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ALTERNATE SOLVENTS FOR BENZENE IN NITROCELLULOSE RECOVERY

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Frankford Arsenal
Philadelphia, Pennsylvania

August 1975

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This study represents one portion of a program directed toward the minimization or elimination of toxicity and flammability hazards associated with the use of benzene in the recovery of nitrocellulose from surplus single base cannon propellants in the manufacture of ball propellants.

It is shown that dichloromethane can replace the current benzene-ethyl

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20. ABSTRACT (cont'd)

acetate cosolvent in nitrocellulose recovery operations while maintaining extraction efficiency, minimizing toxicity dangers. eliminating a fire hazard, simplifying solvent handling, shortening processing time, and reducing energy requirements. It is recommended that pilot plant evaluation of this solvent change be conducted in order to finalize processing conditions for manufacturing operations.

DISPOSITION INSTRUCTIONS

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

INTRODUCTION

Overview of Extraction Step

In the manufacture of ball propellant, surplus single base cannon propellants are used as the cource of nitrocellulose (NC), the major component of the finished product. These surplus propellants contain along with the NC, dinitrotoluene (DNT), dibutylphthalate (DBP), and diphenylamine (DPA), components undesirable in the feedstock for ball propellant processing. In order to utilize the NC in the cannon propellants, the undesirable components must be removed. It is in the extraction or NC recovery step, the first major process step in ball propellant manufacture, that this is achieved.

Description of the Extraction Process

The removal of unwanted modifiers from the cannon propellant is achieved in a 3-step, batch, countercurrent leaching operation. Prior to the extraction operation, the cylindrical multiperforated cannon propellant grains are ground in a hammermill to provide solids with a high surface area to accelerate the leaching rate. This granular feed is pumped in a water slurry to one of the two extraction stills. The feed rests on a perforated false bottom through which water is drained. Following drainage, the cosolvent, containing 90% benzene (B) and 10% ethyl acetate (EA), by weight, is added to the extraction still. The contents are heated to 67°C, the extraction temperature, and agitated for the 90 minute first extraction step. The solvent is then drained and pumped either to recovery for cleanup or to the other extraction still for processing of another batch of propellant. The two stills are operated together in order to achieve countercurrent processing. The schematic in Figure 1 shows how this is achieved. P represents the propellant and S the solvent. Superscripts represent one particular batch of either propellant or solvent. The subscripts of P refer to the number of prior contacts with solvent. Subscripts of S refer to the number of times the solvent has had prior contact with propellant. After three contacts with the B-EA cosolvent, the propellant is pumped as a water slurry, to a stripping still. After solvent has been used three times, it is sent to solvent recovery for removal of the modifiers. After two batches of propellant have been extracted and pumped to the stripping still, the agitated propellant-water slurry is heated and placed under vacuum in order to remove some of the solvent retained either on the surface or in the interstices of the propellant granules. Upon completion of solvent stripping, the propellant chips are pumped forward for the manufacture of ball propellant. Sixteen hours are required to complete two extraction batches and 15 - 17 hours more for the stripping of the retained solvent. The product of the NC recovery operation is solid NC with less than 1% residual extractible material.

