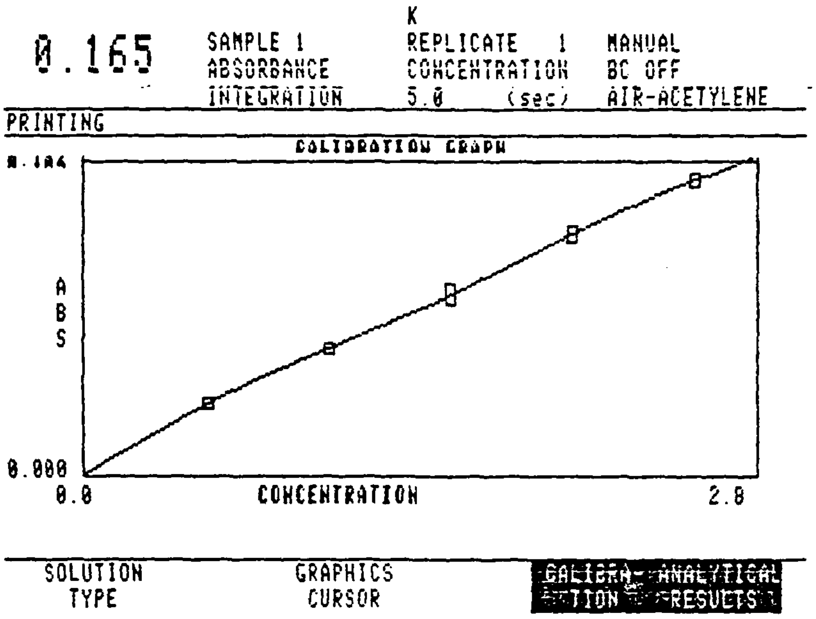
NQ extract samples were not analyzed by the Student's t test due to solubility problems of NQ in the HPLC solvents. Therefore, NQ extracts were prepared in a very large volume of water (500 mL) to circumvent these inherent solubility problems; the results are discussed later in the solvent extraction evaluations for triple-base propellant.

Analysis of water-soluble salts in the propellant extracts was accomplished by atomic absorption spectrometry. A Varian Model Spectra AA-20 was used for all atomic absorption spectrometry determinations. Standards were prepared by volumetric dilution of purchased 1,000-ppm standards (Fisher Scientific, Fairlawn, NJ). Potassium (K^+) cation standards were prepared to be 0, 0.5, 1.0, 1.5, 2.0, and 2.5 ppm; both the lead (Pb^{+2}) and barium (Ba^{+2}) cation standards were prepared to be 0, 1.0, 2.0, 4.0 10.0, and 20.0 ppm. Figures 68 through 70 represent the calibration curves and operating parameters for K^+, Pb^{+2}, and Ba^{+2} cation standards, respectively. The correlation coefficients ranged from 0.999 for the K^+ cation standards to 0.997 for the Pb^{+2} cation standards.

4.2 Solvent Extraction Flow Charts

Solvent extraction procedures were devised for each of the propellants based on the solvent evaluations. Extraction procedures for single-base propellants are shown in figures 71 through 73 for M1, M6, and M10, respectively. The procedures developed for the M1 and M6 propellants contain inherent drawbacks, e.g., high energy consumption in evaporating solvents which can lead to further degradation of stabilizer and separation of three ingredients (DPA, DNT, and DBP) may not be feasible due to solubility differences.

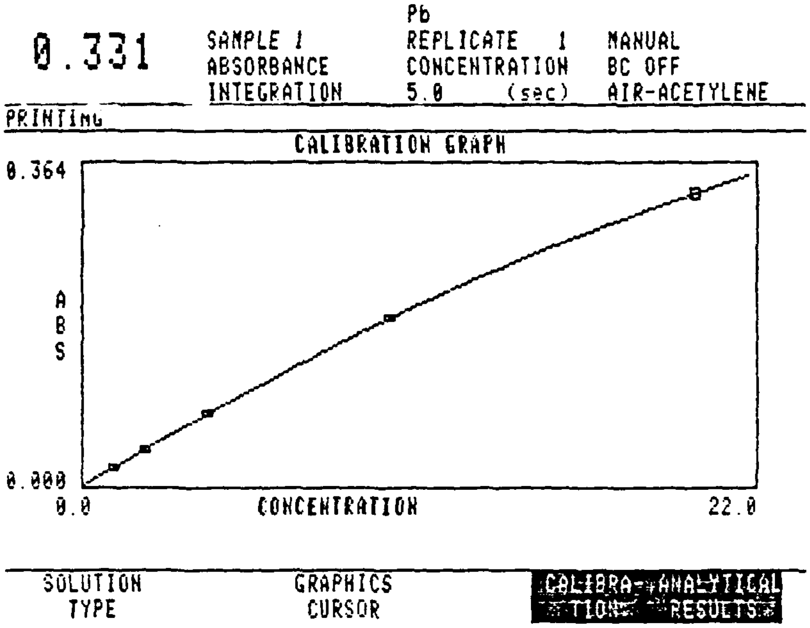
In order to assess the effects of the chosen parameters of interest, e.g., solvent selection and distribution of propellant ingredients in the solvent, testing was conducted with a mixture of propellant ingredients, not the actual propellant itself. In this way, the solvent systems were evaluated without the influence of the propellant matrix in the evaluation. The ingredients contained in M10 single-base propellant, i.e., NC, DPA, and K_2SO_4, were weighed and mixed together as thoroughly as possible. The appropriate extraction scheme was followed, but the results of three extractions indicated that inherent problems existed in the method. For example, DPA analysis, i.e., extraction of the DPA from the NC with ether, revealed the procedure to be irreproducible due to sampling problems encountered as a result of the inhomogeneity of the mixture. The large raw material size, inefficient mixing, and absence of NC plasticization caused an inability to reproducibly sample the mixture, precluding evaluation of the extraction method for individual propellant ingredients.



```
                          K
0.165   SAMPLE 1          REPLICATE     1   MANUAL
        ABSORBANCE        CONCENTRATION     BC OFF
        INTEGRATION       5.0        (sec)  AIR-ACETYLENE
PRINTING
```

Operating Parameters: Air/acetylene flame
5 mA lamp current
766.5 nm wavelength
1.0 nm slit width
sample aspiration

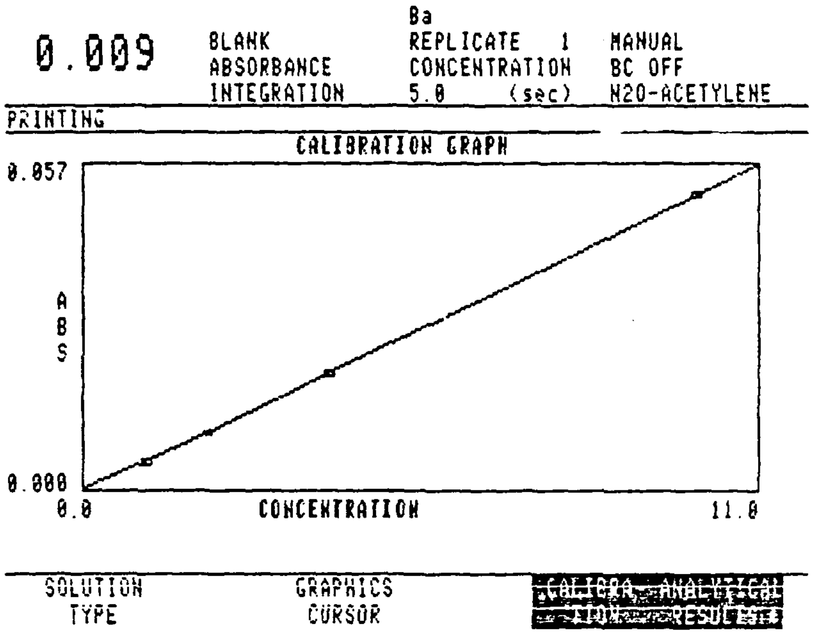
Figure 68. Calibration curve and operating parameters for analysis of potassium (K^+) cation via atomic absorption spectrometry



```
                          Pb
0.331   SAMPLE 1          REPLICATE    1    MANUAL
        ABSORBANCE        CONCENTRATION     BC OFF
        INTEGRATION       5.0      (sec)    AIR-ACETYLENE
PRINTING
```

Operating Parameters: Air/acetylene flame
5 mA lamp current
217.0 nm wavelength
1.0 nm slit width
sample aspiration

Figure 69. Calibration curve and operating parameters for analysis of lead (Pb^{+2}) cation via atomic absorption spectrometry



0.009

BLANK
ABSORBANCE
INTEGRATION

Ba
REPLICATE 1
CONCENTRATION
5.0 (sec)

MANUAL
BC OFF
N2O-ACETYLENE

PRINTING

Operating Parameters: Nitrous oxide/acetylene flame
20 mA lamp current
553.6 nm wavelength
0.5 nm slit width
sample aspiration

Figure 70. Calibration curve and operating parameters for analysis of barium (Ba^{+2}) cation via atomic absorption spectrometry

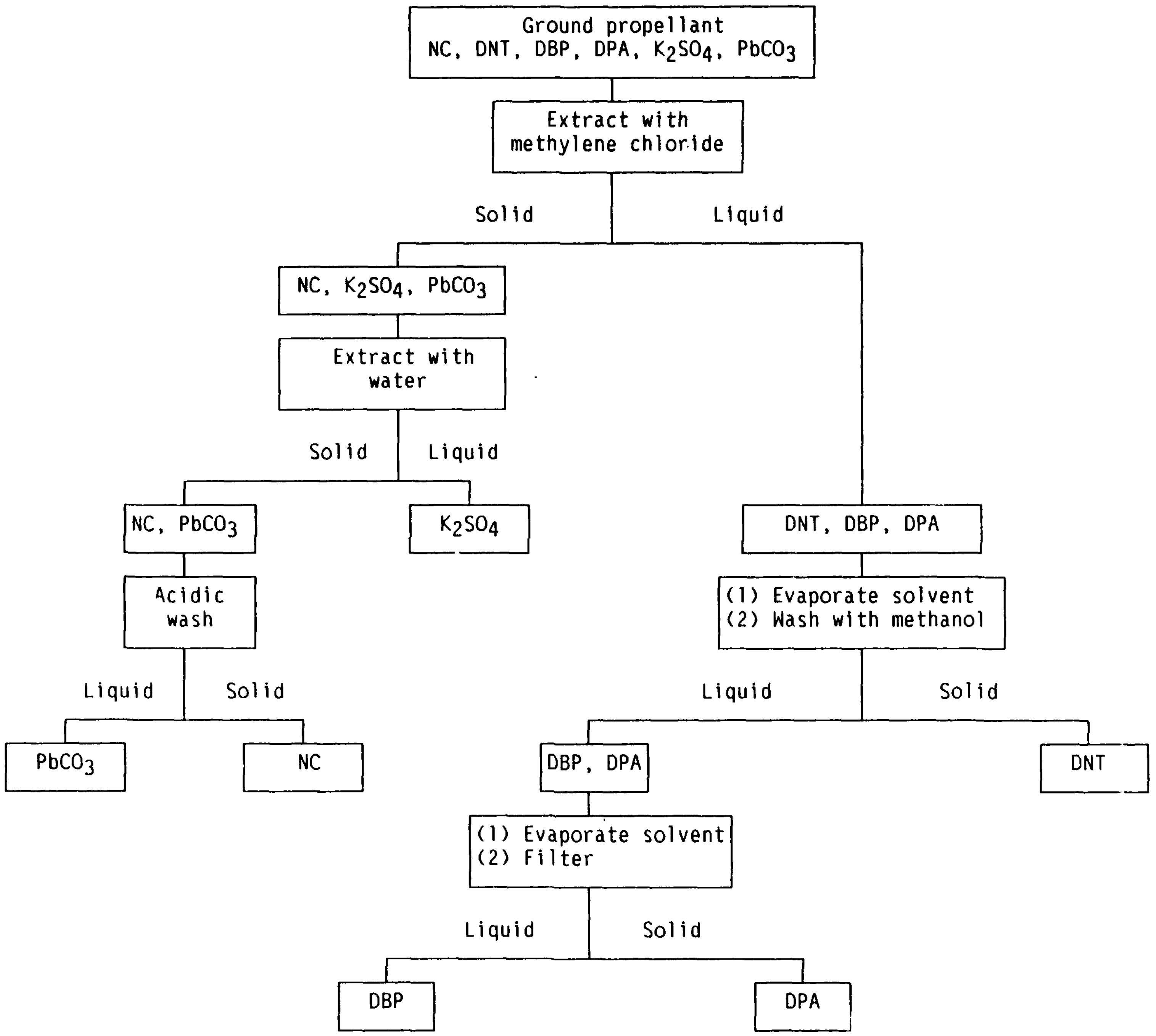


Figure 71. Solvent extraction procedure for M1 single-base propellant

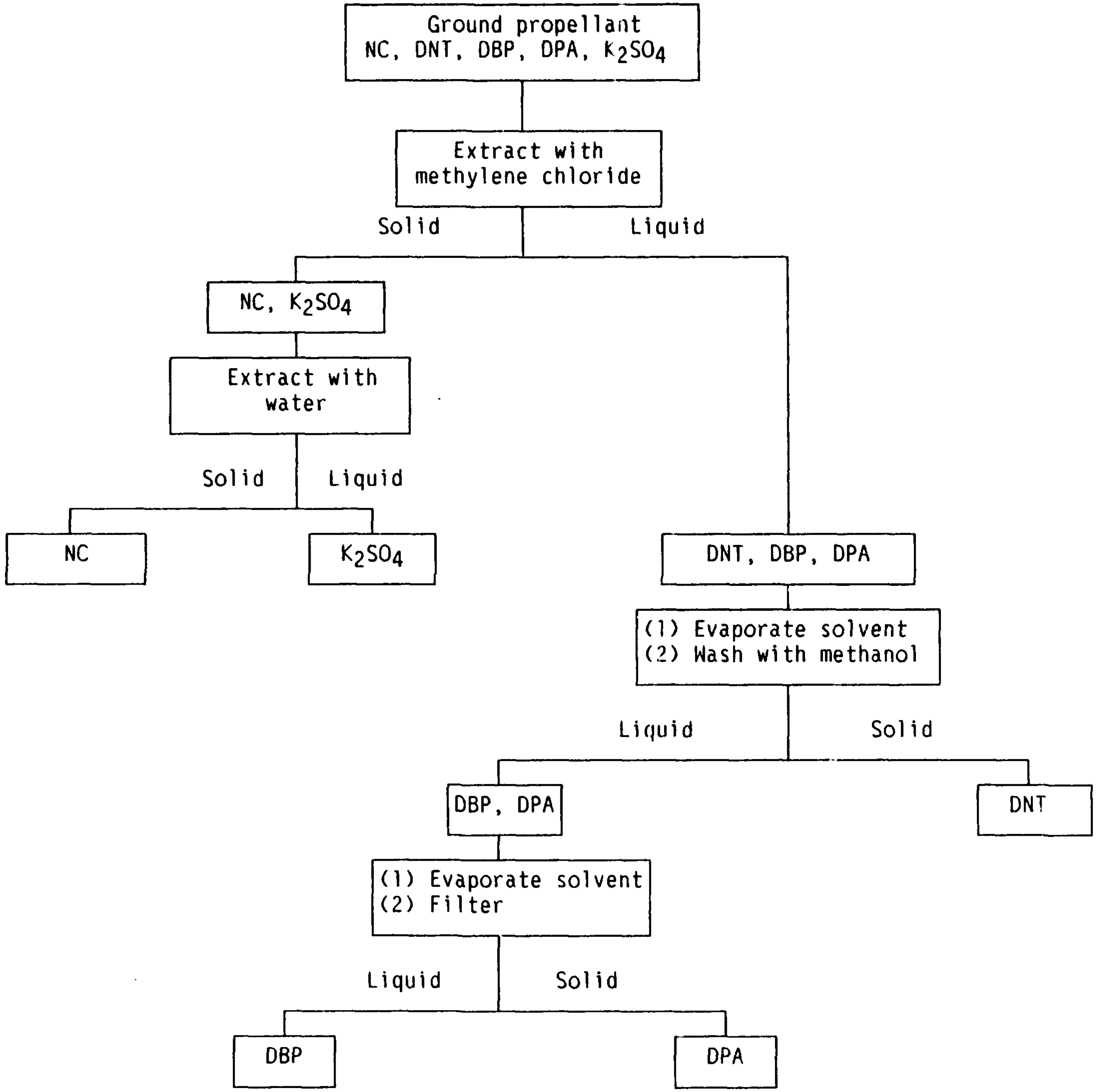


Figure 72. Solvent extraction procedure for M6 single-base propellant

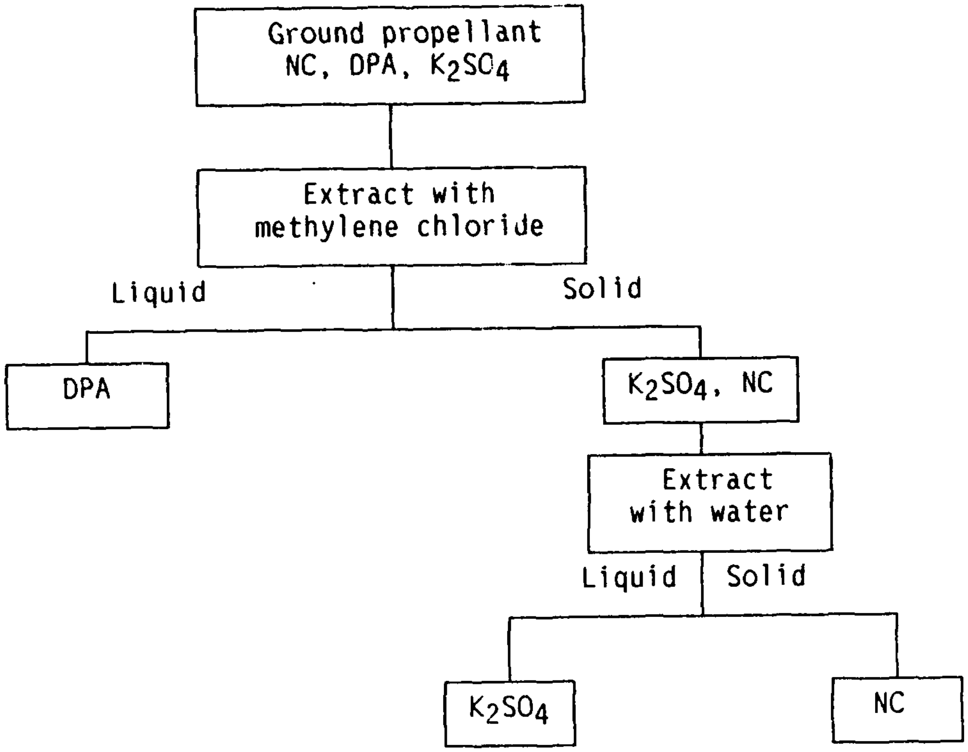


Figure 73. Solvent extraction procedure for M10 single-base propellant

To circumvent this problem and simultaneously evaluate the influence of the propellant matrix, mixture homogeneity was ensured by using ground M10 propellant (particles passing 20-mesh screen and retained on 50-mesh screen). Prior to grinding, the whole grains of propellant were washed to remove as much of the graphite coating as possible. As shown in the flowchart (fig. 73), the ground propellant was then extracted with methylene chloride to remove DPA, resulting in a solid containing K_2SO_4 and NC. This solid was extracted with water to remove K_2SO_4 and leave NC as the solid. This evaluation indicated that the propellant matrix does not adversely affect ingredient extraction.

Double-base propellant extraction procedures are presented in figures 74 through 76 for M2, M7, and M9, respectively. Pretreatment of the M2 and M9 propellant includes washing with water to remove as much excess graphite as possible prior to grinding (particles passing 20-mesh screen and retained on 50-mesh screen). Pretreatment of M7 propellant is limited to grinding. Furthermore, the NG and EC in all double-base propellants are left together in a liquid matrix for safety reasons.

Solvent extraction procedures were developed for the triple-base propellants being investigated. Figure 77 represents the scheme for M30 propellant, with pretreatment of the propellant limited to grinding (particles passing 20-mesh screen and retained on 50-mesh screen); furthermore, the NG and EC are left together in a liquid matrix for safety reasons. Figures 78 and 79 represent the schemes for M30A1 and M31A1 propellants, respectively. For these two propellants, pretreatment consisted of a water-washing step to remove as much excess graphite as possible followed by a grinding step. The NG and EC were left together in a liquid matrix for safety reasons in the M30A1; the DBP and 2-NDPA were also left together with NG in the M31A1 for safety reasons.

The extractions were begun with solvent/propellant ratios of roughly 10 to 1 and 5 to 1 (weight-to-weight). A weighed amount of the ground propellant was placed in a screw-top vial and the extraction solvent added to the vial. The top was replaced and the sample was agitated on an orbital shaker for ~24 hours. At this time, the sample was allowed to settle and the supernatant liquid drawn off. This procedure was repeated three times with all of the extracts being combined. By the third extraction, the samples with a solvent/propellant ratio of 10 to 1 had a supernatant that was clear, while the samples with a solvent/propellant ratio of 5 to 1 ratio had a supernatant that was slight discolored. (The original color of the extract varied depending on which type of stabilizer was added to each propellant.) Based on these results, a solvent/propellant ratio of 10 to 1 was used for all subsequent evaluations. After removing the methylene chloride extract from the vial, the samples were dried under a gentle stream of air to remove any residual solvent. At this point distilled water was added to the vial to begin the extraction of any water solubles. Again, three 24-h extractions were employed with the extracts from each trial being combined.

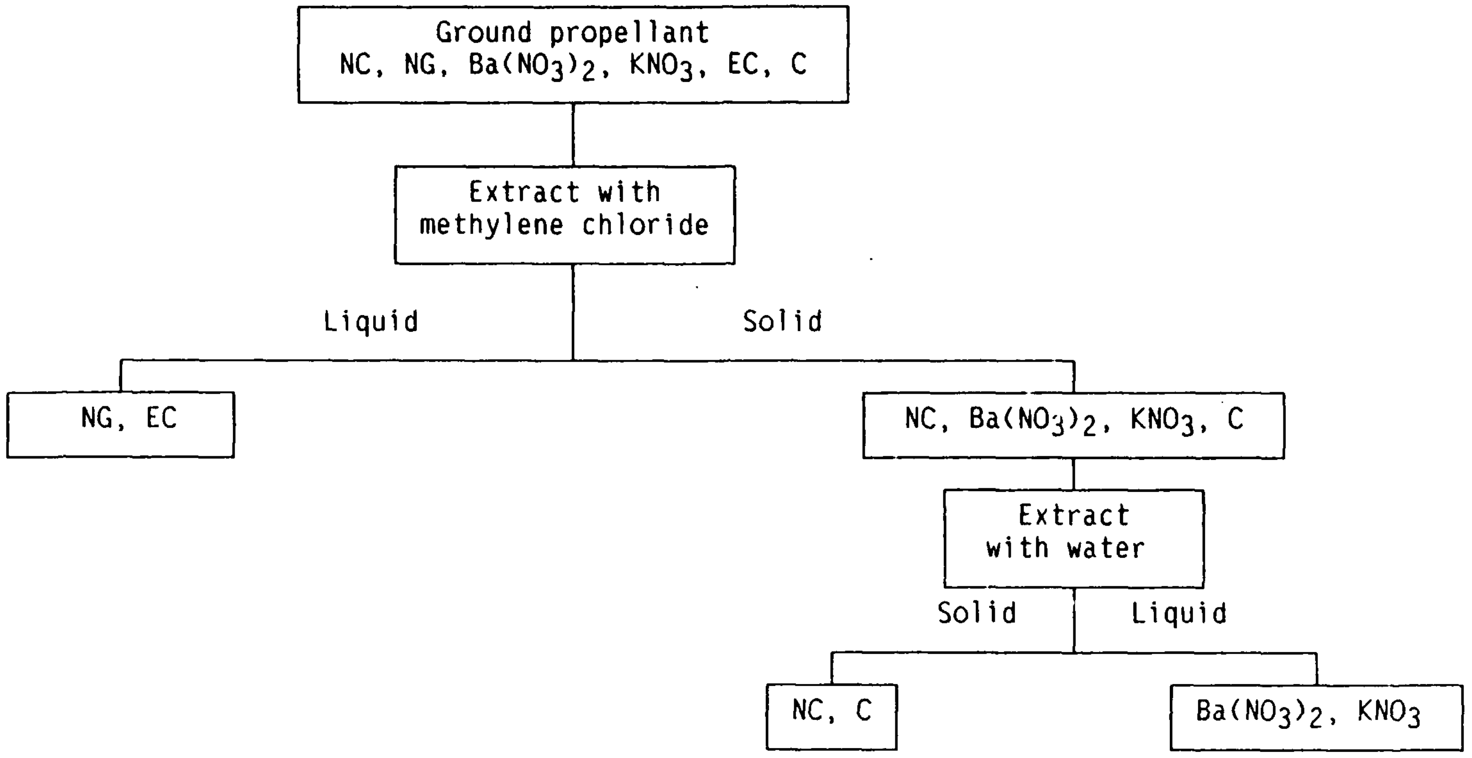


Figure 74. Solvent extraction procedure for M2 double-base propellant

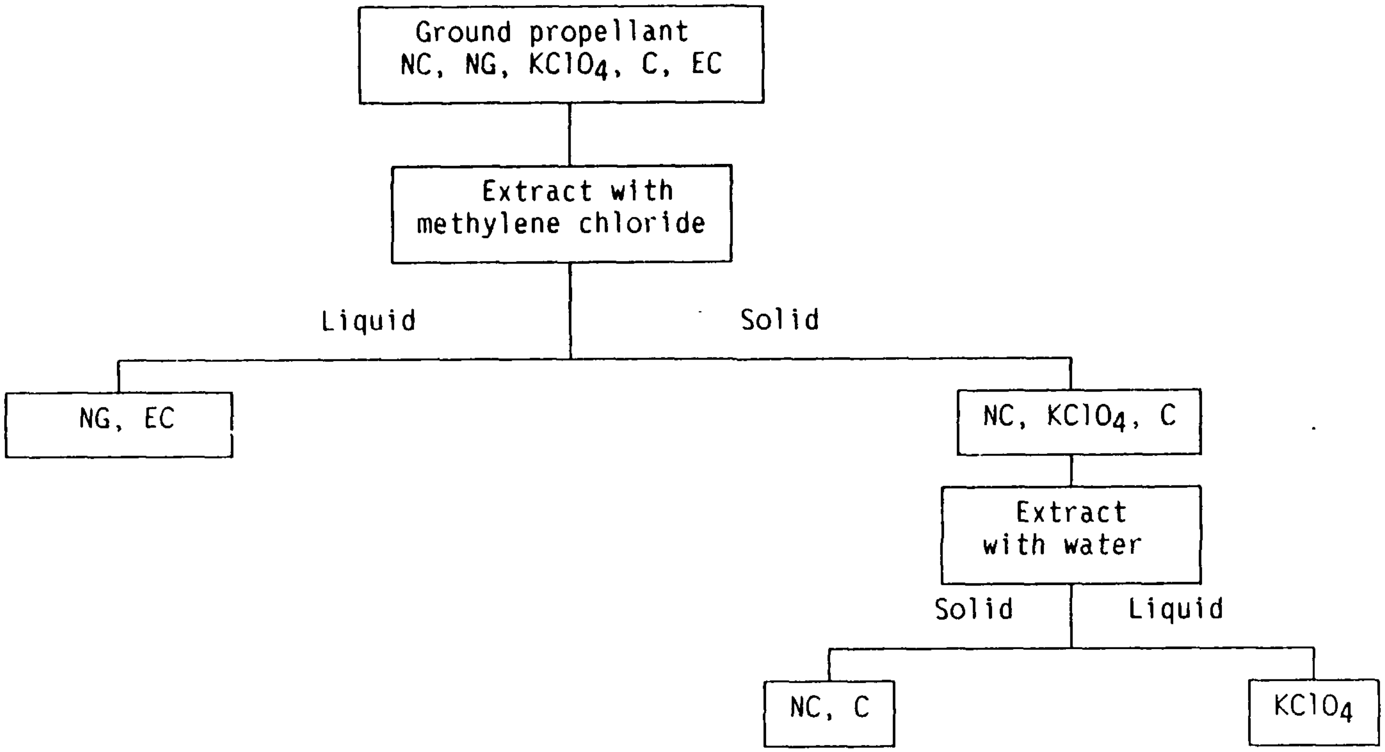


Figure 75. Solvent extraction procedure for M7 double-base propellant

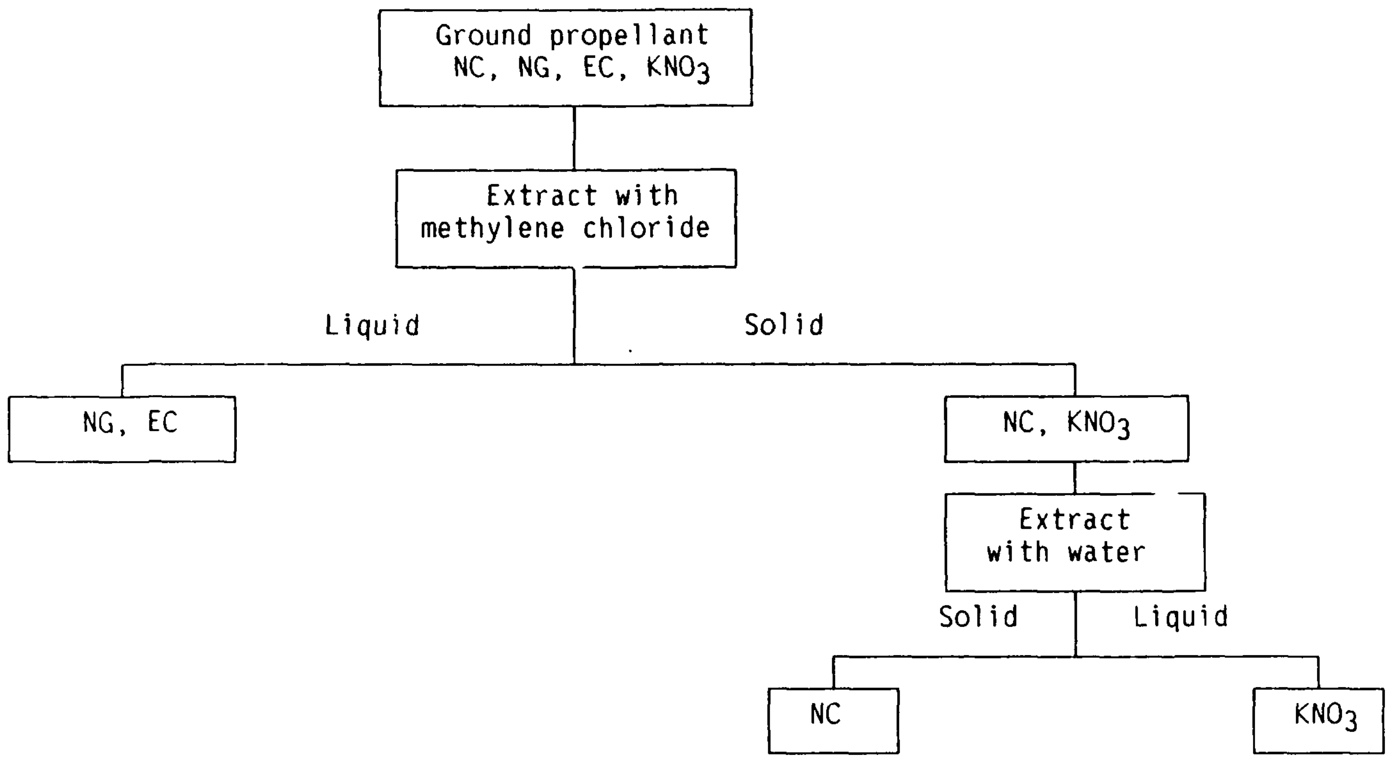


Figure 76. Solvent extraction procedure for M9 double-base propellant

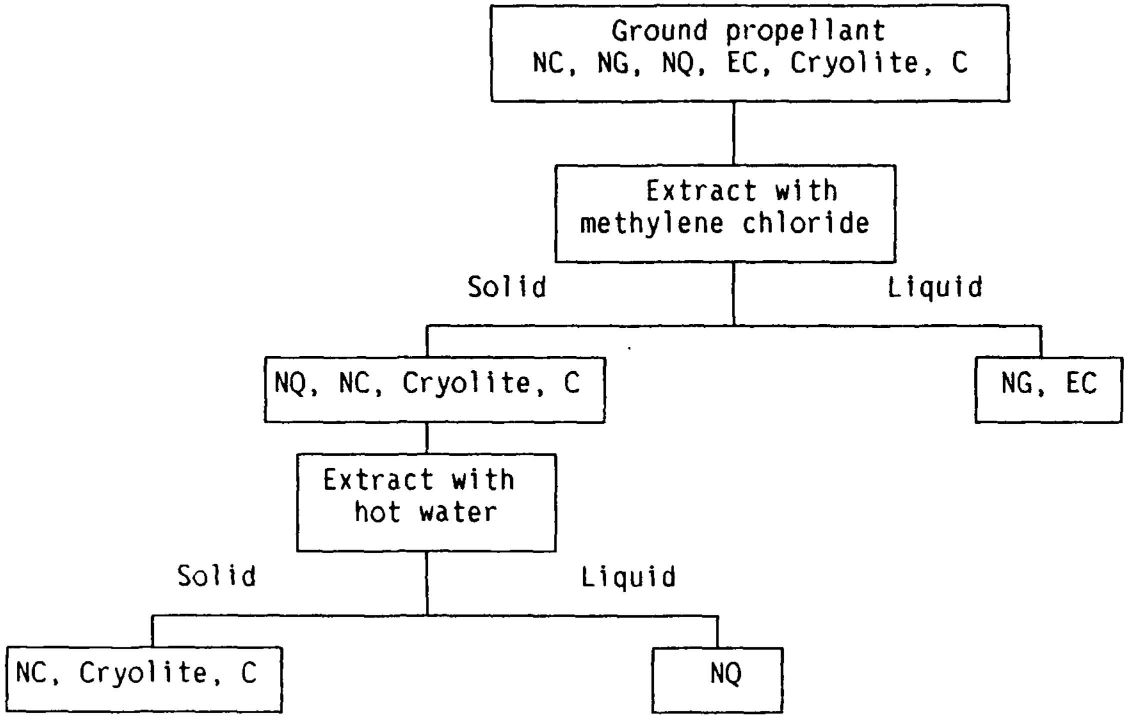


Figure 77. Solvent extraction procedure for M30 triple-base propellant

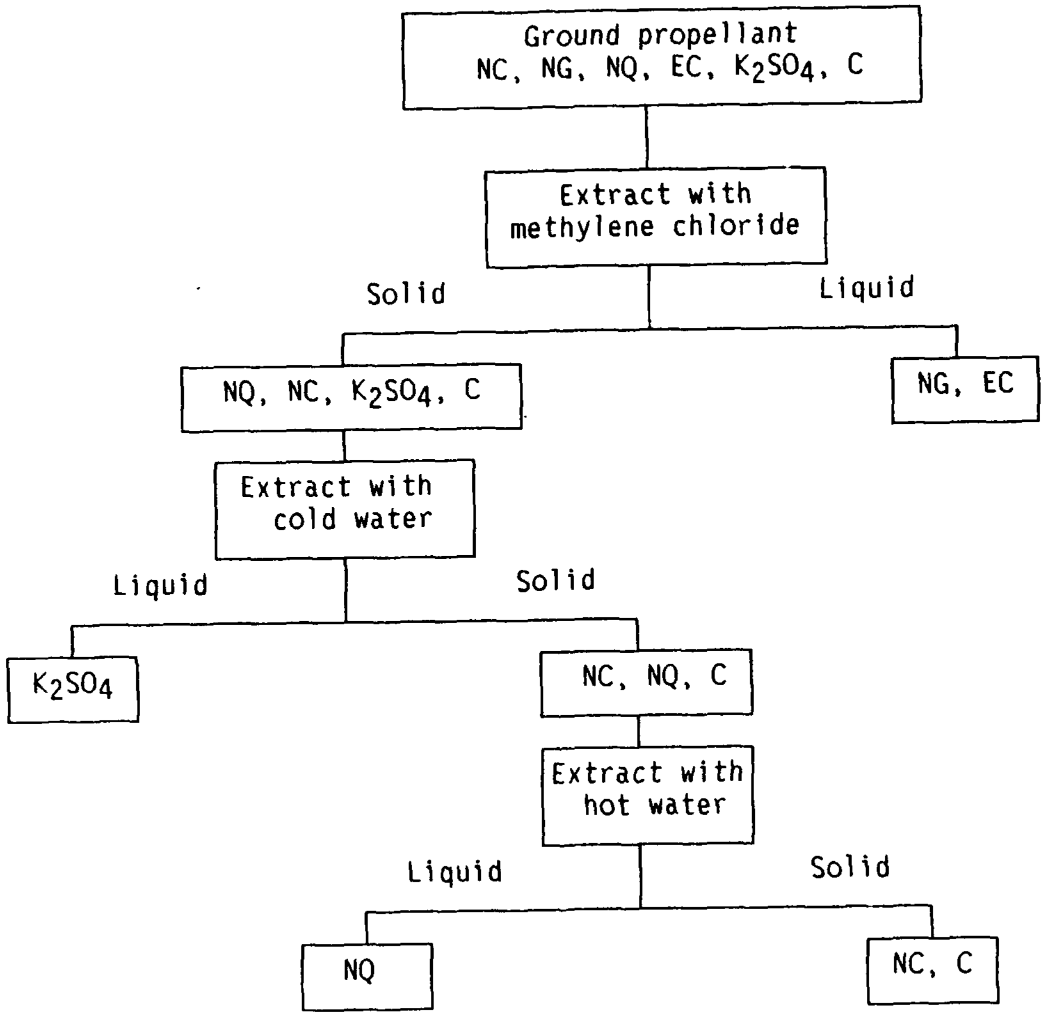


Figure 78. Solvent extraction procedure for M30A1 triple-base propellant

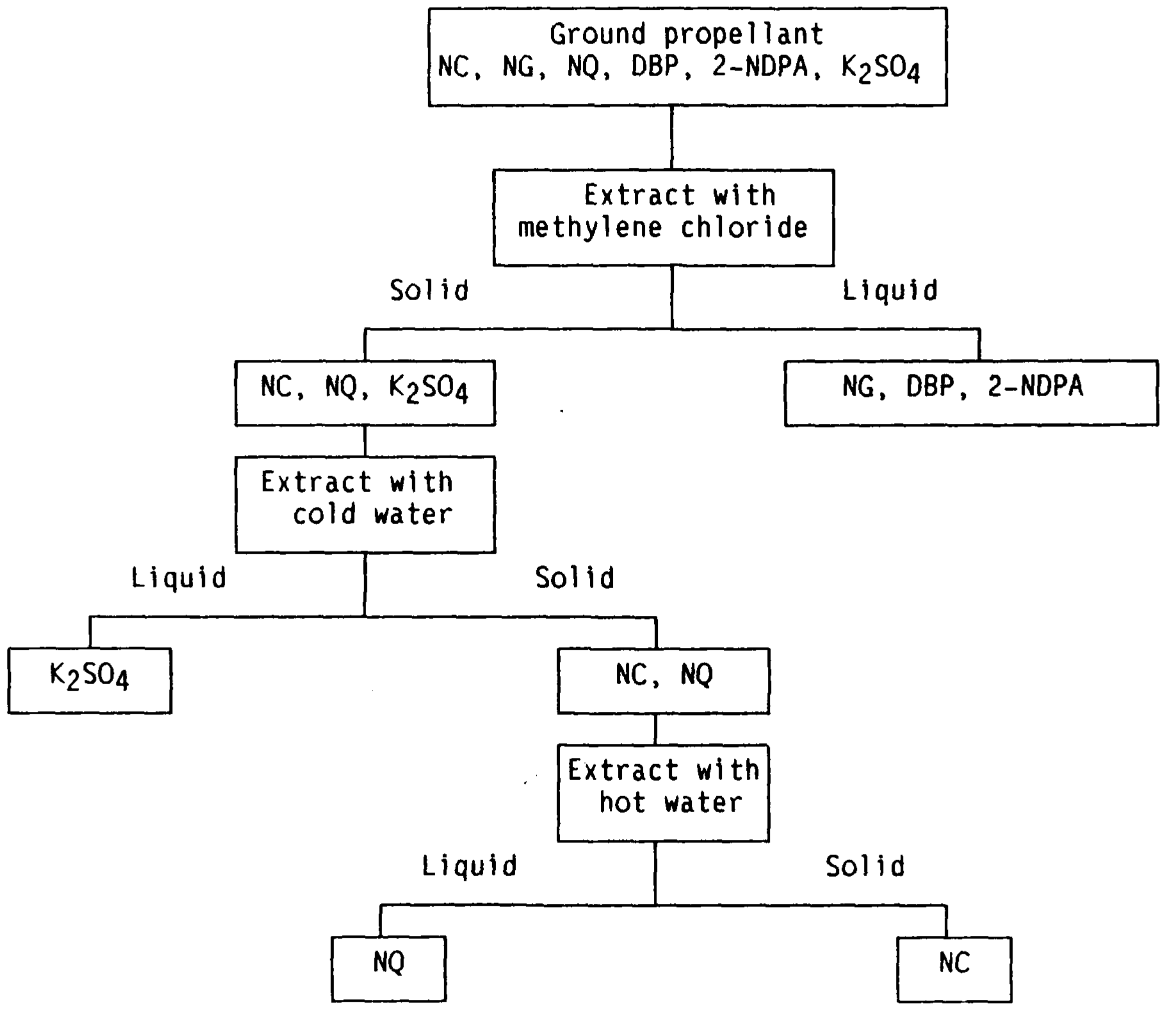


Figure 79. Solvent extraction procedure for M31A1 triple-base propellant

4.3 Solvent Extraction Results for Single-Base Propellants

Solvent extractions using the procedures described earlier were performed on three single-base propellants: M1, M6, and M10 (table 25). As described in the following sections, analyses of the extracts revealed the viability of several of the solvent extraction procedures. The results of the analyses of the extracts indicate that NC recovery from single-base propellants appears feasible. The recovered NC (13.15%N) could be used in any propellant requiring this grade of NC.

4.3.1 M1 Propellant

The first extract, i.e., methylene chloride, of M1 single-base propellant removed the DNT, DPA, and DBP along with any decomposition products of DPA. The methylene chloride was allowed to evaporate and methanol was used to selectively solvate the DPA, DBP, and DPA degradation products. The extracts were filtered and the crystalline material (DNT) was dissolved in acetonitrile. Both extracts were diluted to 100.0 mL with HPLC-grade solvents and subjected to HPLC analysis. The extracts for DNT ranged from colorless to light yellow; the color in this sample was attributed to DPA decomposition products not being thoroughly separated from the DNT. Since the DNT also has a finite solubility in methanol, the longer the extracts were washed with methanol, the greater the chance of obtaining DNT in the DPA/DBP sample. DNT recovery in the DPA/DBP extract ranged from 54 to 82% of the specification value. Recovery in the DNT extract ranged from 0.1 to 35.8%, though these extracts normally contained some DPA and DBP also. DPA and DBP recoveries in the DPA/DBP extracts were fairly consistent. DPA was normally recovered at an average of 75% of the specification value while DBP was recovered around the 90% level. However, due to the inability to effectively separate the individual components of the first methylene chloride extract, this approach does not appear promising for DNT or DPA recovery.

The first water extract removed approximately 32% of the K_2SO_4 in the sample (based on specification value), as determined by atomic absorption spectrometry. Analysis of the extracts by HPLC methods did not reveal the presence of any DNT, DPA, or DBP. The second water extract (acidic water) to remove lead carbonate ($PbCO_3$) from the sample was also analyzed by atomic absorption spectrometry. Since certain M1 propellants contain 1% $PbCO_3$, the extraction procedure was developed to remove and analyze any residual lead following processing. Results indicated that only a very small amount of the $PbCO_3$ was detected, representing 0.04 ppm (mg/L); this amount of $PbCO_3$ apparently was absorbed during the water dry process and remained in the solid material left behind. Again, HPLC analysis of the extracts did not reveal the presence of any DPA, DNT, or DBP. The solid material left behind should contain NC and any of the above-mentioned ingredients that were only partially removed. Calculations assuming only NC present indicate about 98% recovery; even accounting for all the K_2SO_4 and $PbCO_3$ remaining behind, recoveries are still around 96%.