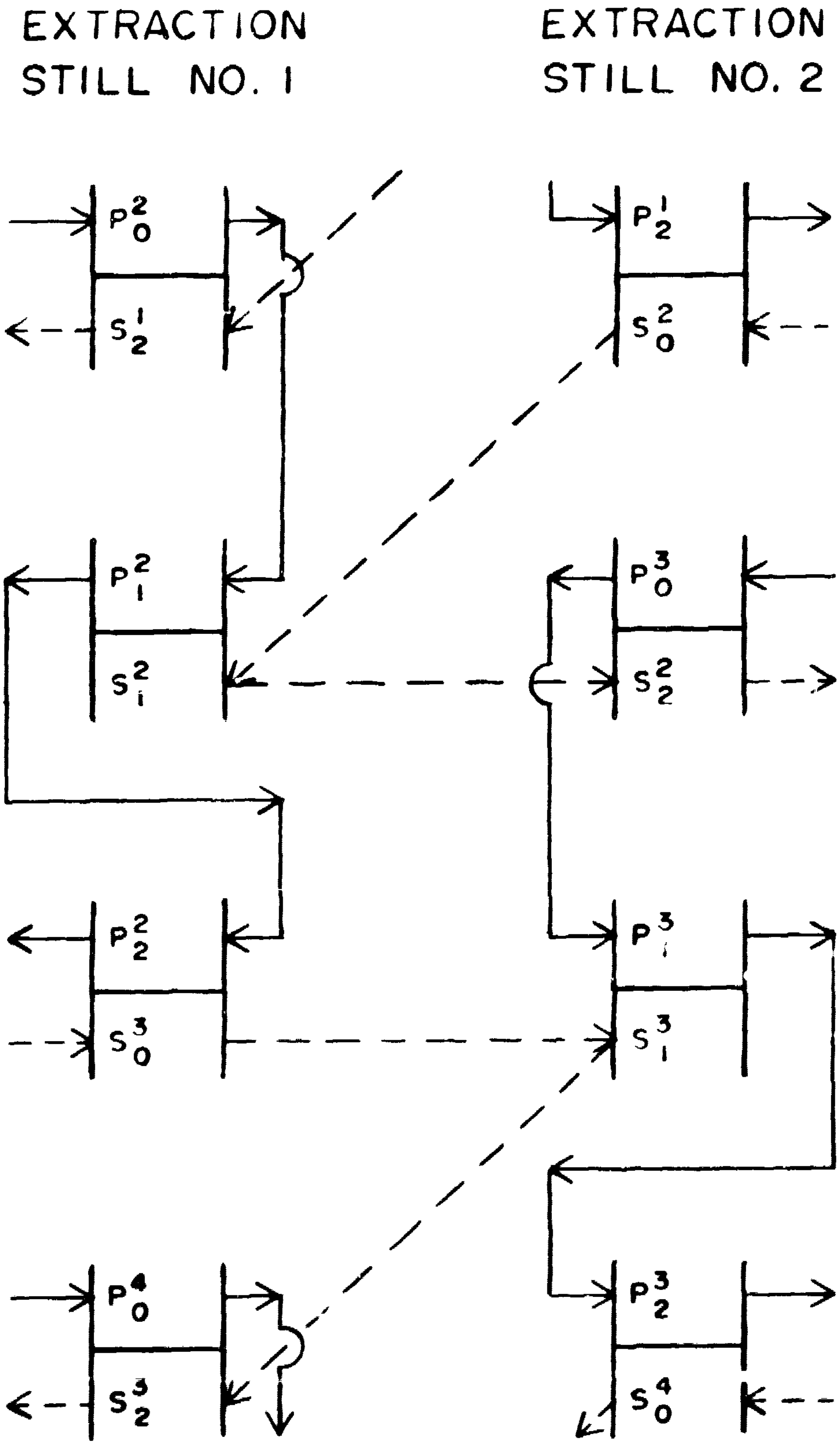

Figure 1. Current Extraction Scheme Using Benzene - Ethyl Acetate Solvent

Problem Statement

The presence of benzene in the NC recovery step has always generated concern among operators and safety engineers. An accidental spill or leakage of vapors is not considered casually because of the extreme toxicity and flammability of benzene.

The toxicity of benzene is considered very severe. The O.S.H.A. assigned Threshold Limit Value (TLV) of 10ppm[1] maximum exposure for an eight hour shift attests to this. If overexposure should occur, underexposure must follow in order to meet the O.S.H.A. guidelines. At low concentrations,[2] prolonged exposure can damage the blood-forming organs. Slightly higher concentrations can result in headache, nausea, and tightness of chest, possibly preventing an operator from removing himself from the contaminated area. At high concentrations, failure of either the central nervous system or respiratory system is a probability. Harmful amounts of benzene may be absorbed by ingestion, inhalation, or direct contact.

During the NC recovery step, extraction stills are opened in order to check if all solvent has drained after a stage. Since high local concentrations of benzene can accumulate when the manhole cover is opened, operators are required to wear air masks or packs to prevent inhalation and possible contamination.

In addition to the severe toxicity exhibited by benzene, it presents a potential for fire and explosion. Because of its low flash point of -11°C and lower explosive limit of 1.3% in air, benzene is considered dangerously flammable.[2]

The concern for operator health and safety in the NC recovery operation led to the creation of a program to replace benzene with a less toxic and, if possible, a non-flammable solvent. Below is presented the program which has resulted in the identification of dichloromethane as an alternate solvent which not only meets the constraints set for toxicity and flammability, but also offers processing advantages for the NC recovery phase of ball propellant manufacture.

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[1] Federal Register, Volume 36, Number 157, August 13, 1971

[2] Sax, N. Irving, Dangerous Properties of Industrial Materials, 1968,

METHODOLOGY OF SOLVENT SELECTION

Selection Criteria

The literature was searched in order to find potential replacements for benzene.[2,3,4,5,6] The criteria were based upon the desire to minimize or eliminate all objectionable characteristics associated with benzene. Therefore, any proposed solvent must have either a higher flash point than benzene or no flash point at all so that the chance of fire or explosion would be less likely. In order to reduce the possibility of a toxic environment and to ease the management of same, a minimum TLV of 100ppm in air for an eight hour work shift was set following consultation with plant safety personnel. The toxic effects a solvent could produce when contacted by humans were considered as a guideline as well, with those solvents having milder effects being more favorably considered.