Table 25. Single-base propellant ingredient recovery

Propellant	Wt % (calculated)	Wt % (specification)	% recovery	
		NC Recovery		
M1	(NC)	(NC)	(NC)	
	84.2	85.0	99.1	
	83.6	85.0	98.4	
	82.4	85.0	96.9	
M6	(NC)	(NC)	(NC)	
	86.1	87.0	99.1	
	85.6	87.0	98.4	
	85.7	87.0	98.5	
M10	(NC + graphite)	(NC + graphite)	(NC + graphite)	
	100.5	98.2	102.4	
	98.9	98.2	100.6	
	83.7	98.2	85.2	
		DPA Recovery		
M1	0.74	1.00	74.0	
	(-)*			
	0.66	1.00	66.0	79.0
	(0.13)		13.0	
	0.77	1.00	77.0	
	(-)			
M6	0.71	1.00	71.3	72.9
	(0.02)		1.6	
	0.75	1.00	75.4	
	(-)			
	0.60	1.00	59.8	75.7
	(0.16)		15.9	
M10	0.88	1.00	87.8	
	0.89	1.00	89.2	
	0.90	1.00	89.5	

Table 25. (cont)

Propellant	Wt % (calculated)	Wt % (specification)	% recovery	
		DNT Recovery		
M1	6.11 (2.65)	10.00	61.1 26.5	87.6
	5.49 (3.58)	10.00	54.9 35.8	90.7
	8.29 (0.66)	10.00	82.9 0.1	83.0
M6	8.01 (0.50)	10.00	80.1 5.0	85.1
	8.74 (0.04)	10.00	87.4 0.4	87.8
	6.63 (2.11)	10.00	66.3 21.1	87.4
		DBP Recovery		
M1	4.48 (-)	5.00	89.6	
	3.95 (-)	5.00	79.0	
	4.67 (-)	5.00	93.4	
M6	2.60 (0.05)	3.00	86.5 1.6	88.1
	2.75 (-)	3.00	91.6	
	2.08 0.55	3.00	69.5 18.4	87.9

Table 25. (cont)

Propellant	Wt % (calculated)	Wt % (specification)	% recovery
		K_2SO_4 Recovery	
M1	0.34	1.00	33.5
	0.32	1.00	31.5
	0.23	1.00	22.5
M6	0.46	1.00	45.7
	0.50	1.00	49.8
	0.52	1.00	52.2
M10	0.10	1.00	10.4
	0.11	1.00	10.6
	0.05	1.00	5.4
		Residual $PbCO_3$	
M1	0.03	---	---
	0.03	---	---
	0.05	---	---

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* The number in parentheses represents the amount in the DNT acetonitrile extraction.

4.3.2 M6 Propellant

The M6 propellant evaluations were performed much the same as the M1 propellant and yielded very similar results. The methylene chloride extract removed the DNT, DBP, DPA and its degradation products. As in the M1 propellant evaluations, the attempt to separate the DNT from the DPA/DBP extract was unsuccessful.

The first water extract removed ~49% of the K_2SO_4 in the specification value, representing a sizable increase from the M1 propellant. HPLC analysis showed no carryover of DNT, DPA, or DBP. Recovery of NC was again around the 99% level, when considering material remaining as NC. Taking the entire amount of K_2SO_4 into account, the recoveries could be as low as 97%.

4.3.3 M10 Propellant

The M10 propellant was evaluated similarly to the other single-base propellants. The methylene chloride extract was analyzed and results revealed that ~90% of the DPA specification value was removed and recovered. The water extract removed only ~10% of the specified value of K_2SO_4. The variability in these levels of removal is uncertain at present. HPLC analysis of the water extract revealed no DPA present.

Recovery of NC was calculated to be ~101%; the recovered NC was contaminated with graphite, accounting for the >100% recovery. Since only 10% of the K_2SO_4 was removed, recoveries are at the 100% level (taking the entire K_2SO_4 amount into account).

4.4 Solvent Extraction Results for Double-Base Propellants

Solvent extractions using the procedures described earlier were performed on three double-base propellants: M2, M7, and M9. The results of the analyses (table 26) of the extracts indicate that NC recovery from double-base propellants appears feasible; however, the recovered NC (12.6%N) should only be used in the production of double-base propellant since the NC has previously been contaminated with insolubles and NG.

4.4.1 M2 Propellant

The first methylene chloride extraction was used to remove NG and EC, leaving NC, graphite, barium nitrate [$Ba(NO_3)_2$], and potassium nitrate (KNO_3) behind. Analysis of this extract revealed NG to be recovered at about the 95% level, based on the specification value. EC was recovered at approximately 98% of the specification value. Because of inherent safety problems, no further separation of this extracted material was performed; furthermore, utilization of this extracted material is not recommended.

Table 26. Double-base propellant ingredient recovery

Propellant	Wt % (calculated)	Wt % (specification)	% recovery
NC Recovery			
M2	(NC + graphite)	(NC + graphite)	(NC + graphite)
	79.1	77.85	101.5
	78.6	77.85	100.9
	78.9	77.85	101.3
M7	(NC + Carbon black)	(NC + Carbon black)	(NC + Carbon black)
	60.1	55.80	107.7
	60.1	55.80	107.7
	60.2	55.80	107.9
M9	(NC + graphite)	(NC + graphite)	(NC + graphite)
	61.0	58.15	104.9
	60.4	58.15	103.9
	60.0	58.15	103.2
NG Recovery			
M2	18.62	19.50	95.5
	18.85	19.50	96.7
	18.28	19.50	93.7
M7	30.23	35.50	85.2
	30.47	35.50	85.8
	30.47	35.50	85.8
M9	33.11	40.00	82.8
	33.22	40.00	83.1
	32.07	40.00	80.2
EC Recovery			
M2	0.60	0.60	100.0
	0.58	0.60	96.7
	0.59	0.60	98.3
M7	0.74	0.80	92.5
	0.75	0.80	93.8
	0.75	0.80	93.8

Table 26. (cont)

Propellant	Wt % (calculated)	Wt % (specification)	% recovery
		EC Recovery (cont)	
M9	0.47	0.75	62.7
	0.48	0.75	64.0
	0.47	0.75	62.7
		Potassium Salt Recovery	
	(KNO_3)	(KNO_3)	(KNO_3)
M2	0.37	0.75	48.8
	0.32	0.75	43.2
	0.37	0.75	49.9
	($KClO_4$)	($KClO_4$)	($KClO_4$)
M7	3.45	8.05	42.9
	4.23	8.05	52.5
	3.40	8.05	42.2
	(KNO_3)	(KNO_3)	(KNO_3)
M9	0.19	1.50	12.5
	0.97	1.50	64.4
	0.82	1.50	54.4
		$Ba(NO_3)_2$ Recovery	
M2	1.22	1.40	87.3
	1.25	1.40	89.5
	1.23	1.40	88.1

The water extraction step removed the $Ba(NO_3)_2$ and KNO_3, leaving only the NC and graphite. Analysis of the water extracts by atomic absorption spectrometry revealed the KNO_3 to be recovered at around the 49% level, and the $Ba(NO_3)_2$ to be recovered around 83%. Analysis of the water extracts used for atomic absorption spectrometry analysis by HPLC showed no indication of either NG or EC in the water.

The NC recovered in this extraction procedure is contaminated with graphite, as well as any other propellant ingredient not completely removed. NC removal was around the 101% level; as noted earlier, the NC was contaminated with graphite . Since most of the other ingredients were not recovered at extremely high levels, it can be assumed that the NC/graphite mixture would be contaminated with low levels of some of these ingredients. Since there is a possibility that NG may be present along with the NC/graphite, this recovered NC/graphite should only be used for the manufacture of double- or triple-base propellants, i.e., the presence of graphite in the reused NC may affect propellant ballistics.

4.4.2 M7 Propellant

The methylene chloride extract removed the NG and EC. NG was recovered at about 85% of specification value while the EC was recovered at about the 93% level. Analysis of the water extract again revealed that no NG or EC was removed in the second step. The second step water extraction did remove the potassium perchlorate ($KClO_4$) at around the 43% level.

The NC and carbon black that should have been left behind were recovered at the 108% level. Again, since all ingredient recoveries were low, the recovered NC is likely contaminated with other propellant ingredients.

4.4.3 M9 Propellant

This propellant is the only one of the double-base propellants that did not contain an insoluble ingredient (refer to table 20) with the NC. The first methylene chloride extract removed the NG around 82% of specification value, while only about 63% of the specification value of EC was removed. Apparently, the higher NG level in this propellant somehow hampers the extraction of the EC in that there is an inverse relationship present between the amount of NG in the double-base propellant and the amount of EC recovered.

The first extract removed roughly 58% of the KNO_3 in the propellant as determined by atomic absorption spectrometry. Analysis of the water extracts by HPLC methods revealed no NG or EC was extracted in the water step. The solid material (NC) left behind calculated to be ~104% of specification value, apparently accounting for the EC or KNO_3 that was not extracted.

Examination of all double-base propellant solvent extraction results indicate that NC recovery may be feasible. However, since the NC in most cases contains other insolubles or contaminants, the recovered NC should only be used in the manufacture of multi-base propellants. Since NG removal is lower than 100%, the recovered NC should not be used in any single-base propellant due to possible NG contamination; furthermore, this blend of NC (12.6%N) is only used in multi-base propellants.

4.5 Solvent Extraction Results for Triple-Base Propellants

Solvent extractions using the procedures described earlier were performed on three triple-base propellants: M30, M30A1, and M31A1 (table 27). The results of the analyses of the extracts indicate that recovery of NQ is very feasible; the recovered NC (12.6%N)/graphite mixture could be reused but only in the production of triple-base propellant, assuming no ballistic effects from the graphite.

4.5.1 M30 Propellant

The first methylene chloride extract removed the NG and EC. The NG was recovered at around 96% of the specification value. However, the EC was recovered at a relatively consistent 127% of the specification value. Since this analysis is based on separation, i.e., HPLC analysis. determination of the cause of this discrepancy is difficult; this behavior was also present in the M30A1 propellant evaluations.

Hot water extraction was used to remove NQ. The extraction was conducted by placing the extraction vial on a hot plate (~95 °C) and loosely replacing the cap. The NQ, which was extracted into the hot water, tended to recrystallize at the top level of the liquid as seen in figure 80. The liquid containing the NQ was saturated and precipitated on the pipettes and flasks used for collection. Removal of this precipitate was easily accomplished by washing with copious amounts of water. The crystalline material was not removed from the vial; rather, it was allowed to redissolve in the next aliquot of water added for extraction. Analysis of these extracts by HPLC revealed the NQ to be recovered at around 88% of the specification value; analysis of the NQ extracts for NG and EC revealed none to be present.

The solid material remaining behind should contain NC, cryolite, and graphite. Calculations indicated that from 97 to 111% of the specification value for these three components was recovered. Further separation of these components by solvent extraction is not possible.

4.5.2 M30A1 Propellant

This propellant, as well as the M31A1 discussed in the next section, required an additional extraction step to remove ambient water solubles. The methylene chloride extraction removed NG at around 98% of the specification value and EC at about 165% of the specification value. Again, as with the M30 propellant, the reason for this unreasonably large

Table 27. Triple-base propellant ingredient recovery

NC Recovery

Propellant	Wt % (calculated)	Wt % (specification)	% recovery
M30	(NC+Cryolite+ graphite)	(NC+Cryolite+ graphite)	(NC+Cryolite+ graphite)
	31.7	28.50	111.2
	28.2	28.50	98.9
	27.8	28.50	97.6
M30A1	(NC + graphite)	(NC + graphite)	(NC + graphite)
	29.9	28.15	106.2
	29.3	28.15	104.1
	37.7	28.15	133.9
M31A1	(NC + graphite)	(NC + graphite)	(NC + graphite)
	18.8	20.15	93.3
	16.0	20.15	79.4
	19.0	20.15	94.3
		NQ Recovery	
M30	42.59	47.70	89.3
	41.60	47.70	87.2
	42.79	47.70	89.7
M30A1	39.09 (1.96)*	47.00	83.2 4.2
	38.59 (1.98)	47.00	82.1 4.2
	31.97 (1.83)	47.00	68.0 3.9
M31A1	39.90 (2.09)	54.00	73.9 3.9
	37.96 (2.04)	54.00	70.3 2.0
	42.47 (2.29)	54.00	78.6 4.2

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*The number in parentheses represents the amount in the ambient water wash.

Table 27. (cont)

NG Recovery

Propellant	Wt % (calculated)	Wt % (specification)	% recovery
M30	22.35	22.50	99.3
	21.83	22.50	97.0
	20.92	22.50	93.0
M30A1	22.36	22.50	99.4
	22.29	22.50	99.1
	21.80	22.50	96.9
M31A1	19.93	19.00	104.9
	20.04	19.00	105.5
	18.46	19.00	97.2
	EC Recovery		
M30	1.90	1.50	126.7
	1.91	1.50	127.3
	1.92	1.50	128.0
M30A1	2.58	1.50	172.0
	2.47	1.50	164.7
	2.34	1.50	156.0
	2-NDPA Recovery		
M31A1	1.37	1.50	91.3
	1.42	1.50	94.7
	1.64	1.50	109.3
	DBP Recovery		
M31A1	4.40	4.50	97.8
	4.39	4.50	97.6
	4.01	4.50	89.1
	K_2SO_4 Recovery		
M30A1	0.78	1.00	77.5
	0.89	1.00	88.6
	0.94	1.00	93.5
M31A1	0.88	1.00	88.4
	0.89	1.00	88.8
	0.82	1.00	82.5

Figure 80. Nitroguanidine (NQ) crystallization resulting from hot water extraction

value is unknown. There is no other propellant ingredient in either of these propellants that would co-elute with the EC.

The second extraction step was an ambient water wash. By atomic absorption spectrometry analysis, between 75 to 79% of the K_2SO_4 was removed. Analysis of this water wash by HPLC did not indicate the presence of any NG or EC but did indicate that roughly 4% of the NQ present in the sample was extracted.

The hot water extract, which showed formation of crystals, removed NQ around 68 to 83% of the specification value. The lowest level was due to incomplete extraction, as evidenced by the NQ crystals which were visible in the solid left behind. The NQ extracts were analyzed by HPLC and no NG or EC was present, nor was any K_2SO_4 indicated by atomic absorption spectrometry.

The solid material left after all extractions contains NC and graphite, as well as any component not completely removed. Taking the NC and graphite into account, recovery was around the 105% level. One sample indicated a 134% recovery; however, residual NQ (as evidenced by the lowest, i.e., 70.3%, NQ recovery shown in table 27) was present, thereby distorting the actual recoveries of NC and graphite.

4.5.3 M31A1 Propellant

The methylene chloride extract removed NG, 2-NDPA, and DBP. The NG recovery was from 97 to 105% of the specification value, while the 2-NDPA ranged from 91-109% and the DBP ranged from 89-98% recovery. The ambient water extraction removed about 88% of the K_2SO_4, and, as in the M30A1 propellant evaluations, about 4% of the specification value for NQ. No NG, 2-NDPA, or DBP was detected in these extractions when analyzed by HPLC.

The hot water extract removed the NQ from 70 to 79% of the specification value. HPLC analysis of this extract showed no NG, 2-NDPA, or DBP; atomic absorption spectroscopy analysis did not detect K_2SO_4. The NC/graphite mixture that remained after all extractions represented from 79 to 94% of the specified value.

Examination of all triple-base results indicate that recovery of NQ is very feasible and that the NC/graphite mixture could be reused, but only in a triple-base propellant. However, the NQ particle size and graphite may affect ballistics.

5.0 Design Criteria Information

Preliminary design criteria were established for pilot plant propellant resolvation studies and bench-scale solvent extraction of selected ingredients. The common requirement for both technologies is particle size reduction of the propellant with minimal ingredient loss during size reduction operations. After size reduction is accomplished, preparation of the propellant to be processed via either technology consists of reducing the moisture and/or ingredient addition or separation for resolvation or solvent extraction, respectively. Based on the results of the earlier testing, preliminary operating plans have been formulated for both the propellant resolvation and ingredient extraction technologies.

5.1 Particle Size Reduction

Particle size reduction consists of grinding the propellant in a safe manner for reuse. Previous studies at RAAP surveyed various size reduction equipment to obtain a uniform distribution of particles from the grinding operations.[6] The review of size reduction equipment such as hammer mills, dicing machines, attrition mills, and knife grinders (granulators) showed knife grinders to be superior for reducing the various propellant sizes manufactured at RAAP. The Mitts and Merrill grinder (fig. 45) has been very successful in size reduction of propellants for feed to the incinerators[6], in previous resolvation studies conducted at RAAP[7], and for the bench-scale study of this project. Based on RAAP production experience and the abbreviated grinding time requirements for incinerator feeds, the optimal screen size for the grinder has been established to be 3/16-in. diameter holes. Fouling and blinding of screens less than this size occurs to due to the grinding time requirements; screens of larger size result in large particles of propellant being discharged in the slurry, hindering subsequent pumping operations.

The optimal propellant particle size requirement was established for M1 single-base propellant during the bench-scale resolvation study. This requirement is that propellant particles passing a 12-mesh screen will resolvate in the 2-1/2 gal. Baker-Perkins mixer (sigma blade configuration). Particles of M7 propellant greater than those retained on a 12-mesh screen have successfully been resolvated in a production-size sigma blade mixer.[7] Therefore, additional studies are required on the various propellants (single-, double-, and triple-base) to determine optimum particle size requirements. If propellant particles that pass a 12-mesh screen are required for the resolvation of the various propellants, either the grinding time can be increased to obtain the smaller particles and reduce fouling of the grinder screen or screening operations following grinding can be optimized to obtain correct propellant particle sizes.

The optimal propellant particle size requirement was not established for solvent extraction of selected propellant ingredients. The solvent extraction studies utilized ground propellants that passed a 20-mesh screen and were retained on a 50-mesh screen.

The major drawback of the Mitts and Merrill grinder is the safety requirement of using water as the coolant for grinding[8] and the resultant excess surface moisture on the ground propellant. However, previous laboratory studies of various coolant media for grinding (100% water, 50%

water/50% ethanol, and 100% ethanol) at various temperatures (hot and cold) showed minimal ingredient losses with water as the coolant.[1] Ethanol was evaluated as a coolant because it is a common solvent for processing both single- and multi-base propellants and will not plasticize the propellants as the ether/ethanol and acetone systems; plasticization would preclude pumping of the slurry to the dewatering operations. These studies showed that 100% water as a coolant media resulted in losses, i.e., leaching, of salts and NQ. In 50% water/50% ethanol, greater salt losses along with stabilizer and NG losses occurred; however, the amount of NQ loss decreased. The least NQ loss occurred in 100% ethanol; however, the greatest losses of salts, stabilizers, and NG resulted.

Therefore, water was selected as the grinding coolant media due to minimal leaching of propellant ingredients, e.g., salts and NQ. In order for the propellant to meet final specifications, these ingredients can be added directly to a production mix whereas NG needs to be added as premix for safety reasons. The stabilizers can be added to a mix by solvating them in the ether or acetone to be added to the mix for resolvation. Water was also selected as the coolant media based on previous hazards analysis studies[6,8] and the hazards analysis performed for this project (appendix B). With water as the selected coolant media, excess surface moisture accumulates on the propellant particles due to the ground propellant being discharged from the grinder as a slurry. Excessive surface moisture interferes with subsequent processing; therefore, surface moisture must be reduced to <3% via dewatering and drying.

In previous resolvation studies conducted at RAAP[7], dewatering was effected by collecting the slurry in muslin bags to permit excess water drainage from the ground propellant. These bags were then stored in the water-wet condition in plastic drums until the propellant could be dried for resolvation studies. During storage, significant ingredient losses occurred as a result of being stored in the water-wet condition. Several evaluations were conducted to dry the propellant, i.e., remove the surface moisture; the most acceptable method was drying the ground propellant in a FAD for 96 h at 140°F. After cooling, the propellant was manually transferred from the bags into grounded conductive plastic-lined tubs. Ethanol was then added to the tubs to reduce dust during propellant transfer from the tubs into the mixer. Additional ingredient loss, e.g., approximately 3% NG, was incurred since the propellant was stored throughout the testing period in the ethanol-wet condition.

During the bench-scale evaluations of the current study, the ground propellant was dewatered on a Sweco® Vibro-Energy separator in order to reduce the time required for drying in the FAD. This dewatering approach reduced the total drying time to 24 h. Drying ground propellant in a FAD to reduce surface moisture is advantageous in that flake propellants (M10 and M9) are currently dried in FADs, remote dumping of trays is an established operation, and no solvent vapors are present for vapor ignition. However, use of the FADs to dry ground propellant has two inherent disadvantages. The operation is labor intensive, resulting in increased costs. Furthermore, personnel would be exposed to the dust generated from transferring the dried propellant from the remotely filled drums into the mixer.

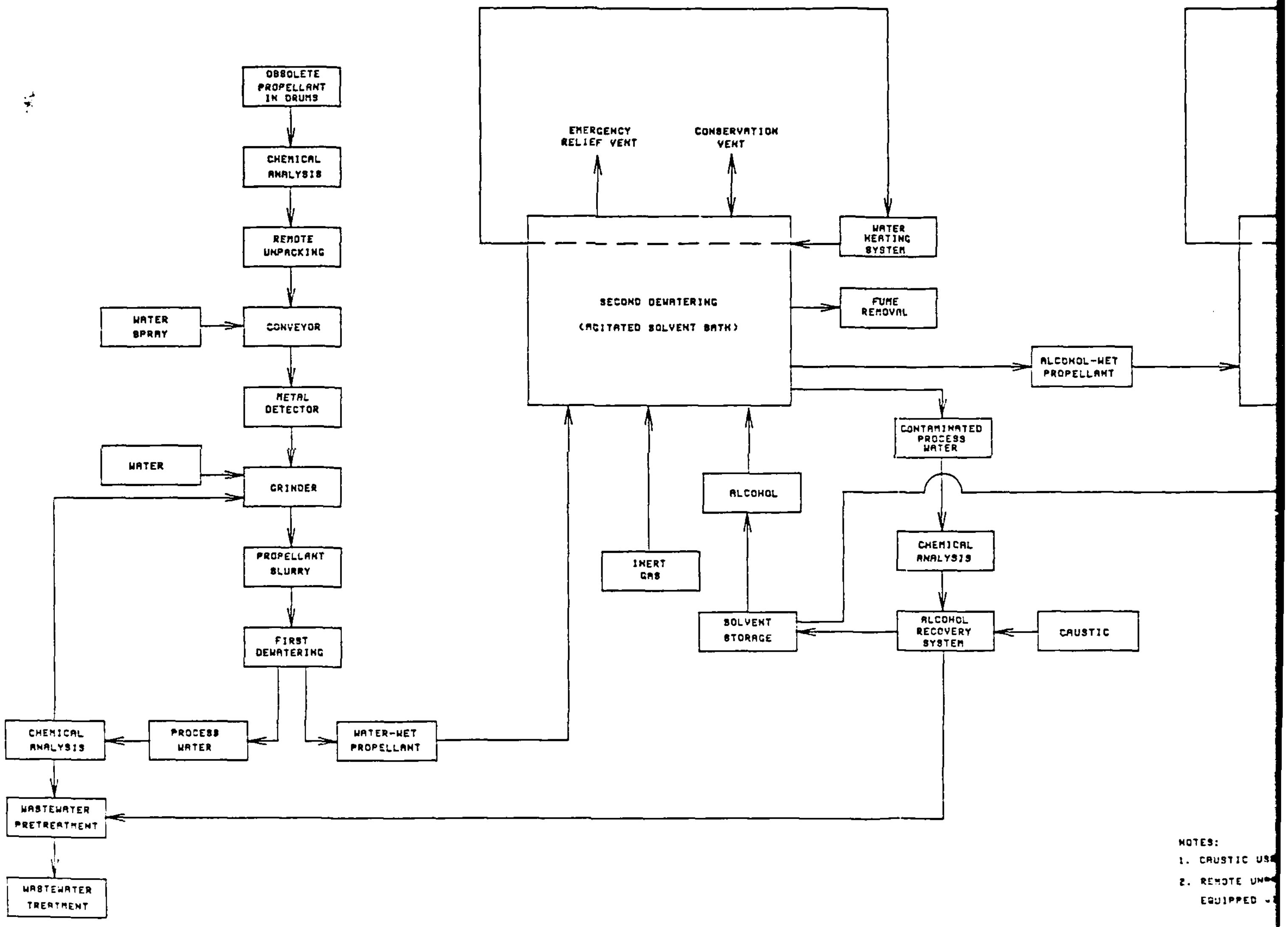
Even though potential static discharge from propellant dust has been shown to be within acceptable safety limits,[9] minimal dust generation is desirable to alleviate personnel exposure. As demonstrated in previous studies,[7] transfer of ethanol-wet propellant reduces personnel exposure to dust during handling, i.e., transfer from grounded conductive plastic-lined tubs into the mixer. The use of ethanol-wet propellant could be considered for propellant resolvation in pilot-scale studies; however, ethanol should be added immediately before the ground propellant is added to the mixer and not during storage. On the other hand, ethanol-wet propellant is undesirable for solvent extraction of propellant ingredients since the initial extraction step utilizes methylene chloride; the interaction of the two solvents would adversely affect solubility separation of the selected ingredients.

5.2 Propellant Resolvation

Pertinent operational aspects, including safety and quality considerations, were addressed in the propellant resolvation studies. The results of the bench-scale study showed that in order to obtain a processible single-base propellant mix, a 60-min cycle to permit solvent sorption is required prior to a 15-min mix cycle. Production-established solvent systems can be utilized with solvent/propellant ratios as low as 0.75/1 for single-base propellants; for multi-base propellants, the initial solvent/propellant ratios can be those optimized in the laboratory-scale study since a production line mix of ground, dried M7 propellant was successfully processed in a previous study[7] using a solvent/propellant ratio of 0.4/1.

Two significant points of departure from standard production mixes should to be considered. One is the method of contacting the ground propellant with the solvent mixture, i.e., the solvent mixture should be added to the mixer followed by an even distribution of the ground propellant. If the propellant is added to the mixer first followed by the solvents, a gelatinous layer forms on the propellant limiting solvent sorption throughout the mix. The second point of departure is that the bench-scale mixes were made with a sigma blade mixer rather than the Beken mixer which is normally used in single-base propellant production.

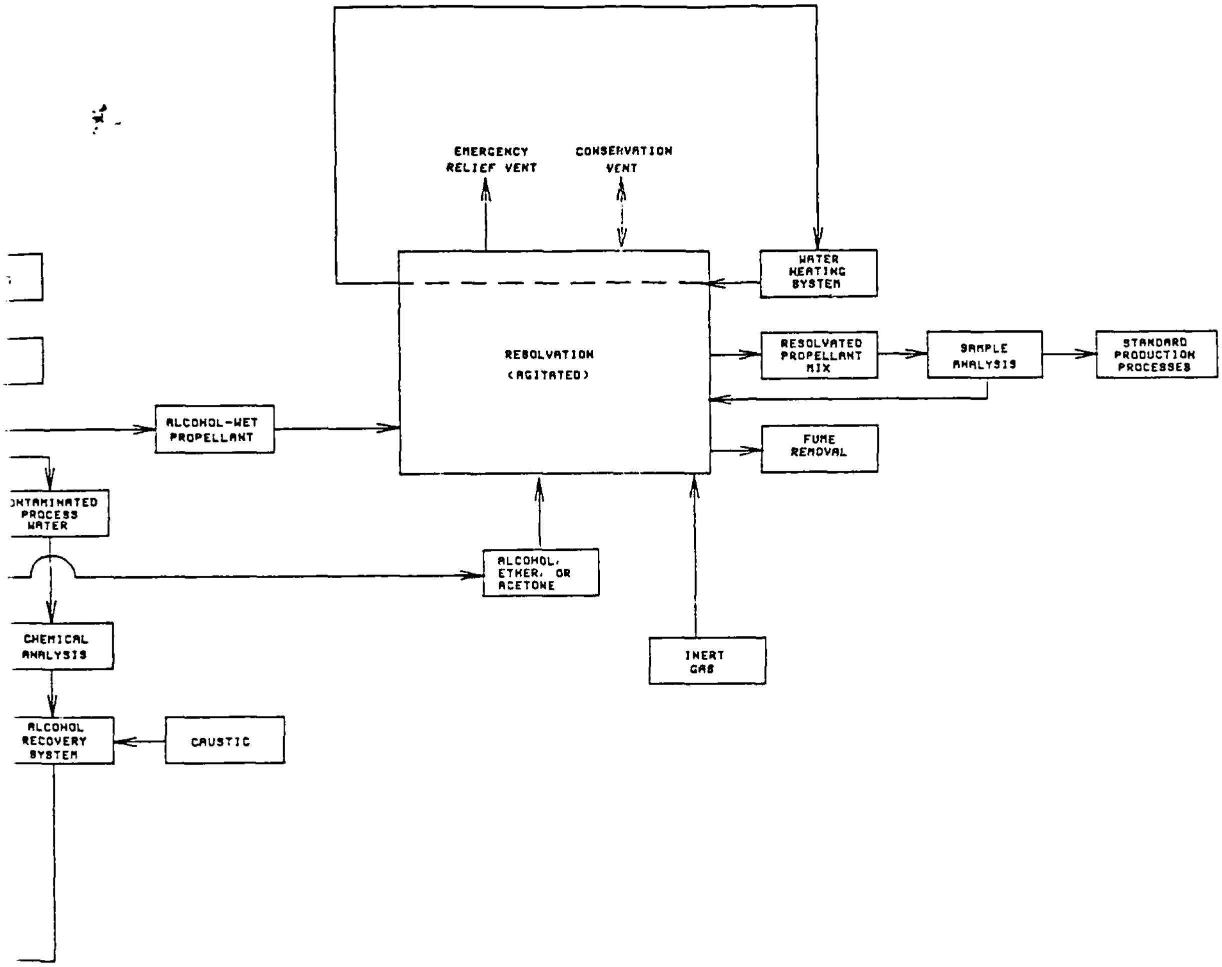
Preliminary safety design criteria for follow-on pilot plant operations were developed in the bench-scale studies; the complete hazards analysis report is presented in appendix B. Figure 81 depicts a flow diagram of the pilot-scale propellant resolvation process. Pertinent quality assurance considerations, e.g., ingredient addition at the mixer, were also addressed during the bench-scale studies in order to ensure the production of specification-grade propellant. The following design criteria information for a pilot-scale propellant resolvation process are based on the parameter constraints established from the results of the laboratory and bench-scale resolvation studies:



NOTES:
1. CAUSTIC US
2. REMOTE UN
EQUIPPED

Figure 81. Flow diagram of pilot-scale propellant resolvation process

~~2 of 2~~
1 of 2



NOTES:

1. CAUSTIC USED FOR NITROGLYCERIN DESTRUCTION.
2. REMOTE UNPACKING, SECOND DEWATERING, AND RESOLVATION OPERATIONS EQUIPPED WITH FIRE SUPPRESSION SYSTEMS.

f pilot-scale propellant
ocess

2 of 2

1. Single-base propellant particles passing an 8-mesh screen were determined to be the optimum size for resolvation in the bench-scale studies; however, additional testing should be conducted to determine if this particle size is the optimal particle size requirement for multi-base propellants.

2. The production-established solvent/solvent ratios adequately resolvated both single- and multi-base propellants.

3. A solvent/propellant ratio ranging between 0.70/1 to 0.75/1 proved optimal for single-base propellants; the solvent/propellant ratios established in the laboratory-scale resolvation studies should be used as a point of departure to define the optimal ratios for multi-base propellants.

4. A 1-h sorption cycle is required for single-base propellants; the length of the sorption cycle for multi-base propellants must be established.

5. A 15-min mixing cycle is required for single-base propellants; the length of the mixing cycle for multi-base propellants must be established.

6. The necessity and required length of the drying cycle times (required to remove the excess solvent from over-solvated propellant following mixing) must be established for the production of specification-grade products.

7. Following resolvation, standard production operations established for the formulation-specific propellant should be utilized to produce a finished product.

8. The existing hazards analyses (appendixes A and B) must be upgraded for pilot-scale evaluations. All equipment and operating procedures must also be reviewed by the RAAP Hazards Analysis Department for each propellant to be evaluated. Safety-related considerations requiring additional evaluation include remote materials handling, equipment and facility clean-up, and containment of potential spillage.

9. Resolvated propellant should be utilized in selected propellant formulations; proper chemical, physical, and ballistic testing should be conducted on propellants manufactured to assure specification compliance.

5.3 Solvent Extraction of Selected Ingredients

Preliminary bench-scale criteria information for solvent extraction of selected ingredients from ground propellant was based on the results of the laboratory investigations. The following design criteria information for a bench-scale solvent extraction process of propellant ingredients are based on the parameter constraints established from the results of the laboratory-scale studies:

1. Particles passing a 20-mesh screen and retained on a 50-mesh screen were utilized in the laboratory studies. Additional testing should be conducted to determine if this particle size is optimal.

2. The solvents, methylene chloride and water, used independently as described in the laboratory studies, can selectively extract the ingredients using 10 to 1 (weight-to-weight) extraction ratios (solvent/propellant) for each solvent.

3. The solvent/propellant ratio used for the extractions should be 10 to 1 (weight-to-weight).

4. Three 24-h extractions followed by combining the extracts are necessary for optimal ingredient recovery.

5. Orbital shakers were used in the laboratory studies; additional testing is required to determine bench-scale equipment.

6. The main ingredient for recovery is NC from both single- and multi-base propellants followed by NQ recovery from triple-base propellants. Quality parameters of the extracted ingredients must be established due to contamination constraints:

    a. The 13.25%N NC from single-base propellant is contaminated with graphite in certain cases, e.g., M10 single-base propellant.

    b. The 12.6%N NC from double-base propellant is contaminated with insolubles and NG.

    c. The 12.6%N NC from triple-base propellant is contaminated with insolubles, NG, and NQ; furthermore, the NQ crystals could be contaminated with other triple-base ingredients.

7. Extracted ingredients should be utilized in selected propellant formulations [i.e., NC (13.25%N) is only used in single-base propellants] and proper chemical, physical, and ballistic testing should be conducted on propellants manufactured with the reused ingredients to assure specification compliance.

8. Solvent (methylene chloride) use considerations such as conducting extractions below the lower explosive level or above the upper explosive level, equipment compatibility, personnel exposure, solvent reuse or disposal, and solvent handling should be assessed by the RAAP Hazards Analysis Department.

6.0 CONCLUSIONS

1. The percent nitrogen (%N) and viscosity of the nitrocellulose (NC) determine the solvent/solvent and solvent/propellant ratios required to properly resolvate propellant.

2. Testing of M10 propellant, which has the greatest NC content, indicate that deviation from production-established solvent/solvent ratios was not necessary.

3. Single-base propellants resolvate more readily with increased solvent/propellant ratios (i.e., greater than production-established ratios).

4. Most multi-base propellants resolvate using production-established or slightly increased solvent/propellant ratios.

5. Smaller particle sizes, which reduce the case-hardened area in the propellant, allow greater solvent penetration to soften the NC matrix, thus reducing the solvent/propellant ratios required for resolvation.

6. Obsolete or out-of-specification propellant can be successfully resolvated.

7. The results of the statistical study verified that the high-performance liquid chromatographic (HPLC) methods developed for these evaluations were equivalent, with regard to precision and accuracy, to the analytical methods delineated in MIL-STD-286B.

8. NC recovery from single-base propellants ranged from 96 to 100%; the recovered NC (13.15%N) could be used in any propellant requiring NC having this nitrogen content.

9. The maximum recovery of dinitrotoluene (DNT) in single-base propellants was ~35%; however, complete recovery of the remaining ingredients represents only ~5% of the formulation-specification ingredients.

10. NC recovery from double-base propellants averaged ~100%; however, the recovered NC (12.6%N) should only be used in the production of multi-base propellant since the NC has previously been contaminated with nitroglycerin (NG) and insolubles, e.g., carbon black and graphite.

11. NG recovery of ~80% is attainable in double-base propellants; however, only 2 to 10% of the remaining formulation-specification ingredients can be recovered.

12. Separate recoveries of NC and nitroguanidine (NQ) from triple-base propellants averaged ~88 and 82%, respectively; however, the recovered NC (12.6%N) should only be used in the production of triple-base propellant since the NC has previously been contaminated with NG and insolubles. Furthermore, the recovered NC should not be used in

the production of double-base propellant due to possible contamination by NQ.

13. Virtually 100% recovery of NG is attainable in triple-base propellants; however, only 2 to 7% of the remaining formulation-specification ingredients can be recovered.

14. Safety in handling represents the major concern in the reuse of NG recovered from the multi-base propellants.

7.0 RECOMMENDATIONS

1. Pilot-scale resolvation studies should be conducted for single-, double-, and triple-base propellant.

2. Additional grinding/screening studies should be performed to obtain propellant particles passing a 12-mesh screen to ensure adequate resolvation.

3. Alternate methods of drying of the ground propellant (other than a forced air dry (FAD) facility) for resolvation should be investigated.

4. Bench-scale solvent extraction studies to optimize the extraction of single-, double-, and triple-base propellant ingredients should be performed.

5. The HPLC methods developed under this project should be utilized to determine both ingredient addition in pilot-scale propellant resolvation studies and ingredient recovery in bench-scale solvent extraction studies.

6. Final users' specification requirements should be delineated to permit the use of obsolete or out-of-specification resolvated propellant in current military weapon systems.

8.0 REFERENCES

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APPENDIX A

Total Systems Hazards Analysis on Propellant Reuse-Recovery Technology

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Attachment

Memorandum

April 1, 1987

HI-87-M-44
Total Systems Hazards Analysis on Propellant Reuse - Recovery Technology
Report No. 1

DIGEST

Objective

The objective of this study is to conduct a Total Systems Hazards Analysis (TSHA) on propellant reuse-recovery technology from laboratory-scale investigations to the development of design criteria for pilot plant design and testing. This specific report identifies and evaluates the potential hazards to personnel and facility during (1) laboratory-scale solubility determinations of selected essential materials in different solvents and (2) extraction of selected essential materials from single- and multi-based propellants.

Summary and Conclusions

This interim safety review documents the Preliminary Hazards Analysis (PHA) of laboratory propellant resolvation studies for extraction of propellants and essential materials using selective solvents.

The planned propellant resolvation/extraction studies can be safely performed at Radford because personnel are well versed in both safety and operating procedures and small quantities (100 grams) of energetic materials are involved. Table 1 lists typical operating procedures and specific safety precautions for controlling potential hazards to personnel. These controls are applied to each step in the laboratory studies. The personnel and operational safety controls listed in Table 1 evolved from years of laboratory and propellant experience.

This hazard study is being done to fulfill partial requirements of a contract between Hercules Aerospace Company and Arthur D. Little, Inc. (ADL) who is the prime contractor for U. S. Army Toxic and Hazardous Materials Agency (USATHAMA). The total contract is identified as TASK ORDER NUMBER 7.

Recommendations

No recommendations are given for the laboratory phase of the reuse/reclamation program at this time.

Future Work

This is the initial report on the reuse and recovery technology. The remaining hazards analysis studies are outlined in Table 2.

INTRODUCTION

The military has stocks of chemically acceptable propellants which are obsolete for one reason or another. For example, the gun system may have changed and a safe and efficient method is needed to reprocess the propellant into a new configuration that can be used for a different weapon.

Also, propellants that are nonconforming to chemical and ballistic specifications are available for reclaiming/reprocessing into chemically and ballistically acceptable products.

Past practice has been to burn or detonate unneeded or unacceptable propellant. This technique requires a waiver to destroy any quantity of propellant and unnecessarily destroys reuseable material.

This hazards analysis study consists of multiple phase safety assessments. This initial effort is devoted to performing the initial PHA of laboratory-scale studies that will: (1) determine solubility of selected propellants and essential materials, (2) determine extraction capability of selected essential materials from propellants, and (3) determine resolvating and extrusion parameters. This safety review is being done as concepts are presented; no specific equipment or process design are yet available.

DISCUSSION

Methodology

The TSHA of the Propellant Reuse/Recovery Technology is being conducted using the Hercules Evaluation and Risk Control (HERC®) technique. The HERC technique is a practical method of hazards isolation, evaluation, elimination, and control; it is a formal engineering approach to quantitatively evaluate processing hazards. The basic objectives of this safety analysis program are: (1) identify hazards, (2) eliminate or control the hazard, and (3) provide system design and operating criteria. The procedures for performing the quantitative risk analysis is described in references 1 and 2 and the HERC technique fulfills the requirements for system safety specified in MPBMA OSM 385-1.

Inherent Safety Features

Radford personnel have extensive experience in the handling and testing of potentially hazardous explosives and solvents. Over the years, operating procedures have been developed to safely sample, store, process propellants and explosives for testing and dispose of small quantities of materials used to manufacture these products. The sample, preparation, and analytical laboratories used for these tests have specific operating procedures and safety features that preclude discharge to the atmosphere. Numerous examples of operating procedure controls and/or safety features are listed in Table 1. These safety controls and precautions are self-explanatory.

Laboratory Extrusion Studies

Procedures, equipment, and instrumentation to measure extrusion pressure and rate does not exist within the laboratory. It is essential that measurable data be obtained during the resolvation study for comparison with full-scale press results. The simple device shown in Figure 1 was used for an initial effort at measuring extrusion pressure and extrusion flow.

A sample of resolvated propellant was placed in the plastic extruder (syringe). The following parameters were known: (1) volume, (2) density, (3) weight, (4) total volatiles, and (5) diameter or area of nozzle.

The pressure applied to the air cylinder was measured. The time to extrude the strand and the strand length were measured. The overall pressure on the sample was calculated. This simple device allowed measurable initial attempts for quantification of extrusion results.

This type test can be safely done within the laboratory because only small volumes (~20 mL) of propellants are used and the plastic walls of the extrusion vessel will rupture prior to sufficient pressure being applied for initiation. To further improve safety, this operation is performed under a hood to reduce solvent exposure. A shield is also used for personnel protection.

WARRANTY AND DISCLAIMER

Within the scope of work, Hercules warrants that it has exercised its best efforts in performing the hazards analysis reported herein, but specifically disclaims any warranty, expressed or implied, that hazards or accidents will be completely eliminated or that any particular standard or criterion of hazard or accident elimination has been achieved.

MAH:bpw

Attachments

REFERENCES

[1] HERC® Engineering Analysis Manual, Edition 1, Hercules Incorporated, Allegany Ballistics Laboratory, HERC No. 73-116, December 1973, Hercules Proprietary.

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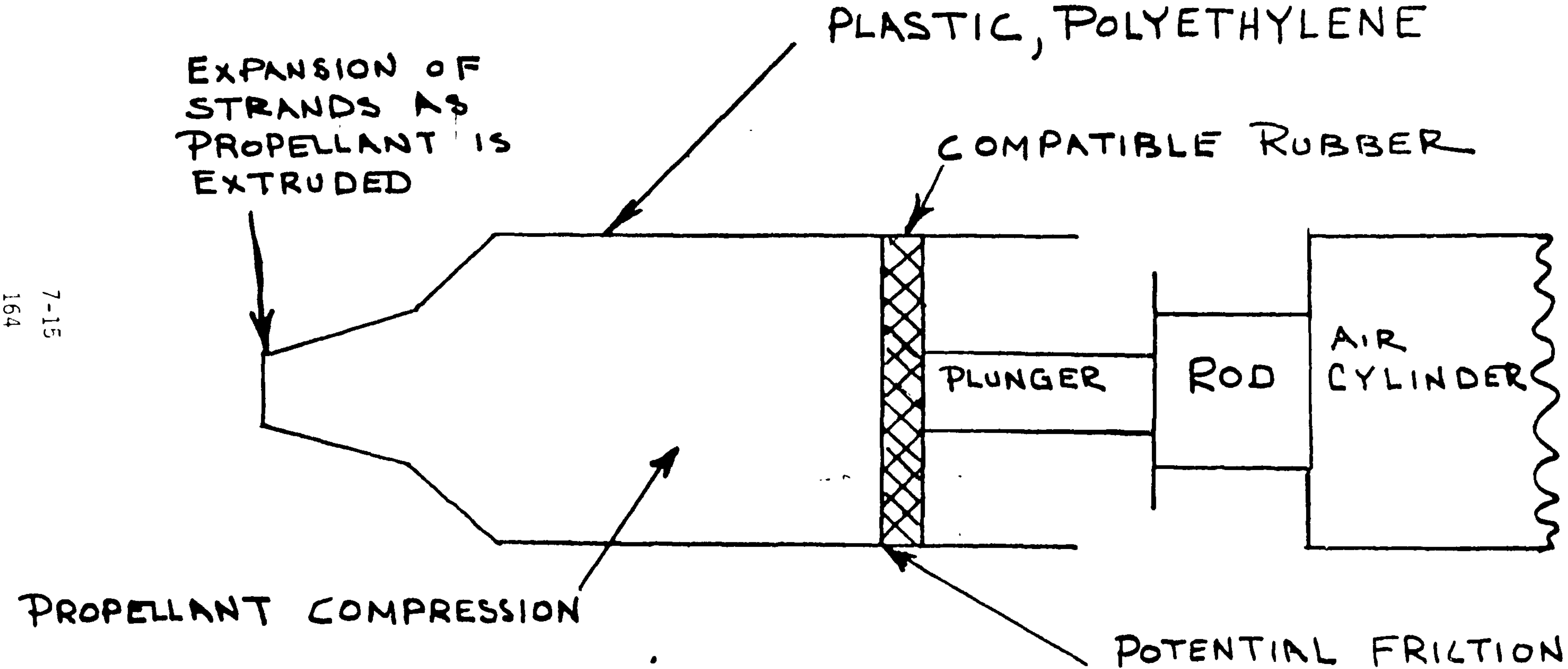

Figure 1

Laboratory Scale Propellant Extruder

Table 1

Preliminary Hazards Analysis

Item Reviewed	Potential Problem Area	Existing Safety Design Features	Recommendations for Improving Safety	Applicable Documentation	Building
Propellant Storage					
1. Proper Propellant Identification	Use of incorrect propellant in evaluation	Each sample in storage area arrives from Finishing Area with full identification	None	GOP 4-20-10 GOP 4-20-28	7105 or 7108
		Internal documentation from engineering provides standard propellant lot numbers for tests.	None	PEI-ADL-7-2 and PEI-ADL-7-1	
		Storage personnel verify that correct lot is in storage by comparison of propellant identification against PEI documents.			
		Fire protection provided for samples.			
2. Storage	Propellant initiation	Stored at ambient temperature.	None		7105 or 7108
		Absence of credible initiation stimuli.			
		Fire protection (red head) for storage area.			
		Minimum quantity of propellant stored in building.			
		Approved procedure for storage and disposal of samples.		GOP-4-A-5 GOP-4-18-49A GOP-4-18-1A GOP-4-18-41A	7105 or 7108
3. Propellant Sample Preparation	Use of incorrect propellant samples	See safety features listed in No. 1 above.	None	PEI-ADL-7-1 PEI-ADL-7-2	7105
	Initiation of propellant during grinding	Approved procedure for Grinding of *Propellant Samples.*	None	UOP-4-18-6A	3739
		Small sample (≤10 grams) ground at a time.		UOP-4-18-6A	3739
		Extra personnel safety equipment required when grinding propellant with Wiley Mill.		UOP-4-18-6A	3739
		Only one grinding operation performed at one time.		UOP-4-18-6A	3739

Table 1 (cont)

Item Reviewed	Potential Problem Area	Existing Safety Design Features	Recommendations for Improving Safety	Applicable Documentation	Building
Propellant Storage (cont)					
3. Propellant Sample Preparation (cont)	Initiation of propellant during grinding (cont)	10 grams is maximum amount of propellant that is allowed to accumulate.		UOP-4-18-6A	3739
		Mill fed propellant by wooden or plastic probe to protect fingers.		UOP-4-18-6A	3739
		Fire protection provided for area.			
	Frictional initiation during sample screening	*10 grams screened at at time.		UOP-4-18-6A	3739
		Fire protection (Redhead) provided for area.			
		Extra personnel safety equipment required for screening-(Nitrometer face shield and long cuff cotton gloves).		UOP-4-18-6A	3739
	Ignition of sample after screening	Small samples handled.		UOP-4-18-6A	3739
		Fire protection provided (Redhead)			
		Absence of credible ignition stimuli.			
	Ignition of propellant during equipment clean up	Small quantities of propellant-gram quantities.		UOP-4-18-6A GOP-4-18-1A	3739
		Fire protection provided (Redhead)			
		Equipment is cleaned after <u>each</u> sample is processed.		UOP-4-18-6A	3739
		Wiley Mill <u>LOCKED</u> off during clean up.		UOP-4-18-6A	3739
		Waste propellants disposed of according to approved procedures.		GOP-4-18-1A GOP-4-18-42A GOP-4-18-43A	3739
Propellant Transfer					
4. Propellant Identification for Transfer to Laboratory	Incorrect propellant sample used for testing	See safety features in No. 1 above.	None	PEI-ADL-7-1 PEI-ADL-7-2	
		Quality Control documents identify which sample to deliver.		PEI-ADL-7-1 PEI-ADL-7-2	

Table 1 (cont)

Item Reviewed	Potential Problem Area	Existing Safety Design Features	Recommendations for Improving Safety	Applicable Documentation	Building
Propellant Transfer (cont)					
5. Sample Transfer by Quality Control	Propellant initiation	Small quantity of material in sample (100 grams).			
		Approved procedures for sample pickup and delivery.		GOP-4-20-1 GOP-4-20-10 GOP-4-20-11 GOP-4-20-28	Sample transported in specially equipped trucks
		Samples carried in special containers.			
		Absence of credible ignition stimuli-sample vehicle travels very slow.			
		Samples segregated during transportation.			
6. Sample Arrival at Appropriate Laboratory	Incorrect propellant sample left by Quality Control for tests	Approved procedure for acceptance of laboratory sample from Quality Control.		L-6 GOP-4-19-28 GOP-4-19-50 GOP-4-20-10 GOP-4-20-12	201
		Instructions on sample specify individual to receive sample.		PEI-ADL-7-1 PEI-ADL-7-2	201
		Sample cross-checked by receiver at laboratory.		PEI-ADL-7-1 PEI-ADL-7-2	201
Laboratory Storage					
7. Laboratory Storage of Propellant Samples	Propellant ignition	Small sample stored in building.			
		Fire protection (Redhead) for storage area.			
		Credible ignition stimuli lacking.			
	Incorrect sample used for testing	Samples identified and cross-checked before start of analysis.		PEI-ADL-7-1 PEI-ADL-7-2 RA-271	201
8. Laboratory Analysis Laboratory Scale I and II Tests	Personnel protection	Approved test procedures prepared and approved by appropriate supervision.		Technical Analytical Book - Book 1 TIP T-20 TIP T-21	201

Table 1 (cont)

Item Reviewed	Potential Problem Area	Existing Safety Design Features	Recommendations for Improving Safety	Applicable Documentation	Building
Laboratory Storage (cont)					
8. Laboratory Analysis Laboratory Scale I and II Tests	Personnel protection (cont)	Small quantities of propellant used for testing (<100 grams per test).		PEI-ADL-7-1 PEI-ADL-7-2	201
		Procedures available for handling the solvents used in tests.		L-6	201
		Procedures available for sampling and handling the essential materials that are tested.		UOP-4-20-4 GOP-4-20-20 UOP-4-20-21	3024 3026
		Procedure forbids sampling Nitroglycerin.		PEI-ADL-7-1	
		Small volume of solvents, propellant and essential materials used for solvent extraction test (100 gm solids and 100 mL liquid).		L-6	201
		Fume hoods used for reduction of fume exposure.		L-6	201
		Approved disposal methods for samples.			201
	Propellant/solvent ignition	Small volume of solvent (100 mL) and propellant weight in grams used.		L-6	201
		Absence of credible initiation stimuli.			201
		Many samples analyzed by instrument and concentration is in ppm range.		Applicable instrument operating instructions	201
	Personnel exposure to potentially harmful solvents in laboratory	Work performed under approved safety hoods.		L-6	201
		Small volume of solvents (<100 mL).		L-6	201
		Use of hazardous solvents and materials are under control of Plant Toxicity Board.		Management Manual Committee Charter No. 16	201

Table 1 (cont)

Item Reviewed	Potential Problem Area	Existing Safety Design Features	Recommendations for Improving Safety	Applicable Documentation	Building
9. Propellant Extrusion	Propellant ignition during sample extrusion	Small quantity (20 grams) extruded at a time.		TLP-T-20	201
		Extrusion takes place behind a shield.		TLP-T-20	201
		Extrusion device constructed of plastic and ruptures easily.		TLP-T-20	201
		Procedure available to control extrusion.		TLP-T-20	201
		Propellant samples are not allowed to dry prior to extrusion.		TLP-T-20	201
		Extrusion is done under a hood behind a shield.		TLP-T-20	201
10. Sample Disposal	Ignition of propellant sample/solvent after test completion	Absence of ignition stimuli.			
		Waste propellant samples are stored under a water blanket until incinerated.		GOP-4-19-28 GOP-4-19-49	201
		Solvent samples are absorbed in sawdust and incinerated.		L-6	201
		Samples are kept segregated and in special containers.		GOP-4-A-5	201 and Incineration
		Waste samples incinerated on a regular schedule.		GOP-4-A-5 GOP-4-A-25 GOP-4-1-1 GOP-4-3-1 GOP-4-3-2H GOP-4-3-4 UOP-4-3-4A	201 and Incineration

Table 2

Schedule for Hazards Analysis Events

Event	Time 1987								
	April	May	June	July	Aug	Sept	Oct	Nov	Dec
1. Completion of PHA on Laboratory Scale Reuse/ Reclamation Technology	▲								
2. Repair of 2.5 Gallon Mixer (by others)	△		▲						
3. Risk Assessment of 2.5 Gallon Mixer for Single-Base Use	△					▲			
4. Procedure Review for 2.5 Gallon Mixer	△			▲					
5. Submit Safety/Design Criteria for a Pilot Plant to Reclaim/Reuse Single-Base Propellant					△			▲	
6. Final Report							△	▲	

△ = Start

▲ = Completion

APPENDIX B

Hazards Analysis of Equipment, Procedures, and Operations Planned for a Reclamation Process for the Recovery of Obsolete Cannon Propellant

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HI-87-M-125
Hazards Analysis of Equipment, Procedures, and Operations Planned for a Reclamation Process for the Recovery of Obsolete Cannon Propellants

DIGEST

Objective

The objective of this study is to perform a Total Systems Hazards Analysis (TSHA) of equipment, procedures and operations planned for a reclamation process for the recovery of obsolete cannon propellants. This study was conducted to ensure safety to personnel and facility and to determine compliance with safety risk requirements of Army safety document MPBMA OSM 385-1.

Summary and Conclusions

This final report documents the TSHA performed of equipment, procedures, and operations planned for reclamation of obsolete cannon propellants. Planned operations from storage through finished propellant operations were subjected to an engineering risk assessment. These assessments were extracted from previous reports where applicable and updated if required. Appropriate analyses were performed on equipment and/or procedure changes made in these particular operations.

Upon implementation of the study recommendations in Table 1, the planned propellant grinding (size reduction), resolvating, and extrusion of reused M1 propellant can be safely performed. The overall risk to personnel and facility will then conform to Army safety requirement MPBMA OSM 385-1 as shown in Table 2.

Safety design criteria are provided for the design of a pilot plant to reclaim cannon propellants.

Any changes to the system design or operations as planned to date will invalidate the findings of this study and require reassessment.

Recommendations

Recommendations to eliminate and/or control real or potential hazards to acceptable levels are listed in Table 1.

Future Work

Table 3 outlines the initial Hazards Analysis effort for the single-base propellant reclamation project. Procedure reviews and completion of an Operating Hazards Analysis (OHA) of dry-run reclamation operations have been done.

INTRODUCTION

The military has stocks of acceptable propellants which are obsolete for one reason or another. For example, the gun system may have changed and a safe and efficient method is needed to recover and reprocess the propellant for a different weapon. Also, propellants that are nonconforming to ballistic specifications are available for reclaiming into chemically and ballistically acceptable products.

Past practice has been to burn or detonate unneeded or nonconforming propellant. This technique unnecessarily destroys reuseable material.

This hazards analysis study consists of multiple-phase safety assessments. The initial phase was a Preliminary Hazards Analysis (PHA) of laboratory scale studies to determine (1) the solubility of selected propellants, (2) extraction capability, and (3) resolvating and extrusion parameters. This report documents the quantitative assessments of equipment and operations planned for reclamation process for recovery of obsolete cannon propellants from initial storage through size reduction, resolvating, extrusion, cutting, drying, and storage.

DISCUSSION

The following sections discuss the methodology and material response data used to risk assess the equipment, procedures and operations planned for reclaiming obsolete cannon propellants.

Methodology

This safety assessment used the Hercules-developed Hazards Evaluation and Risk Control (HERC®) safety technique[1,2] to quantitatively assess the risk potential for injury to personnel or facility damage to equipment, procedures, and operations planned for a reclamation project that will recover obsolete cannon propellants. This study will use existing plant equipment and procedures to transport, grind (size reduction) and cut the finished propellant. The HERC® technique permits identification and quantitative assessment of in-process energies for starting fires or explosions when applied to propellant during handling and processing. For this study, in-process energies are compared to M1 propellant material initiation data to establish safety margins and determine the probability (risk) for fire, explosion, or personnel injury during the recovery of obsolete cannon propellants. Requirements for operational safety risk levels are defined in Army safety document MPBMA OSM 385-1 for four hazard levels in terms of risk to personnel and facility.[3] Unacceptable risks are eliminated or controlled to acceptable levels by engineering changes to equipment and/or facilities or by procedural changes as feasible.

The Hazards Analysis techniques used during this study to identify, eliminate, or control hazards are the PHA and engineering risk assessment. An Operating Hazards Analysis (OHA) was performed during the dry-run reclamation process when equipment, procedures and operating conditions were safety assessed. Table 3 indicates when each task is done.

Preliminary Hazards Analysis

The PHA qualitatively identifies potential hazards during concept and design stages when it is most economical to make changes. References 4-7 are examples of PHA's performed previously on equipment planned for propellant reclamation.

Engineering Risk Assessment

The engineering analyses quantitatively assesses the probability of potentially hazardous events identified and assigns an accident severity level as shown in Appendix A. This assessment is used to quantify potential hazards identified during the PHA and the OHA and assures that an acceptable risk is achieved in accordance with MPBMA OSM 385-1. The process flow in the reclamation program is briefly described in Appendix B and is depicted in Figure 1. The engineering risk assessment is followed by the OHA. The OHA is explained after an explanation of what frequencies, events, and material present columns in Table 4 represent.

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Value assignment and calculations of frequencies, event, and material present probabilities in support of the line items of Table 4 are shown in Appendix C.

Operating Hazards Analysis

This safety technique assesses humans as a potential contributor of initiation into the system analysis; it combines operating procedures and equipment to determine where human error can occur and attempts to evaluate the consequences of such error.

Material Response

Background

An important aspect of any hazards investigation is to define the initiation and explosive characteristics of the propellant physical and chemical states present. This testing has been done for the various process mixtures of M1 propellant as shown in Table 5. As can be seen by reference to Table 5, M1 propellant is not unduly sensitive to mechanical impact and friction stimuli.

Fine particles of M1 are sensitive to Electrostatic Discharge (ESD), see Table 5, but the reclamation project is designed to minimize the generation of fines.

M1 propellant does not react readily to flame initiation (Critical Height) and shock (Critical Diameter) but a brief explanation of each test is needed. Critical Height to Explosion (C_{he}) tests are performed to define the susceptibility of a material to transit from a burning to an explosion reaction once initiation has occurred. The Critical Diameter Test (C_D) for explosive propagation determines a material's susceptibility to propagate an explosive reaction. Again, a double-base propellant is provided for comparison of the two propellants. The data in Table 5 indicates that the M1 should not transit from a burning to an explosive reaction in the planned operations of this reclamation project. The data indicates that the M1 can propagate an explosive reaction, if confined. Confinement necessary for the propagation was not identified in the equipment to be used.

Hazards Analysis

1. Removal from Storage

The hazards analysis was performed starting with movement of the propellant from the New River Storage Area, see Figure 1, and is completed upon chemical, physical, and ballistic testing after the M1 propellant has been processed through the Finishing Area. Obsolete propellant that will be used for this study must be removed from storage, transported to Radford, and stored until it can be passed through the size reduction operation just as if the propellant were to be incinerated.

2. Grinding and Dewatering

Radford has a long and safe history of grinding waste propellant for incineration. References 8-10 are Hazards Analysis reports that discuss why this operation is safe. However, briefly stated, this operation is safe because the propellant is ground in the presence of copious volumes of water and water flow failure automatically deactivates the grinder. Minor fires have occurred during propellant grinding without consequence or facility damage. Pump casings and impellers are lined with energy-absorbing rubber to reduce propellant initiation by mechanical stimuli during movement.

The propellant recovery process makes use of the SWECO system to dewater ground propellant. This system can be safely used, see Table 4, but is not the updated SWECO normally associated with propellant screening. The SWECO at the Incinerator has a metal tie down in the center of the screen. The tie down provides unnecessary metal-to-metal friction and impact points. This deficiency has been controlled by "potting" the entire area around the tie down. Periodic reexaminations are needed to assure that the "potting" has not deteriorated. Also, piece marks should be aligned on the SWECO frame, where they can be easily seen, in order to detect slippage which can lead to excessive friction. The volume of water present in this equipment will be sufficient to inhibit a sustained propellant burning reaction.

The SWECO separator equipment design and operations are not ready for use; pumps and parts need replacement. Current procedures and training are not up-to-date. These items must receive attention prior to starting propellant grinding and screening.

If a SWECO is to be used in the pilot operation, the hollow ring holding the screen should be replaced with a solid ring. The hollow ring could fill with propellant fines during extended use and present a propellant confinement hazard.

Capability exists to spill contaminated water and propellant on the scales and floor around the SWECO. Spillage provides two potential hazards: (1) personnel exposure during cleanup and (2) capability to contaminate area outside the building since the water can flow outside. Provisions must be made, before operations, to contain any spillage within the building.

3. Propellant Traying and Drying

Normal practice after propellant grinding is incineration. However, in the reclamation project, the propellant will be trayed or bagged after it has been dewatered by the SWECO. The ground propellant will have excess surface moisture (≈1% moisture) removed in a Forced Air Dry (FAD) building.

Risk assessment of potential friction, impact, electrostatics and thermal energies associated with both manual and equipment operations, as related to planned drying were assessed. Examples of operations/equipment subjected to risk analysis were:

1. Operation of the SWECO Separator.

2. Manual traying or bagging of ground propellant.

3. Manual handling and equipment movement in FAD operations such as:

    a. Opening FAD doors--impact and friction.

    b. Temperature controller operation.

    c. Buggies passing over spilled propellant.

    d. ESD.

These operations were assessed to be acceptably safe, see Table 2 for a summary of the data and refer to Table 4 for complete details on the risk assessment.

4. Resolvating and Remixing

Small samples of ground, dried M1 propellant will be brought to Building 3677, C-9 Mix House, for resolvating and mixing in the 2.5-Gallon Mixer. Approximately three pounds of the ground M1 will be placed into the mixer and approximately four pounds of alcohol and ether added for resolvation. This operation has several potential hazards that merit discussion and these individual events are discussed in the following paragraphs.

5. Baker-Perkins 2.5-Gallon Mixer

This equipment has been subjected to several hazard assessments.[4-7] Each of these safety reviews outlined work required to allow the processing of multi-base or high-energy propellants. In Reference 7 are all the recommendations that have been made that will allow the mixer to be used for processing multi-base and high-energy propellants. However, this study is directed toward using the mixer for M1 single-base propellant only. Those recommendations that are applicable to single-base have been extracted from Reference 7 and are included in Table 1 with a note on status.

a. Propellant Contamination

The Baker-Perkins 2.5-Gallon Mixer was not designed as a production propellant mixer. It has open gears for spilled propellant to fall into, dry, and to be easily ignited by the rotating gears. The mixer was built prior to Occupational Safety and Health Administration

(OSHA) regulations; an open rotating shaft serves as a point for potentially igniting spilled propellant and as a hand hazard. If operated as designed, the system has an unacceptable probability of 2.5×10^{-4}/h for an incident. The gears and shaft are now protected from propellant contamination by covers. Once these covers are in place and the operating procedure requires effective housekeeping (current procedure is deficient in this area) the probability for an accident falls to an acceptable 2.5×10^{-10}/h, see numbers 71 and 72 of Table 4.

Another potential thermal initiation hazard exists from propellant getting into the mixer glands. The glands are not typical mixer glands in use at Radford. Maintenance records do not identify the packing or the last time the glands were refurbished.[11] Calculations were made, see Appendix D, that show the ability of the glands, if tightened excessively, to ignite propellant. Therefore, the glands were inspected and replaced before the reclamation project began and a work order (700139) accomplished this task. When this repair work has been completed there is an acceptable probability of 3×10^{-8}/h for an incident, see Table 4 number 62.

b. Volatile Vapor Ignition

The electric motor that drives the 2.5-Gallon Mixer is rated for Class I, Group D vapors. Both diethyl ether and alcohol are required during resolvation and the motor is not rated for ether. This need not disqualify the motor for use, however. Currently, the motor has a modified purge which does not work effectively, see Figure 2. Changes were made to the system as follows:

> The sheet metal pipe was capped at the cut shown on Figure 2; air from the plant system is applied directly against the motor end and forced out at the other end. Measurements and calculations show a minimum of 94 cubic feet per minute of air passing over the motor. The bay volume is in excess of 4,680 cubic feet, see Appendix E. The bay fumes are removed by an air driven eductor at approximately 1,560 cubic feet per minute or a complete air change about every five minutes.
>
> The flammability limit for the solvent system is[12] 1.9 to 36% by volume.
>
> Calculations show a volume of 0.064 cubic feet per minute, see Appendix E, of solvents being released. Thus, it can be seen that the evaporated solvents released in the bay are considerably below the flammability limits.

The air purge for the electric motor is not a complete Type X purge as required by the National Fire Code. Power is cut off on purge loss. However, no time delay exists to electronically assure the required volume of purge air passes past the electric motor. However, the amount of purge air passed is sufficient because procedures require the purge to be started during initial equipment checkout and sufficient air volume will have passed the motor before the current is applied.

The probability of this system malfunctioning and causing an incident is an acceptable 1 x 10^{-10} per operating hour, see Table 4, number 59.

6. Extrusion and Cutting Resolvated Propellant

a. General

By reference to Figure 1, it can be seen that small quantities of M1 made in the 2.5-Gallon Mixer will be extruded using the four-inch press; normal practice is to use the 12-inch press for extruding single-base propellants. Another difference is the absence of the preblock step. Both actions are being taken because the quantity of material produced in the 2.5-Gallon Mixer is small, approximately four pounds of propellant per mix.

Personnel and facility are protected during the extrusion of propellant from the press. Operation is remote, blow-out panels relieve bay pressure, and fire protection exists. Inert gas is used to inhibit the potential for adiabatic initiation hazard (during ram insertion and withdrawal). Several abnormal events could lead to an incident with the press and are worthy of discussion.

b. Frictional Heating

It has been demonstrated that grit in propellant (foreign material) can cause ignition at low velocity by friction between steel and Delrin.[13] The probability for an incident with the four-inch press is an unacceptable 5 x 10^{-4}/h, if foreign material is present, see Table 4, number 80. Without the foreign material present, the probability for an incident is an acceptable <1 x 10^{-10}/h, see Table 4, number 79. Thus, it is imperative that the mix be free of foreign material. The M1 is passed through a metal detector prior to grinding and is hand loaded into and out of the mixer. Since the resolvated propellant is also hand loaded into the four-inch press, any foreign material should be detected and removed before extrusion.

c. Compressional Heating

Compressional heating of air bubbles during propellant extrusion has been suspected as a potential initiation source. Using the computer model for a 12-inch press, resulted in a three-inch diameter bubble raising the temperature to about 149°C,[14] which is near the M1 initiation point. However, a three-inch diameter bubble is not expected since the material will be hand loaded into the four-inch press.

d. Impact Initiation

The potential for an impact initiation hazard due to an out-of-alignment ram head impacting propellant on the basket top could easily cause initiation. Such an event provided an unacceptable risk of 5×10^{-4}/h, see Table 4, number 83.

Procedures require observation to assure that alignment does exist and it will be easy to wipe off any excess propellant after loading. With these events controlled, an acceptable probability of 5×10^{-9}/h exists, see Table 4, number 82.

7. Cutting, Solvent Recovery, and Water Dry

These are standard operations; the only difference is the smaller quantity of M1 propellant involved. These events have been assessed previously and assessed to be safe.[15]

Safety Design Criteria for Design and Operation of a Pilot Plant for Obsolete Cannon Propellant Recovery

One of the safety objectives of this small-scale study is to provide safety design criteria for a pilot plant capable of reclaiming several thousand pounds of propellant per day. Although this specific study was directed toward single-base propellant, the pilot plant would need to process multi-base to be economically feasible.

Shown in Figure 3 is a simplified flow sheet for the reclamation of propellant.[16] Based on this concept, the guidelines in Table 6 were formulated.

MAH:bpw

Attachments

REFERENCES

[1] HERC® Engineering Analysis Manual, Edition 1, Hercules Incorporated, Allegany Ballistics Laboratory, HERC No. 73-116, December 1973, Hercules Proprietary.

[2] HERC® Risk Analysis Manual, Edition 1, Hercules Incorporated, HERC No. 75-79, October 1975, Hercules Proprietary.

[3] Safety Program for Modernization and Expansion System projects, 12 May 1980. MPBMA OSM 385-1.

[4] J. R. Murray, "Hazards Analysis of the 2.5-Gallon Baker-Perkins Mixer (Building 3677)," HI-75-M-1, March 6, 1975.

[5] J. R. Murray, "Hazards Analysis of the Baker-Perkins 2.5-Gallon Mixer," HI-75-M-2, June 12, 1975.

[6] M. A. Hundley, "Safety Review of the Baker-Perkins 2.5-Gallon Mixer Facility," HA-80-M-50, October 3, 1980.

[7] T. W. Ewing, "Updated Hazards Analysis Study of the 2.5-Gallon Baker-Perkins Mixer," HI-86-M-103, November 6, 1986.

[8] M. L. Griffith, "Hazards Analysis Evaluation of the Proposed Methods of Incinerating Liquid Explosive Waste," November 7, 1978, HA-78-27-M.

[9] H. W. Carter, "Hazards Analysis Study of the Automated Incinerator Facility - Report No. 1," February 24, 1972, HI-72-M-1.

[10] M. L. Griffith, "Risk Analysis of Grinding and Dewatering of Some Propellants and TNT Based Explosives," HA-81-R-8, June 12, 1981.

[11] Review of Records by Maintenance Personnel, July 1987.

[12] Fire Protection Guide on Hazardous Materials, Fourth Edition, 1972.

[13] Investigation of a Press Fire During Extrusion of M31A1 Triple-Base Propellant, October 2, 1985.

[14] G. A. Insley, Calculation of Bubble Temperature, July 30, 1987.

[15] R. L. Asbury, J. L. Evans, "Production Engineering Project PE-406," July 1977.

[16] M. A. Hundley, "Hazards Analysis Review of Propellant Reuse Technology," HI-86-M-24, February 28, 1986.

Table 1

Safety Recommendations That Resulted From This Safety Assessment

Item or Process	Recommendation	Safety Benefit	M or S[a]	Authority	Status
Incinerator	1. Reinspect and replace, if necessary, all potting on SWECO separator.	Reduce metal-to-metal impact and friction initiation potential.	M	Standard Safety Practice	
	2. Align piece marks on SWECO frame, if required.	Misaligned marks will notify operator of potential hazard.	M	Standard Safety Practice	
	3. Provide method to reduce contamination of scale and area around SWECO and to retain contaminated material in the building.	Reduce personnel exposure during clean-up.	M	Standard Safety Practice	
Mixing and Resolvation	4. Inspect/repair mixer glands prior to mixing resolvated MI.	Reduce potential for thermal initiation.	M	Standard Safety Practice	Completed
	5. Repair air purge system for electric motor.	Reduce potential for vapor flash.	M	Hazards Analysis Study	Completed
	6.[b] Install energy-absorbing, compatible plastic cushions on the steel anvils at the mixer bowl tilt and rest positions.	Minimize the risk of metal/metal impact initiation of combustibles.	M	Hazards Analysis Study	Completed
	7.[b] Shield or enclose mixer drive gears from ingredient or propellant mix contamination. Note: It is suggested that air purge of the enclosures be considered.	Preclude contamination of gears with combustibles and minimize chance for propellant initiation.	M	Hazards Analysis Study	Completed
	8.[b] Replace metal lid and pan with conductive plastic ones.	Minimize risk of dropping lid or pan during mixing operations and propellant propellant initiation by metal/metal impact or friction.	M	Hazards Analysis Study	Lid contact points "potted" with compatible plastic. Lid is equipped with a ground wire.

---

[a] M-mandatory recommendation, S=suggested recommendation.

[b] See Reference 7.

Table 1 (cont)

Item or Process	Recommendation	Safety Benefit	M or S[a]	Authority	Status
	9.[b] Upgrade condition of bay to meet plant requirements.	Facilitate cleaning of bay. Preclude accumulation of explosives in cracks and possible fire during subsequent maintenance operations.	M	Standard Safety Practice	To be implemented.
	10.[b] Provide funnel to direct propellant dumped from mixer into receiver.	Minimize the potential for contamination of the bay floor.	M	Standard Safety Practice	
	Note: A grounded, conductive, compatible plastic funnel is suitable for all types of receivers (tubs, drums, etc.) and is recommended. A grounded, non-sparking, metal (Al or other) funnel is acceptable if plastic tubs are used as receivers.				
	11.[b] Provide drip pans beneath glands/slinger rings to catch propellant and/or solvents passing through mixer glands.	Facilitate cleanup of mixer. Minimize accumulation of combustibles or solvents on bay floor.	M	Standard Safety Practice	Will be done.
	12.[b] Mount inert gas supply more securely. Also design to be remotely operated.	Preclude risk of metal distributor falling into mixer and causing a fire.	M	Standard Safety Practice	Metal wand has been replaced with a plastic wand with clamps.
	13.[b] Pot exposed threaded fasteners.	Minimize thread contamination with combustibles and possible personnel injury during maintenance operations.	M	Standard Safety Practice	Completed
	14.[b] Provide guard on exposed 11.5-inch long portion of rotating shaft.	Reduce potential for personnel injury.	M	Standard Safety Practice	Shield installed.

---

[a] M-mandatory recommendation, S-suggested recommendation.

[b] See Reference 7.

Table 1 (cont)

Item or Process		Recommendation	Safety Benefit	M or S[a]	Authority	Status
	15.[b]	Restrict mixer to use of Class I, Group D solvents. Alternative No. 1 Upgrade existing motor fresh air purge system to meet the National Electric Code (NFPA). Alternative No. 2 Replace existing motor and fresh air purge system with motor rated for Class I, Groups C and D, and Class II, Groups E, F and G.	Preclude initiation of solvent vapors by the drive motor.	M	Standard Safety Practice	Installed modified purge on Class D motor. Have not been able to buy group C motor small enough to fit mixer and single-base propellant requires use of group C solvents.
Procedures	16.	Revise/update or prepare detailed operating procedures for: A. SWECO operation and bagging or traying. B. FAD handling of M1 propellant. C. 2.5-Gallon Mixer Operation. D. 4-Inch Press Operation. E. Cutting, Drying.	Minimize the risk of propellant fire and potential for personnel injury or equipment damage.	M	Standard Safety Practice	
Hazards Analysis	17.	Complete the total systems hazards analysis, perform operating hazards analysis of the operation.	Ensure adequate safety to personnel and facilitate and ensure compliance with Army risk criteria.	M	AMC R 385-100	This report completes study.

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[a] M=mandatory recommendation, S=suggested recommendation.

[b] See Reference 7.

Table 2

Summary of Probabilistic Analyses

Operations	Facilities Accident Category, Accidents/Facility-h			Personnel Accident Category, Accidents/Man-h			
	I_α	II_α	IIIα	Iβ	IIβ	IIIβ	IV
Materials Handling	-	1.5E-7	-	-	2.5E-7	-	-
Grinding, Slurrying, Traying, Drying, etc.	3E-10	1.5E-8	-	2E-10	3E-7	-	-
Mixing, Resolvating, Extrusion, and Cutting	2E-10	1.8E-7	3E-8	<1E-10	1.1E-7	3.1E-8	-
Total	5E-10	3.5E-7	3E-8	3E-10	6.6E-7	3.1E-8	-
MPBMA OSM 385-1	1E-6	1E-5	1E-3	1E-7	1E-6*	1E-6*	-

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*Sum of IIβ and IIIβ probabilities shall be 1E-6 per man-h or lower.

Table 3

Schedule for Hazards Analysis Events for Reuse-Recovery of M1 Propellant

	Time 1987								
Event	April	May	June	July	Aug	Sept	Oct	Nov	Dec
1. Completion of PHA on Laboratory Scale Reuse/ Reclamation Technology	▲	Completed April 1, 1987							
2. Prepare 2.5-Gallon Mixer for Single-Base Use (by others)	△				▲				
3. Risk Assessment of 2.5-Gallon Mixer for Single-Base Use	△					▲		This report completes this item	
4. Procedure Review for 2.5-Gallon Mixer	△						▲		
5. Submit Safety/Design Criteria for a Pilot Plant to Reclaim/Reuse Single-Base Propellant					△			▲	
6. Final Report							△		▲

△ = Start

▲ = Completion

Table 4
Probabilistic Assessment of Reuse-Recovery of Obsolete M1 Propellant to Manufacture a Usable M1 Product

SYSTEM: See individual listings in OPERATIONS Column

PAGE 1 OF 10 DATE: October 28, 1987
ANALYST: M. A. Hundley

	ENGINEERING ANALYSIS						PROBABILITIES								
OPERATION	UNITS OF ANALYSIS	MATERIAL OF CONSTR.	COMBUST.	PROCESS POTENTIAL*	MATERIAL RESPONSE *	SAFETY MARGIN *	FREQUENCY (f)*	EVENT	MATERIAL PRESENT (C_p)*	INITIATION* (I_p)	SUST. BURNING (S_p)*	FIRE (F_p)*	TRANSITION (T_p)	EXPLOSION* (X_i)	HAZARD CATEGORY
Materials Handling in the Magazine - New River Magazine Area, Radford															
Truck Loading															
1.*Impact as fork lift tines puncture drum.	ft-lb/in.^{2}	Steel/Propellant	M1	2	6.7	>2	6	1E-6	1	5E-5	1	3.E-10	0	0	IIα/β
2.*Friction as fork lift travels over M1 propellant.	psi @ fps	Rubber/Concrete	M1	2000 @ 2	6E4 @ 8	V=4 F >10	6	1	1E-3	1E-7	1	6E-10	0	0	IIα/β
3.*Impact as drum falls onto concrete floor.	ft-lb/in.^{2}	Paper/Concrete	M1	>6.7	31.8	1	6	1E-4	1E-3	3E-2	1	1.8E-8	0	0	IIα/β
Material Handling on Arrival at Radford															16
4. Repeat No. 3 at Radford												1.8E-8	0	0	IIα/β
5. Repeat No. 2 at Radford	These are reverse of numbers 1-3											6E-10	C	0	IIα/β
6. Repeat No. 1 at Radford												3E-10	0	0	IIα/β
Storage in Magazine															
7. Storage	No ignition stimuli present during storage.														
Material Handling															
8. Impact as fiber drums are manually loaded onto truck.	ft-lb/in.^{2}	Concrete or Wood	M1	·7.8	31.8	> 3	26	1E-4	1E-3	1E-6	1	<1E-10	0	0	IIα/β
9.*Friction as hand buggy runs over spilled propellant.	psi @ @ fps	Concrete/Rubber	M1	1000 @ 2	6E-4 @ 8	V=2 F>10	26	1E-3	1E-3	1E-7	1	<1E-10	0	0	IIα/β

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*Items identified are considered abnormal.

* F = >10

Table 4 (cont)

SYSTEM: See individual listings in OPERATIONS Column

PAGE 2 OF 10 DATE: October 28, 1987
ANALYST: M. A. Hundley

	ENGINEERING ANALYSIS						PROBABILITIES								
OPERATION	UNITS OF ANALYSIS	MATERIAL OF CONSTR.	COMBUST.	PROCESS POTENTIAL*	MATERIAL RESPONSE *	SAFETY MARGIN *	FREQUENCY (f)*	EVENT	MATERIAL PRESENT (C_p)*	INITIATION* (I_p)	SUST. BURNING (S_p)*	FIRE (F_p)*	TRANSITION (T_p)	EXPLOSION* (X_p)	HAZARD CATEGORY
Materials Handling in the Magazine - New River Magazine Area and Radford															
Material Handling (cont)															
10.*Electrostatic Discharge from an ungrounded operator	J	N/A	M1	2.3E-5	1.3E-2	>100	26	1E-3	1E-3	1E-9	1	<1E-10	0	0	IIα/β
Transportation															
11. Materials Handling from magazine to remote dumping operation	ft-lb/in.^{2}	Steel/Steel	M1	>6.7	6.7	0	1	1E-3	1	9.4E-5	1	9.4E-8	0	0	IIα/β
Manual Dumping of M1 from Fiber Drums															
12. Impact generated as fiber drums are removed from vehicle and placed in building	ft-lb/in.^{2}	Concrete	M1	<1	6.7	>6	3.3	1E-4	1E-3	1E-7	1	<1E-10	0	0	IIα/β
13. Friction generated by placing drums in building, i.e., sliding across floor.	psi @ fps	Concrete/Steel	M1	540 @ <1	6E4 @ 8	F >10 V=7	3.3	1E-3	1E-3	1E-7	1	<1E-10	0	0	IIα/β
14.*Electrostatic Discharge by charged operator.	J	N/A	M1	2.3E-5	1.3E-2	>100	3.3	1E-6	1	1E-9	1	<1E-10	0	0	IIα/β
15. Impact as M1 propellant is poured out of container.	ft-lb/in.^{2}	Steel	M1	2.3E-2	7.8	>100	7.4	1	1	1E-9	1	7.4E-9	0	0	IIα/β
16. Friction applied by raking M1 granules.	psi @ fps	Steel	M1	<1 @ <1	6E4 @ 8	F >10 V=7	7.4	1E-3	1	1E-13	1	<1E-10	0	0	IIα/β
17. Electrostatic Discharge created by falling M1 propellant.	J	N/A	M1	2.3E-5	1.3E-2	>20	7.4	1	1	1E-9	1	7.4E-9	0	0	IIα/β

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*Items identified are considered abnormal.

* F = :10

Table 4 (cont)

SYSTEM: See individual listings in OPERATIONS Column

PAGE 3 OF 10 DATE: October 28, 1987
ANALYST: M. A. Hundley

OPERATION	ENGINEERING ANALYSIS						PROBABILITIES								HAZARD CATEGORY
	UNITS OF ANALYSIS	MATERIAL OF CONSTR.	COMBUST.	PROCESS POTENTIAL*	MATERIAL RESPONSE *	SAFETY MARGIN *	FREQUENCY (f)*	EVENT	MATERIAL PRESENT (C_p)*	INITIATION* (I_p)	SUST. BURNING (S_p)*	FIRE (F_p)*	TRANSITION (T_p)	EXPLOSION* (X_p)	
Materials Handling in the Magazine - New River Magazine Area and Radford															
18. Impact as granules fall into container.	ft-lb/ in.^{2}	Plastic	M1	<2	>230	>20	7.4	1	1	1E-9	1	7.4E-9	0	0	IIα/β
19. Friction generated by sliding a polyethylene can across propellant.	psi @ fps	Plastic/ Concrete	M1	170 @ 1.3	6E4 @ 8	F>10 V=5	7.4	1E-3	1E-3	1E-7	1	<1E-10	0	0	IIα/β
20. Impact generated by placing cans onto vehicle.	ft-lb/ in.^{2}	Plastic/ Wood	M1	<1	7.8	>6	7.4	1E-4	1E-3	1E-7	1	<1E-10	0	0	IIα/β
21. Materials Handling enroute to the Waste Propellant Incinerator.	ft-lb/	Steel/ Steel	M1	6.7	6.7	0	1	1E-3	1	9.4E-5	1	9.4E-8	0	0	IIβ
<u>Unloading Waste Propellant Cans Into Storage</u>															
22. Impact as polyethylene cans are placed on floor.	ft-lb/ in.^{2}	Poly-ethylene	M1	<10	>230	>20	59	1E-4	1E-3	1E-9	1	<1E-10	0	0	IIα/β
23. Friction generated by sliding can on floor.	psi @ fps	Poly-ethyl-ene/ Concrete	M1	<170 @ 1.3	>6E4 @ 8	F >10 V >5	59	1E-3	1E-3	1E-7	1	<1E-10	0	0	IIα/β
24. *Electrostatic Discharge from ungrounded operator.	J	N/A	M1	2.3E-5	1.3E-2	>20	59	1E-7	1	1E-9	1	<1E-10	0	0	IIα/β
25. Grinder clean-up prior to grinding M1 propellant.	- Consists of a continuous fresh water wash until all propellant is washed out of grinder into a slurry tank. Wash will require approximately two hours.														
<u>Draining and Cleaning Slurry Tank</u>															
26. Impeller impacts on tank walls in presence of propellant.	ft-lb/ in.^{2}	Steel	M1	>7.8	7.8	<1	1	1E-3	1	5E-16	1	<1E-10	0	0	IIα

*Items identified are considered abnormal.

* F = >10

Table 4 (cont)

SYSTEM: See individual listings in OPERATIONS Column

PAGE 4 OF 10 DATE: October 28, 1987
ANALYST: M. A. Hundley

OPERATION	ENGINEERING ANALYSIS						PROBABILITIES								HAZARD CATEGORY
	UNITS OF ANALYSIS	MATERIAL OF CONSTR.	COMBUST.	PROCESS POTENTIAL*	MATERIAL RESPONSE *	SAFETY MARGIN *	FREQUENCY (f)*	EVENT	MATERIAL PRESENT (C_p)*	INITIATION* (I_p)	SUST. BURNING (S_p)*	FIRE (F_p)*	TRANSITION (T_p)	EXPLOSION* (X_p)	
<u>Draining and Cleaning Slurry Tank (cont)</u>															
27. *Friction as impeller blades strike wall.	psi @ fps	Steel	M1	8.5E4	6E4 @ 8	1	1	1E-3	1	5E-16	1	<1E-10	0	0	IIα
28. Pump Operation, Impact and Friction.	- Values extracted from Reference 10.											<1E-10	0	0	IIα
<u>Loading M1 Propellant Cans onto Conveyor</u>															
29. Impact as can is placed on conveyor.	ft-lb/in.^{2}	Steel Plastic	M1	<10	>230	>20	1	1E-4	1E-3	1E-9	1	<1E-10	0	0	IIα/β
30. Impact as can lid discarded.	ft-lb/in.^{2}	Concrete/Plastic	M1	<1	>230	>20	1	1E-3	1E-3	1E-9	1	<1E-10	0	0	IIα/β
31. Friction between trolley parts as conveyor moves.	psi @ fps	Steel	M1	9.5E4 @ 1	6E4 @ 8	F<1 V>7	1	1	1E-3	1E-5	1	1E-9	0	0	IIα/β
32. Impact as M1 falls into grinder.	ft-lb/in.^{2}	Steel	M1	<1	6.7	>5	1	1	1	1E-7	0	0	0	0	IIIα
<u>Grinding M1 Propellant</u>															
33. Impact and friction between metal and propellant.	Conventional engineering analysis indicate that propellant will initiate. However, the copious volume of water immediately drowns the reaction and prevents sustained burning.														
34. Slurrying, dewatering, bagging and traying.	Data extracted from Reference 10.											1.1E-8	0	0	IIα/β
35. Materials Handling from incinerator to FAB area.	ft-lb/in.^{2}	Steel/	M1	6.7	6.7	0	1	1E-3	1	9.4E-5	1	9.4E-8	0	0	IIβ

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*Items identified are considered abnormal.

* F = :10

19

Table 4 (cont)

SYSTEM: See individual listings in OPERATIONS Column

PAGE 5 OF 10 DATE: October 28, 1987
ANALYST: M. A. Hundley

	ENGINEERING ANALYSIS						PROBABILITIES								
OPERATION	UNITS OF ANALYSIS	MATERIAL OF CONSTR.	COMBUST.	PROCESS POTEN-TIAL*	MATERIAL RESPONSE *	SAFETY MARGIN *	FRE-QUENCY (f)*	EVENT	MATERIAL PRESENT (C_p)*	INITIA-TION* (I_p)	SUST. BURNING (S_p)*	FIRE (F_p)*	TRAN-SITION (T_p)	EXPLO-SION* (X_p)	HAZARD CATEGORY
Propellant Drying to 1% Moisture															
36.[a] Friction generated by opening FAD doors (hinges).	psi @ fps	Steel/ Steel	M1	1.3E4 @ 3	6E4 @ 8	F>3 V>1	1	1	1E-3	3E-7	1	3E-10	0	0	IIα/β
37.[a] Friction generated by door and frame.	psi @ fps	Wood/ Rubber	M1	5E3 @ 3	6E4 @ 8	F>10 V>1	1	1	1E-3	3E-9	1	<1E-10	0	0	IIα/β
38.[a] Impact or door is closed.	ft-lb/ in.^{2}	Wood/ Rubber	M1	<100	1191	>10	1	1	1E-3	1E-8	1	<1E-10	0	0	IIα/β
39.[a] Friction generated as louvres open and close.	psi @ fps	Steel/ Lead	M1	1.3E4 @ 3	6E4 @ 8	F>3 V>2	1	1	1E-3	2E-9	1	<1E-10	0	0	IIα/β
40.[a] Friction generated by loaded cabinet rolling over propellant.	psi @ fps	Rubber/ Lead	M1	3.6E3 @ 2	6E4 @ 8	F>10 V>3	10	1	1E-3	1E-10	1	<1E-10	0	0	Iα/β
41. *Temperature controllers fail.	°F	N/A	M1	245°F	329°F	>3	1	1	1	1E-11	1	<1E-10	0	0	Iα
42.[b]*Electrostatic discharge from ungrounded operator.	J	N/A	M1	2.3E-5	1.3E-2	>10	10	1E-7	1	1E-8	1	<1E-10	0	0	Iα/β
43. Materials Handling from FAD to Finishing Area.	ft-lb/ in.^{2}	Steel/	M1	6.7	6.7	0	1	1E-3	1	9.4E-5	1	9.4E-8	0	0	IIβ

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[a] Was assumed that only M1 is involved - normally NG film would be combustible in FAD analysis.

[b] Combustible would normally be vapors; in this case M1 dust used.

*Items identified are considered abnormal.

* F = >10

Table 4 (cont)

SYSTEM: See individual listings in OPERATIONS Column

PAGE 6 OF 10 DATE: October 28, 1987
ANALYST: M. A. Hundley

	ENGINEERING ANALYSIS						PROBABILITIES								
OPERATION	UNITS OF ANALYSIS	MATERIAL OF CONSTR.	COMBUST.	PROCESS POTENTIAL*	MATERIAL RESPONSE *	SAFETY MARGIN *	FREQUENCY (f)*	EVENT	MATERIAL PRESENT (C_p)*	INITIATION* (I_p)	SUST. BURNING (S_p)*	FIRE (F_p)*	TRANSITION (T_p)	EXPLOSION* (X_p)	HAZARD CATEGORY
<u>Placing M1 Into Fiber Drums by Remote Control</u>															
44. Friction generated by loaded cabinet rolling over propellant.	psi @ fps	Rubber/ Concrete	M1	1E3 @ 2	6E4 @ 8	F>10 V=73	1	1	1E-3	1E-7	1	1E-10	0	0	IIα/β
45. Impact as valve liner closes on propellant.	ft-lb/ in.^{2}	Rubber	M1	<1	>1000	>20	1	1	1	1E-9	1	1E-9	0	0	IIα
46. Friction as full drums are moved.	psi @ fps	Concrete/ Steel	M1	540 @< 1	6E-4 @ 8	F>10 V>7	1	1	1	1E-13	1	<1E-10	0	0	IIα/β
47. Impact as full drums are moved.	ft-lb/ in.^{2}	Concrete	M1	<1	6.7	6	1	1E-4	1E-3	1E-7	1	<1E-10	0	0	IIα/β
48.*Friction as hand truck runs over spilled propellant.	psi @ fps	Concrete/ Rubber	M1	1000 @ 2	6E4 @ 8	V=2 F>10	1	1E-3	1E-3	1E-7	1	<1E-10	0	0	IIα/β
49.*Electrostatic discharge by charged operator.	J	N/A	M1	2.3E-5	1.3E-2	>100	1	1E-6	1	1E-9	1	<1E-10	0	0	IIα/β
50.*Thermal initiation of dust due to malfunctioning dust system.	°F	Steel	M1	300°F	329°F	<1	1	1.3E-4	1	1E-9	1	<1E-10	0	0	IIα/β
51. Materials Handling of filled containers to storage.	ft-lb/ in.^{2}	Steel/ Steel	M1	6.7	6.7	0	1	1E-3	1	9.4E-5	1	9.4E-8	0	0	IIβ
<u>Unloading Full Containers Into Storage</u>															
52. Impact as fiber drums are unloaded.	ft-lb/ in.^{2}	Concrete	M1	<7.8	31.8	>3	26	1E-4	1E-3	1E-6	1	<1E-10	0	0	IIα/β

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*Items identified are considered abnormal.

* F = >10

Table 4 (cont)

SYSTEM: See individual listings in OPERATIONS Column

PAGE 7 OF 10 DATE: October 28, 1987
ANALYST: M. A. Hundley

OPERATION	ENGINEERING ANALYSIS						PROBABILITIES								HAZARD CATEGORY
	UNITS OF ANALYSIS	MATERIAL OF CONSTR.	COMBUST.	PROCESS POTENTIAL*	MATERIAL RESPONSE *	SAFETY MARGIN *	FREQUENCY (f)*	EVENT	MATERIAL PRESENT (C_p)*	INITIATION* (I_p)	SUST. BURNING (S_p)*	FIRE (F_p)*	TRANSITION (T_p)	EXPLOSION* (X_p)	
Unloading Full Containers Into Storage (cont)															
53.*Friction as hand truck runs over spilled propellant.	psi @ fps	Concrete/ Rubber	Ml	1000 @ 2	6E4 @ 8	F>10 V=2	26	1E-3	1E-3	1E-7	1	<1E-10	0	0	IIα/β
54.*Electrostatic discharge from an ungrounded operator.	J	N/A	Ml	2.3E-5	1.3E-2	>100	1	1E-3	1E-3	1E-9	1	<1E-10	0	0	IIα/β
55. Storage.	No creditable initiation stimuli present during storage.														
Removal of Small Samples of Ml to Mixer Building and Resolvation															
Loading the Mixer															
56. Impact. Dropping Ml mix onto the mixer.	ft-lb/in.^{2}	Steel	Ml	3	6.7	>1	1	1E-4	1E-3	5E-5	1	<1E-10	0	0	IIβ
57. Impact. Dropping Ml onto the concrete floor.	ft-lb/in.^{2}	Concrete	Ml	2	6.7	>2	1	1E-4	1E-3	5E-5	1	<1E-10	0	0	IIβ
58.*Electrostatic discharge. Personnel produces sufficient energy to ignite ether-alcohol vapors during loading.	J	N/A	Ether	2.3E-5	1.3E-4	>4	1	1E-3	1E-3	1E-6	1	<1E-10	1	<1E-10	Iβ
59.*Vapor ignition from electric motor.	J	N/A	Ether	>1.3E-4	1.3E-4	0	0.25	4E-5	1E-5	1	1	1E-10	1	1E-10	Iα

22

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*Items identified are considered abnormal.

[illegible] 10

Table 4 (cont)

SYSTEM: See individual listings in OPERATIONS Column

PAGE 8 OF 10 DATE: October 28, 1987
ANALYST: M. A. Hundley

OPERATION	ENGINEERING ANALYSIS						PROBABILITIES								HAZARD CATEGORY
	UNITS OF ANALYSIS	MATERIAL OF CONSTR.	COMBUST.	PROCESS POTENTIAL*	MATERIAL RESPONSE *	SAFETY MARGIN *	FREQUENCY (f)*	EVENT	MATERIAL PRESENT (C_p)*	INITIATION* (I_p)	SUST. BURNING (S_p)*	FIRE (F_p)*	TRANSITION (T_p)	EXPLOSION* (X_p)	
Removal of Small Samples of MI to Mixer Building and Resolvation (cont)															
Mixing															
60. *Friction as blades scrape wall of mixer with propellant and foreign material present.	psi @ fps	Steel	MI	1E5 @ <2 fps	1.8E5 @ 8 fps	<1	0.25	1E-9	1	1	1	2.5E-10	0	0	IIα
61. *Blade scrapes wall of mixer with propellant present and blades out of alignment.	psi @ fps	Steel	MI	1E5 @ <2 fps	1.8E5 @ 8 fps	< 1	0.25	1E-5	1	3E-2	1	7.5E-8	0	0	IIα
62. *Propellant and solvents get into glands and ignite from frictional heating.	°F	Steel/ Plastic	MI	472°F	329°F	N/A	1	1E-6	1	3E-2	1	3E-8	0	0	IIIα/ IIIβ
Impact															
63. Mixer impacts stops as mixer is lowered into position.	ft-lb/ in.^{2}	Steel	MI	682	7.8	0	1	1E-9	1E-3	1	1	<1E-10	0	0	IIIβ
64. Lift handle impacts mixer in presence of propellant.	ft-lb/ in.^{2}	Steel	MI	2	7.8	>2	1	2E-6	1E-3	5E-5	1	<1E-10	0	0	IIIβ
65. Impact. Inert gas wand impacts mixer with propellant present.	ft-lb/ in.^{2}	Steel	MI	1	7.8	6	1	1E-4	1E-3	1E-7	1	<1E-10	0	0	IIβ
66. *Impact. Mixer lid dropped onto mixer with propellant present.	ft-lb/ in.^{2}	Steel/ Steel	MI	3.6	7.8	>1	1	1E-4	1E-3	3E-2	1	3E-9	0	0	IIβ
67. *Impact. Mixer lid dropped onto propellant on concrete floor.	ft-lb/ in.^{2}	Steel/ Concrete	MI	7.2	14.8	1	1	1E-4	1E-3	3E-2	1	<1E-10	0	0	IIIβ

*Items identified are considered abnormal.

* F = >10

le 4 (cont)

SYSTEM: See individual listings in OPERATIONS Column

PAGE 9 OF 10 DATE: October 28, 1987
ANALYST: M. A. Hundley

OPERATION	ENGINEERING ANALYSIS						PROBABILITIES									HAZARD CATEGORY
	UNITS OF ANALYSIS	MATERIAL OF CONSTR.	COMBUST.	PROCESS POTENTIAL*	MATERIAL RESPONSE *	SAFETY MARGIN *	FREQUENCY (f)*	EVENT	MATERIAL PRESENT (C_p)*	INITIATION* (I_p)	SUST. BURNING (S_p)*	FIRE (F_p)*	TRANSITION (T_p)	EXPLOSION* (X_p)	
Removal of Small Samples of M1 to Mixer Building and Resolvation (cont)															
Impact															
68. Impact. Mixer cover with energy-absorbing strips slammed onto mixer.	ft-lb/in.^{2}	Steel/ Plastic	M1	<10	>100	>2	1	1E-3	1E-3	1E-6	1	<1E-10	0	0	IIβ
69. Friction. Lift handle creates friction as it is actuated.	psi @ fps	Steel	M1	1000 @ 2	1.8E5 @ 8	>10	1	1	1E-3	1E-7	1	<1E-10	0	0	IIIβ
70. Friction. Actuator rod moves in the presence of propellant.	psi @ fps	Steel	M1	500 @ 0.5	1.8E-5 @ 8	>10	1	1	1E-3	1E-7	1	<1E-10	0	0	IIIβ
71.*Impact. Propellant falls into rotating gears.	ft-lb/in.^{2}	Steel	M1	6.6E4	7.8	0	0.25	1	1E-9	1	1	2.5E-10	0	0	IIα
72.*Friction. Propellant gets onto shaft and into bearings.	psi @ fps	Steel	M1	1E5 @ 2	1.8E5 @ 8	V=2 F=<1	0.25	1	1E-9	1	1	2.5E-10	0	0	IIα
Discharging Mixer															
73. Impact of rake on mixer bowl.	ft-lb/in.^{2}	Wood or Plastic	M1	5.3	31.8	5	1	1E-3	1	1E-7	1	<1E-10	0	0	IIβ
74. Friction between rake and mixer bowl.	psi @ fps	Steel	M1	1.5E3 @ 1	1.5E5 @ 8	V=8 F=>10	1	1	1	5E-13	1	<1E-10	0	0	IIβ
75.*Electrostatic ignition of vapors by ungrounded individual.	J	N/A	Ether	2.3E-5	1.3E-4	>4	1	1E-3	1E-3	1E-7	1	<1E-10	1	1E-10	Iα/β
76. Dropping propellant mix onto floor after mixer is unloaded.	ft-lb/in.^{2}	Concrete	M1	<4	31.5	>6	1	1E-4	1	1E-7	1	<1E-10	0	0	IIIβ

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*Items identified are considered abnormal.

* F = >10

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Table 4 (cont)

SYSTEM: See individual listings in OPERATIONS Column

PAGE 10 **OF** 10 **DATE:** October 28, 1987
ANALYST: M. A. Hundley

	ENGINEERING ANALYSIS						PROBABILITIES								
OPERATION	UNITS OF ANALYSIS	MATERIAL OF CONSTR.	COMBUST.	PROCESS POTENTIAL*	MATERIAL RESPONSE *	SAFETY MARGIN *	FREQUENCY (f)*	EVENT	MATERIAL PRESENT (C_p)*	INITIATION* (I_p)	SUST. BURNING (S_p)*	FIRE (F_p)*	TRANSITION (T_p)	EXPLOSION* (X_p)	HAZARD CATEGORY
Removal of Small Samples of MI to Mixer Building and Resolvation (cont)															
<u>Discharging Mixer</u> (cont)															
77.*Excess vapors present in bay.	See calculations in Appendix E.														
78. <u>Preblocker Operation for 4-Inch Press</u>	This equipment will not be used since the weight of the mix will not be sufficient for a charge for a Preblocker.														
<u>Operation of the 4-Inch Press</u>															
79. Friction generated as Delrin inserts rub on steel walls - normal condition.	psi @ fps	Delrin/ Steel	MI	2.9E4 @ <1	1E5 @ 8	F=3 V>6	0.5	1	1	1E-11	1	<1E-10	0	0	IIα
80.*Abnormal friction generated by gritty material being present between Delrin and press walls.	psi @ fps	Delrin/ Steel	MI	>2.9E4 @ <1	2.9E4 @ 2	F<1 V=1	0.5	1E-3	1	1	1	5E-4	0	0	IIα
	(When corrected, this value is same as No. 79).														
81. Friction generated between ram head and barrel.	psi @ fps	Bronze/ Steel	MI	4.2E4 @ <1	1.8E5 @ 8	F>3 V>7	0.5	1E-3	1	5E-11	1	<1E-10	0	0	IIα
82. Impact by the ram head - normal.	ft-lb/ in.^{2}	Brass/ Steel	MI	<1	20.4	>10	0.5	1	1	1E-8	1	5E-9	0	0	IIα
83. *Impact by the ram head - abnormal - ram out of alignment.	ft-lb/	Brass/ Steel	MI	>20.4	20.4	0	0.5	1E-3	1	1	1	5E-4	1	5E-4	IIα
	(When corrected, this value is same as No. 82)														
84. <u>Cutting of Propellant</u>	Extracted from previous studies - Reference 5.											4.6E-9	0	0	IIβ
85. Solvent Recovery, Water Dry, Final Blend, Pack, etc.	Data extracted from Reference 15.											1E-7	1	1E-7	IIα/β

*Items identified are considered abnormal.

* F ≥ 10

Table 5

Sensitivity Initiation Characteristics for Different Forms of M1 Single-Base Propellant with M26 Double-Base for Comparison

Initiation Method	Units	Test Condition	Composition	Temperature	Test Value
Explosive					
Impact[a]	ft-lb/in.^{2}	Steel-Steel	M1 fines	Ambient	6.7
			M1 Extruded Strand 12-25% TV	Ambient	20
			M1 Granule After Solvent Recovery 19% TV	Ambient	24.7
			M1 Granules Dry	Ambient	8.0
Sliding[a] Friction	psi @ fps	Steel-Steel	M1 Dry Flakes	Ambient	60,000 @8
			M1 Green Mix Solvent Wet 30% TV	Ambient	176,900 @ 8
			M1 Extruded Strands 12-25% TV	Ambient	70,000 @ 8
			M1 After Solvent Recovery 19% TV	Ambient	77,285 @ 8
			M1 Finished Dry Granules	Ambient	69,165 @ 8
Electrostatic[a] Discharge	Joules	N/A	M1 fines	Ambient	0.0013
			M1 Cut Granules Solvent Wet 20-29% TV	Ambient	≤5.0
			M1 Finished Granule Dry	Ambient	≤5.0
			Diethyl Ether Vapor Air Mixture	Ambient	0.0013
			Ethyl Alcohol Vapor Air Mixture	Ambient	0.075

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[a] The Threshold Initiation Level (TIL) is described as the level above which initiation can occur as established by 20 failures at the indicated level, with at least one initiation at the next test level.

Table 5 (cont)

Initiation Method	Units	Test Condition	Composition	Temperature	Test Value
Thermal					
Autoignition[a]	°F	N/A	M1	N/A	329
Exposure to Flame and Shock					
Flame[b] Critical Height to Explosion	Inches Height At / Diameter				
	1-inch diameter pipe	Steel pipe	M1 Dry Granules	Ambient	>7
			M1 Granules Water Wet-Soaked in H_2O for 4 1/2 minutes prior to test	Ambient	>35
			M1 Macerated Propellant 35% TV	Ambient	>48
Critical[c] Diameter for Explosive Propagation	Inch	Steel pipe	M1 Dry Granules Approximately 0.5-0.6% moisture	Ambient	<0.25
				Ambient	>2.0 (unconfined)
			M1 Paste Lumps	Ambient	1.4

Volatile Materials

Diethyl Ether Vapor: Flammable limits by volume 1.9 to 36 percent

Ethyl Alcohol Vapor: Flammable limits by volume 3.3 to 19 percent

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[a] Autoignition Temperature or temperature where propellant automatically ignites.

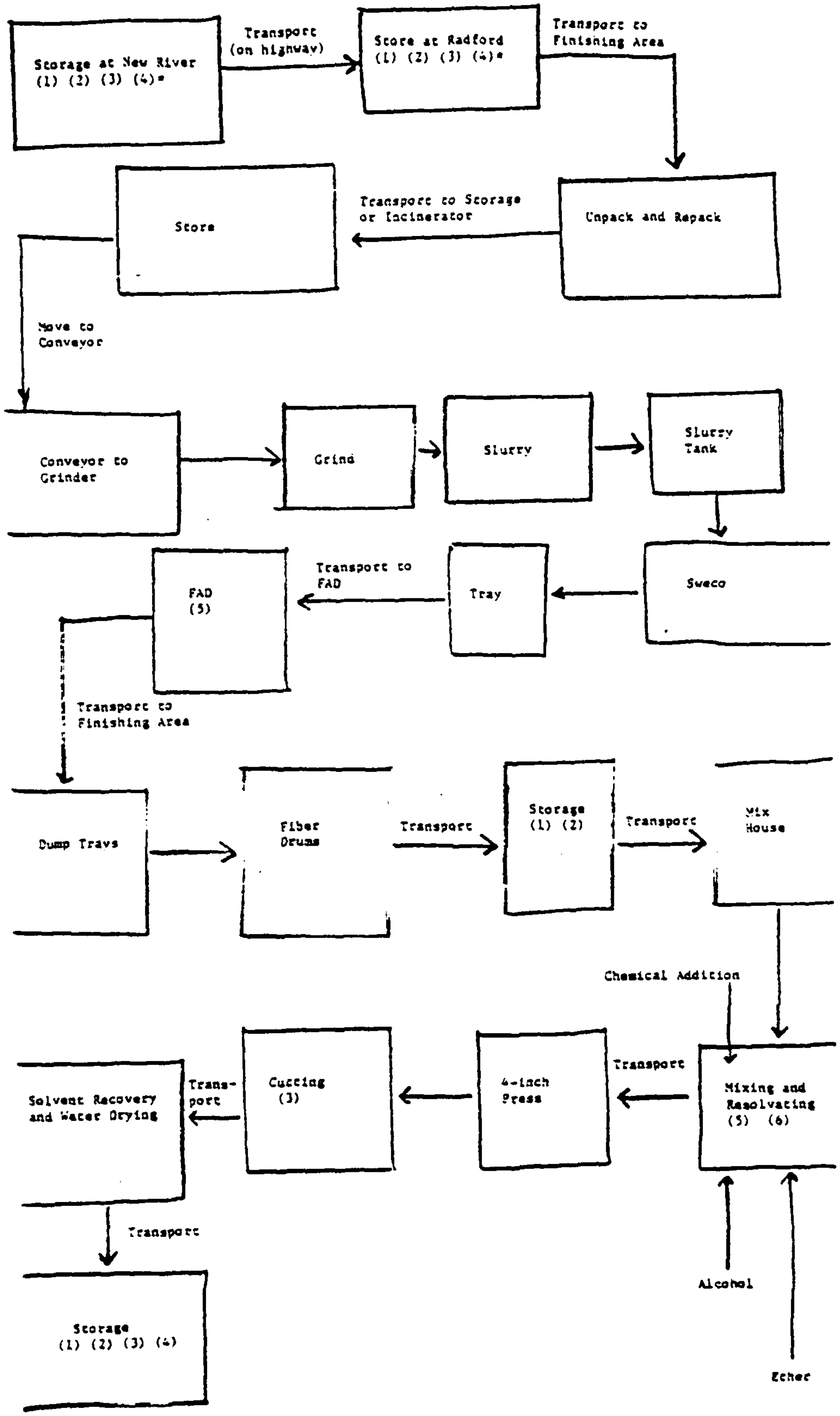
[b] Critical height is defined as the confined material height above which an explosion can occur when subjected to bottom flame initiation produced by a 12-gram bag igniter (50/50 mixture of 2056 casting powder and Class 6 black powder).

[c] Critical Diameter is defined as the confined material dimension above which an explosive reaction can be propagated when subjected to a shock impulse produced by a Composition C-4 donor (L:D ratio of 3:1 plug 1 inch for blasting cap).

Table 6

Preliminary Safety Design Criteria for the Design of a Pilot Plant to Reuse Propellant

1. The Propellant Reuse Operation should be one continuous operation in one location and extensive manual material handling steps should be eliminated thereby reducing personnel exposure. For example, propellant should be unpacked by mechanical methods to reduce exposure. Slurry movement or similar material handling steps should be employed.
2. Each reuse operation run should be type propellant specific. For example, the line should be cleaned prior to the M1 run and cleaned upon completion of the M1 run.
3. Propellant size reduction should be done using equipment similar to that used in the Waste Propellant Incinerator operation. The grinder has been damaged by tramp metal in propellants but sustained burning reactions have not resulted during grinding due to the large volumes of water present.
4. The only coolant used in the size reduction operation should be water and an excess of water must always be present.
5. Initial dewatering of propellant is to be done in approved dewatering systems such as a SWECO separator with modifications necessary for propellant operations.
6. All equipment must be approved type for explosive service.
7. Entire plant layout should be in a sump to facilitate clean-up and to recapture any spills.



Tests:

(1) Chemical
(2) Stability
(3) Physical dimensions
(4) Ballistics
(5) Moisture and Total Volatiles
(6) Sensitivity - Impact - Friction - ESD

*Test only once

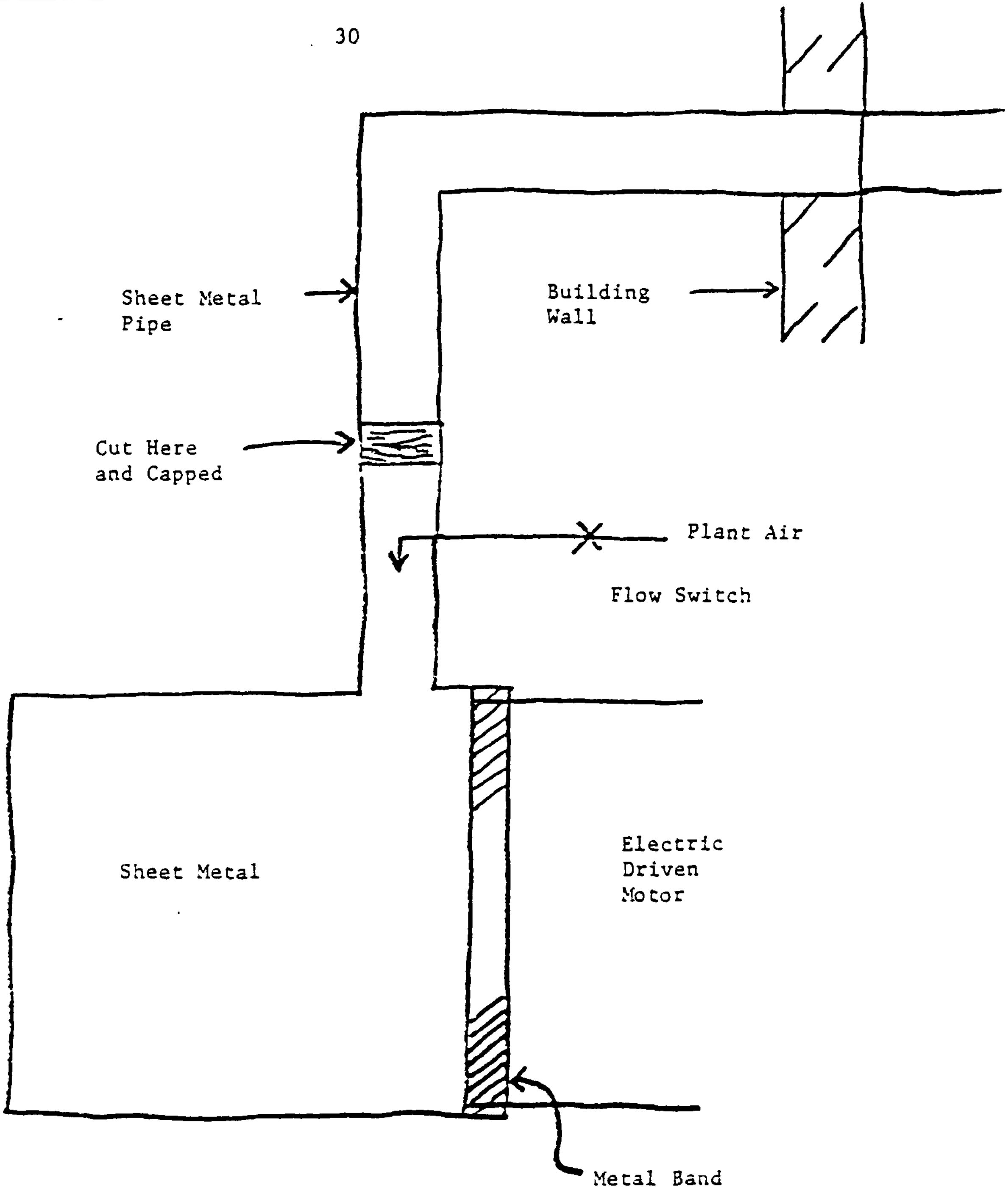


Figure 2. Schematic of Modified Purge System of the Electric Motor

APPENDIX A

EXPLANATION OF HAZARD EVALUATION/PROBABILISTIC ANALYSIS TABLES

Column No.	Title	Description
1	Operation	States the operation, specific task, and whether normal or abnormal operation is being assessed.
2	Units of Analysis	States the appropriate energy units for Process Potential (Col. 5) and Material Response (Col. 6).
3	Materials of Construction	The materials of construction associated with the potential hazard are specified.
4	Combustible	The combustible (M1 propellant, diethyl ether, and alcohol vapors) that is present where a potential hazard is named.
5	Process Potential (PP)	The process stimuli or energy that can be generated by the potential hazard. This is determined by direct measurement, laboratory simulation, or calculation.
6	Material Response (MR)	The threshold initiation level (highest test level at which no initiation is evidenced in a fixed number of trials, usually 20) established from initiation tests for a given combustible.
7	Safety Margin (SM)	Equal to the material response (MR) divided by the process potential (PP) less one $SM = \frac{MR}{PP} - 1$
8	Frequency (f)	Frequency is 1 where continuous process is involved, or the frequency per hour if an intermittent operation.
9	Probability of Event (E_p)	E_p is the probability of the hazardous event occurring and is numerically equal to one for normally occurring events and is established from the appropriate equipment or human failure rate for abnormal events.

APPENDIX A (cont)

Column No.	Title	Description
10	Probability of Material Present (C_p)	C_p is the probability of combustible material being present where and when the potential hazard occurs. The sequence of events necessary for the combustible to be present (for example, whether normally present or as the result of an accidental condition or procedural error) is considered in establishing the probability.
11	Probability of Initiation (I_p)	I_p is determined statistically comparing material response and process potential. Safety margins and probit plots are used for this determination.
12	Probability of Sustained Burning (S_p)	S_p is the probability of transition from initiation to burning. Where the potential hazard is in the presence of quantities of combustible the most severe condition is taken; that is, $S_p = 1$. Where the combustible is present in smaller amounts, as the result of minor spills, S_p is either 1×10^{-3} or 1×10^{-6}.
13	Probability of Fire (F_p)	F_p is the product of $f \times E_p \times C_p \times I_p \times S_p$.
14	Probability of Transition (T_p)	T_p is the probability of transition from sustained burning to an explosion and is either one or zero, depending on whether the critical height to explosion is exceeded (in-process material height $>C_{he}$) or not (see Table III).
15	Probability of Explosion (X_p)	X_p is the product of $F_p \times T_p$.
16	Hazard Category	The potential hazard is classified in accordance with MPBMA OSM 385-1 to reflect hazard level (see below). The severity of the hazard alone, and not its probability of occurrence, determines hazard category.

APPENDIX A (cont)

Hazard Severity

Hazard Severity Categories/Accident Categories Application:

Hazard severity categories are classified by MIL-STD-882B into four categories, based upon the most severe result of personnel error, procedural deficiencies, environment, design characteristic, or subsystem or component failure or malfunction. When the necessary conditions exist and the necessary sequence of events occur, then a hazard severity category becomes the corresponding category accident. The probability values given in hazard analysis indicate the probability of the transition occurring from hazard to accident. The hazard severity categories are defined as follows:

(1) Category Iα (Catastrophic) - Conditions such that the failure mode occurrence will cause system loss or large-scale environmental damage.

(2) Category Iβ (Catastrophic) - Conditions such that the failure mode occurrence will cause death or permanent total disability to one or more persons.

(3) Category IIα (Critical) - Conditions such that the failure mode occurrence will cause critical system damage or some environmental damage.

(4) Category IIβ (Critical) - Conditions such that the failure mode occurrence will cause permanent partial disability to one or more persons.

(5) Category IIIα (Marginal) - Conditions such that the failure mode occurrence will cause minor system damage or some environmental damage.

(6) Category IIIβ (Marginal) - Conditions such that the failure mode occurrence will cause temporary total disability or lost time injury not covered by category I or II .

(7) Category IV (Negligible) - Conditions such that the failure mode occurrence will not result in injury, occupational illness, or system damage.

The relationships between the accident categories and effects on the system are further explained in Exhibit 1.

APPENDIX A (cont)

Hazard Severity

Exhibit 1. Accident Categories and Effects on System.

ACCIDENT CATEGORY	EFFECTS ON SYSTEM	
	EQUIPMENT	PERSONNEL
Iα	SL or LSED	---
Iβ	---	D or PTD
IIα	CSD or SED	---
IIβ	---	PPD
IIIα	MSD or SED	---
IIIβ	---	TTD or lost time injury not covered by category Iβ or IIβ
IV	No Damage	No Injury

SL = System Loss
CSD = Critical System Damage
MSD = Minor System Damage
LSED = Large Scale Environmental Damage
SED = Some Environmental Damage
D = Death
PTD = Permanent Total Disability
PPD = Permanent Partial Disability
TTD = Temporary Total Disability

APPENDIX B

PROCESS DESCRIPTION FOR REUSE-RECOVERY OF M1 SINGLE-BASE PROPELLANT USING THE 2.5-GALLON MIXER

A small quantity (≈3500 pounds) of M1MP propellant (Lot 413) is stored in the New River Magazine. No further need exists for this propellant; it will be returned to Radford and reclaimed in accordance with the operations shown in Figure 1. As can be seen by reference to Figure 1, the reuse-recovery project is labor intensive and operations will need to be streamlined for a pilot plant to reduce personnel exposure and simultaneously effect processing economics.

APPENDIX C

TABLE OF PROBABILITIES USED IN TABLE 2 RISK ANALYSIS

Item	Type Event	Frequency (f)/h	Event Probabilities Ep/h	Material Present Cp/h
Material Handling	1. Impact	6 Got 6 pallets to load. Can be done in one hour.	1E-6 Probability of tines cutting drum is remote. Combination of at least three errors.	1 Propellant is in drum if puncture drum.
	2. Friction	6 Got 6 pallets to load. Can be done in one hour.	1 Normal Operation	1E-3 Error for propellant to be present.
	3. Impact	6 Got 6 pallets to load. Can be done in one hour.	1 Normal Operation	1E-3 Error for propellant to be present.
Material Handling	4. Impact 5. Friction 6. Impact	6 6 6	Same as Number 1-3, except unloading trailer at Radford.	
Storage and Material Handling	7. Storage	No initiation hazards identified during normal storage.		
	8. Impact	26 Got 26 fiber drums to put on truck.	1E-4 Accidental dropping of drum.	1E-3 Error for propellant to be on floor.
	9. Friction	26 Got 26 drums to move.	1E-3 Failure to follow procedures.	1E-3 Error for propellant to be on floor.
	10. Electrostatic Discharge	26 Got 26 drums to move.	1E-3 Failure to check shoes.	1E-3 Error for propellant dust to be present.
Propellant Movement	11. Impact	1 Takes 0.50 hours to move propellant, but personnel are present.	1E-3 Accident.	1 Normal.
Manual Dumping of M1 From Fiber Drums	12. Impact	3.3 Got 26 drums to unload. Will take eight hours.	1E-4 Generate impact by dropping container or running into something.	1E-3 Error for propellant to be outside where it can receive impact.
	13. Friction	3.3 Got 26 drums to unload. Can do in eight hours.	1E-3 Failure to follow instructions.	1E-3 Error for propellant to be on floor.
	14. Electrostatic Discharge	3.3 Got 26 drums to unload.	1E-6 Multiple events (1) Failure to check shoes (1E-3) (2) Shoe failure (1E-3)	1 Normal

APPENDIX C (cont)

Item	Type Event	Frequency (f)/h	Event Probabilities Ep/h	Material Present Cp/h
Manual Dumping of M1 From Fiber Drums (cont)	15. Impact	7.4 Got 26 drums, 3502 pounds, to unload - unload 59 waste cans.	1 Normal Event	1 Normal for propellant to be present.
	16. Friction	7.4 Got 26 drums, 3502 pounds, to unload - unload into 59 drums in eight hours.	1E-3 Failure to follow instructions if apply friction.	1 Normal event.
	17. Electrostatic Discharge	7.4 Got 26 drums, 3502 pounds, to unload in eight hours into 59 cans.	1 Normal Event	1 Propellant must be present.
	18. Impact	7.4 Got 26 drums, 3502 pounds, to empty in eight hours into 59 cans.	1 Normal Event	1 Propellant must be present.
	19. Friction	7.4 Got 59 tubs to move in eight hours.	1E-3 Failure to follow procedure if drag tub.	1E-3 Error. Propellant out of place.
	20. Impact	See No. 13. - Reverse as tubs placed on vehicle except for f = 7.4		
Propellant Movement	21. Impact	1 Takes one hour to move propellant.	1E-3 Accident.	1 Normal.
Unloading Waste Propellant Cans Into Storage	22. Impact	59 Got 59 tubs to unload. Can do in one hour.	1E-4 Dropping the tub.	1E-3 Error if propellant is on floor.
	23. Friction	59 Got 59 tubs to unload. Can do in one hour.	1E-3 Failure to follow procedure i.e., dragging can.	1E-3 Error for propellant to be on the floor.
	24. Electrostatic Discharge	59 Got 59 cans to unload in one hour.	(1E-4) (1E-3) Shoe failure and Failure to check shoes.	1 Propellant present.

APPENDIX C (cont)

Item	Type Event	Frequency (f)/h	Event Probabilities Ep/h	Material Present Cp/h
Grinder Cleanup Prior to Grinding M1 Propellant	25. See Table 5 - N/A at this operation.			
Draining and Cleaning Slurry Tank	26. Impact	1 Continuous Operation	1E-3 Impeller contacts wall.	1 Fines will be in tank.
	27. Friction	1 Continuous Operation	1E-3 Impeller scrapes wall.	1 Fines will be in tank.
	28. See Reference 10.			
Loading M1 Propellant Cans Onto Conveyor	29. Impact	1 Continuous Operation	1E-4 Drop an item.	1E-3 Error for propellant to be present.
	30. Impact	1 Continuous Operation	1E-4 Drop an item.	1E-3 Error for propellant to be present.
	31. Friction	1 Continuous Operation	1 Normal Operation.	1 Propellant must be present.
	32. Friction	1 Continuous Operation	1 Normal Operation.	1 Propellant must be present.
	33. N/A			
Slurrying, Dewatering, Bagging, and Traying	34. See Reference 10.			
Propellant Movement From Incinerator to FAD	35. Impact	1 Takes 0.50 hours to move propellant, but personnel are present.	1E-3 Accident.	1 Normal.
Propellant Drying to 1% Moisture	36. Friction	1 Personnel are present.	1 Normal. Door must be opened.	1 Error if material is present. Door should have been washed.
	37. Friction	1 Personnel are present.	1 Normal Operation	1E-3 Error. Door should have been washed.

APPENDIX C (cont)

Item	Type Event	Frequency (f)/h	Event Probabilities Ep/h	Material Present Cp/h
Propellant Drying to 1% Moisture	38. Impact	1 Personnel are present.	1 Normal Operation	1E-3 Error. Door should have been washed.
	39. Friction	1 Personnel are present.	1 Normal Operation	1E-3 Error. Door should have been washed.
	40. Friction	10 Takes 10 cabinets to hold propellant. Can load in one hour.	1 Normal Operation.	1E-3 Error. Propellant should have been cleaned up.
	41. Thermal	1 Continuous heating once started.	1 Normal Operation.	1 Propellant normally present.
	42. Electrostatic Discharge	10 Got 10 buggies to move.	(1E-3) (1E-3) Shoe Failure and Failure to check shoes.	1 Propellant present.
Propellant Movement From FAD to Finishing Area	43. Impact	1 Takes 0.50 hour to move propellant, but personnel are pesent.	1E-3 Accident.	1 Normal.
Placing M1 Into Fiber Drums by Remote Control	44. Friction	1 Personnel are present.	1 Normal Operation.	1E-3 Propellant out of place.
	45. Impact	1 Got 10 buggies to unload. Assume will take eight hours and personnel are present.	1 Normal Operation.	1 Propellant present.
	46. Friction	1 Got at least 10 drums @ 100 pounds. Load in one shift and personnel are present.	1 Normal Operation.	1E-3 Error for propellant to be present.
	47. Impact	1 Got at least 10 drums to move in eight hours and personnel are present.	1E-4 Drop item.	1E-3 Error. Propellant out of place.

APPENDIX C (cont)

Item	Type Event	Frequency (f)/h	Event Probabilities Ep/h	Material Present Cp/h
Placing M1 Into Fiber Drums by Remote Control (cont)	48. Friction	1 Got 10 drums to move in eight hours and personnel are present.	1E-3 Failure to follow procedure.	1E-3 Error. Propellant out of place.
	49. Electrostatic Discharge	1 Got 10 drums to move in eight hours and personnel are present.	(1E-3)(1E-3) Shoe Failure and Failure to check shoes.	1 Propellant present.
	50. Thermal	1 Fan runs all time building operates.	1.3E-4 Failure of floor switch.	1 Propellant present.
Propellant Movement	51. Impact	1 Takes 0.50 hours to move propellant, but personnel are present.	1E-3 Accident.	1 Normal.
Unloading Into Storage	52. Impact	26 Got 26 drums to move.	1E-3 Failure to follow procedures.	1E-3 Error for propellant to be on floor.
	53. Friction	26 Got 26 drums to move.	1E-3 Failure to check shoes.	1E-3 Error for propellant dust to be present.
Propellant Movement	54. ESD	1 Takes 0.50 hours to move propellant, but personnel are present.	1E-3 Accident.	1 Normal.
Storage	55. N/A			
Mixing	56. Impact	1 One mix every four hours, but personnel are present.	1E-4 Dropping an item.	1E-3 Out-of-place propellant.
	57. Impact	1 One mix every four hours, but personnel are present.	1E-4 Dropping an item.	1E-3 Out-of-place propellant.
	58. Electrostatic Discharge	1 One mix every four hours, but personnel are present.	1E-3 Failure to check shoes.	1E-3 Failure to activate fume eductor.

APPENDIX C (cont)

Item	Type Event	Frequency (f)/h	Event Probabilities Ep/h	Material Present Cp/h
Mixing (cont)	59. Electrical Initiation	0.25 One mix every four hours.	4E-5 Failure of electric motor.	1E-5 Failure of eductor to withdraw fumes and failure of modified purge.
	60. Friction	0.25 One mix every four hours.	1E-9 (1) Propellant passes metal detector (2) Ground (3) Screened (4) Three pounds loaded so can inspect each load	1 Propellant normally present.
	61. Friction	0.25 One mix every four hours.	1E-5 (1) Alignment checked (2) Can hear grinding	1 Propellant normally present.
	62. Thermal	1 One mix every four hours, but personnel are present.	1E-6 (1) Material trapped in glands and not removed (2) No heat transfer	1 Propellant normally present.
	63. Impact	1 One mix every four hours, but personnel are present.	1E-9 (1) Allowing mixer to fall (2) Failure to install stops (3) Failure to clean up.	1E-3 Error. Propellant out of place.
	64. Impact	1 One mix every four hours, but personnel are present.	2E-6 (1) Deliberate act (2) Failure to install stops.	1E-3 Error. Propellant out of place.
	65. Impact	1 One mix every four hours, but personnel are present.	1E-4 Dropping an item.	1E-3 Error. Propellant out of place.
	66. Impact	1 One mix every four hours, but personnel are present.	1E-4 Dropping an item.	1E-3 Error. Propellant out of place.
	67. Impact	1 One mix every four hours, but personnel are present.	1E-4 Dropping an item.	1E-3 Error for propellant to be on floor.
	68. Impact	1 One mix every four hours, but personnel are present.	1E-3 Deliberate slamming of lid.	1E-3 Error. Propellant out of place.

APPENDIX C (cont)

Item	Type Event	Frequency (f)/h	Event Probabilities Ep/h	Material Present Cp/h
Mixing (cont)	69. Friction	1 One mix every four hours, but personnel are present.	1 Normal Event.	1E-3 Error. Propellant out of place.
	70. Friction	1 One mix every four hours, but personnel are present.	1 Normal Event.	1E-3 Error. Propellant out of place.
	71. Impact	0.25 One mix every four hours.	1 Normal Event. Gears rotate.	1E-3 Error. Propellant out of place. After shield installation and cleanup discipline is added the material present becomes 1E-9.
	72. Friction	0.25 One mix every four hours.	1 Normal. Shaft rotates.	1E-3 Error. Propellant out of place. After shield installation and cleanup discipline is added the material present becomes 1E-9.
Discharging Mixer	73. Impact	1 One mix every four hours, but personnel are present.	1E-3 Must unload mixer but error to impact.	1 Normal. Propellant must be present.
	74. Friction	1 One mix every four hours, but personnel are present.	1 Normal event. Must unload mixer.	1 Normal. Propellant must be present.
	75. Electrostatic Discharge	1 One mix every four hours, but personnel are present.	1 Normal event. Must unload mixer.	1 Normal. Propellant must be present.
	76. Impact	1 One mix every four hours, but personnel are present.	1E-4 Drop the mix.	1 Normal. Propellant must be present.
Vapor Generation	77. Excess Vapors	N/A - See Appendix E.		
Preblocker	78. N/A - This equipment is not being used.			

APPENDIX C (cont)

Item	Type Event	Frequency (f)/h	Event Probabilities Ep/h	Material Present Cp/h
4-Inch Press	79. Friction	0.5 Assume mixer will be able to provide propellant to run 50% of the time.	(1E-6) (1E-5) Based on combination of force and velocity safety factors.	1 Propellant must be present for extrusion.
	80. Friction	0.5 Press runs 50% of time.	1E-3 Failure to detect grit.	1 Propellant must be present.
	81. Friction	0.5 Press runs 50% of time.	1E-3 Press out of alignment.	1 Propellant must be present.
	82. Impact	0.5 Press runs 50% of time.	1 Normal Event.	1 Propellant must be present.
	83. Impact	0.5 Press runs 50% of time.	1E-4 Ram out of alignment and not checked.	1 Propellant must be present.
	84. Data extracted from Reference 15.			
	85. Data extracted from Reference 15.			

APPENDIX D

CALCULATED TEMPERATURE RISE IN A TIGHT GLAND

$H = \frac{35{,}000\ P\ M\ s\ \Delta T}{J}$ where

1 HP = 33,000 ft-lb per minute

J = 778 ft-lb per Btu

P = horsepower loss

M = mass of material in gland - propellant and packing say 0.5 lb

s = specific heat of propellant 0.36 Btu/lb°F

T = temperature, °F

You can rewrite this

$\frac{\Delta T}{\Delta t} = \frac{33{,}000}{J\ M\ s} \approxeq (236P)$ °F per minute

If we assume a 100% loss of hp due to packing

$\frac{\Delta T}{\Delta t} = (236)(2) = 472$°F per minute temperature rise

However, a more realistic loss would be 25-50% loss for the mixer to turn. Thus, (236)(0.5) = 118°F per minute rise in temperature.

For M1 the autoignition temperature is 329°F. Consider normal ambient temperature to be 75°F. Thus, ΔT is 329-75 = 254°F.

$\frac{\Delta T}{\Delta t} = \frac{254}{118} = 2.2$ minutes for the conditions just described to start a fire.

This calculation has assumed that no heat loss occurs from the glands and that absolute ignition results. Actual operating results using full size mixers do not verify these calculations. Solvent-wet propellant is difficult to ignite and even more difficult to sustain burning at atmospheric conditions.

APPENDIX E

GENERATION AND REMOVAL OF FUMES FROM THE MIXER BAY

Mixer Bay Dimensions
L - 19'7" say 19 1/2'
W - 15'11 1/2" say 16'
H - >15'
Bay Volume >4680 ft^3

Bay Openings.

Door: 6' Wide

Air Forced into Bay:

Air Purge for Electric Motor
94 ft^3/min without motor fan running (measured value)

Volume of Solvents Evaporated:

0.064 ft^3/min[a] Ether and Alcohol Mixture

Volume of Air Removed Each Minute by Eductor

$Q = AV$ where

Q = volume removed, ft^3/min

A = cross sectional area of eductor, ft^2

V = velocity of fluid, ft/min

$A = \pi r^2$

$A = \pi [3/12]^2$

$A = 0.196\ ft^2$

V = 8,000 fpm - measured value

$Q = (8000)(0.196) = 1568\ ft^3/min$ removed

Room Volume: >4680 ft^3

$\frac{>4680}{1568}$ = total air change in room about every 3-4 minutes. Say 5 minutes to account for the rafter volume.

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[a] Calculations by W. M. Walasinski.

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