In order for successful removal of unwanted modifiers to be accomplished in a leaching operation, the proposed solvent had to exhibit good solvent power for the modifiers. At the same time, solubility of NC in the solvent was considered detrimental since this would represent a loss of raw material, an unacceptable processing inefficiency. With all these constraints, one additional one was necessary: the proposed alternate solvent would need to be approximately as efficient or more so than the B-EA cosolvent in use.

Soxhlett Extractions

The literature indicated that the most promising alternates fell in the following two classes: (1) halogenated hydrocarbons and (2) short to medium chain length alcohols.[2,3,4,5,6] In order to assess the leaching power of each solvent, duplicate five hour Soxhlett extractions were run for each candidate. A summary of results appears in Table 1.

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[2] Sax, N. Irving, Dangerous Properties of Industrial Materials, 1968

[3] Durran, Thomas H., Solvents, 1957

[4] Mellan, Ibert, Source Book of Industrial Solvents, 1957

[5] Mellan, Ibert, Industrial Solvents, 1950

[6] Doolittle, Arthur K., The Technology of Solvents and Plasticizers, 1954

Table 1. Summary of Soxhlett Extractions and Environmental Data

Solvent	Extractibles Removed % Weight	Explosive Range[2] % Volume	Flash Point[2] °C	TLV,[1] Ppm
Dichloromethane	97.7	None	None	500
n-butanol	86.6	1.4-11.2	29	100
Isobutanol	84.5	1.7-10.9	28	100
Benzene	73.8	1.3-7.1	-11	10
Isopropanol	61.6	2.0-12.0	12	400
Dichloroethylene	46.8	9.7-12.8	4	200
Isoamyl alcohol	39.5	1.2-9.0	43	100
Trichloroethylene	39.1	2.5-90.0	32	100
n-amyl alcohol	14.2	1.2-10.0	33	100
Freon TF	2.7	None	None	1000

The results indicated that three of the solvents being investigated showed better extraction power than benzene. They were, in order of relative extraction efficiency, as follows: (1) dichloromethane, (2) n-butanol, and (3) isobutanol. These three solvents showed improvement in the flammability and the minimum toxicity level considerations, as well.

Batch Extractions

In the Soxhlett extraction phase of this investigation, the candidate solvents could be compared only to benzene, not directly with the 90% benzene-10% ethyl acetate cosolvent in use. Therefore, a series of co-current batch extractions was planned and subsequently conducted in an agitated, temperature-controlled, 1-liter, 3-necked flask. Standard experimental procedure provided for addition and heating up of the solvent followed by addition of the required amount of ground cannon propellant. In every case, the solvent-to-propellant ratio was set at 3:1 by weight. The duration of the extractions was set at four hours, sufficiently long for complete equilibrium to have been reached. Prior to extraction, the propellant was towel-dried; following extraction, the propellant was allowed to air dry overnight prior to analysis for residual extractible material.

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[1] Federal Register, Volume 36, Number 157, August 13, 1971

[2] Sax, N. Irving, Dangerous Properties of Industrial Materials, 1968

In this phase of experimentation, two effects were studied: (1) extraction efficiency as a function of temperature, and (2) the impact of 10% by weight ethyl acetate addition to the solvent upon extraction efficiency. Figure 2 compares the extraction efficiencies of the candidate solvents and the B-EA cosolvent. In all cases, more extractible matter is removed as the temperature is elevated. The extraction efficiency of dichloromethane, over its usable range, is much less sensitive to temperature. Equivalent removal of extractibles can be achieved using dichloromethane (boiling point: 40.1°C) at 35°C as compared to 65°C for the B-EA cosolvent. Similarly, nearly equivalent removal of extractibles was achieved using n-butanol at 105°C. Isobutanol was shown to be much less effective and was removed from further consideration.

The effects of addition of ethyl acetate on removal of extractibles from cannon propellant are shown in Table 2.

Table 2. Influence of EA on Extraction Efficiency

Solvent	Temperature, °C	Residual Extractibles,% Weight
Benzene	65	6.35
Benzene-EA	65	3.33
Dichloromethane	35	3.33
Dichloromethane-EA	35	3.39
n-butanol	90	4.15
n-butanol-EA	90	4.52

The advantage of using ethyl acetate with benzene is clearly shown; however, no improvement in extraction efficiency is shown when EA is combined with either dichloromethane or n-butanol. In fact, the addition of EA to n-butanol was somewhat detrimental.

Solvent Selection

As a result of the batch extractions discussed above a decision was made to withdraw n-butanol from further consideration. N-butanol demonstrated extraction efficiency nearly equivalent to that of dichloromethane and the B-EA cosolvent at 105°C (See Figure 2), a temperature considered unsafe for processing of NC in its unstable condition (DPA removed). Furthermore, the fact that n-butanol boils at a higher temperature (117.9°C) than water would present difficulty in its recovery and recycle.

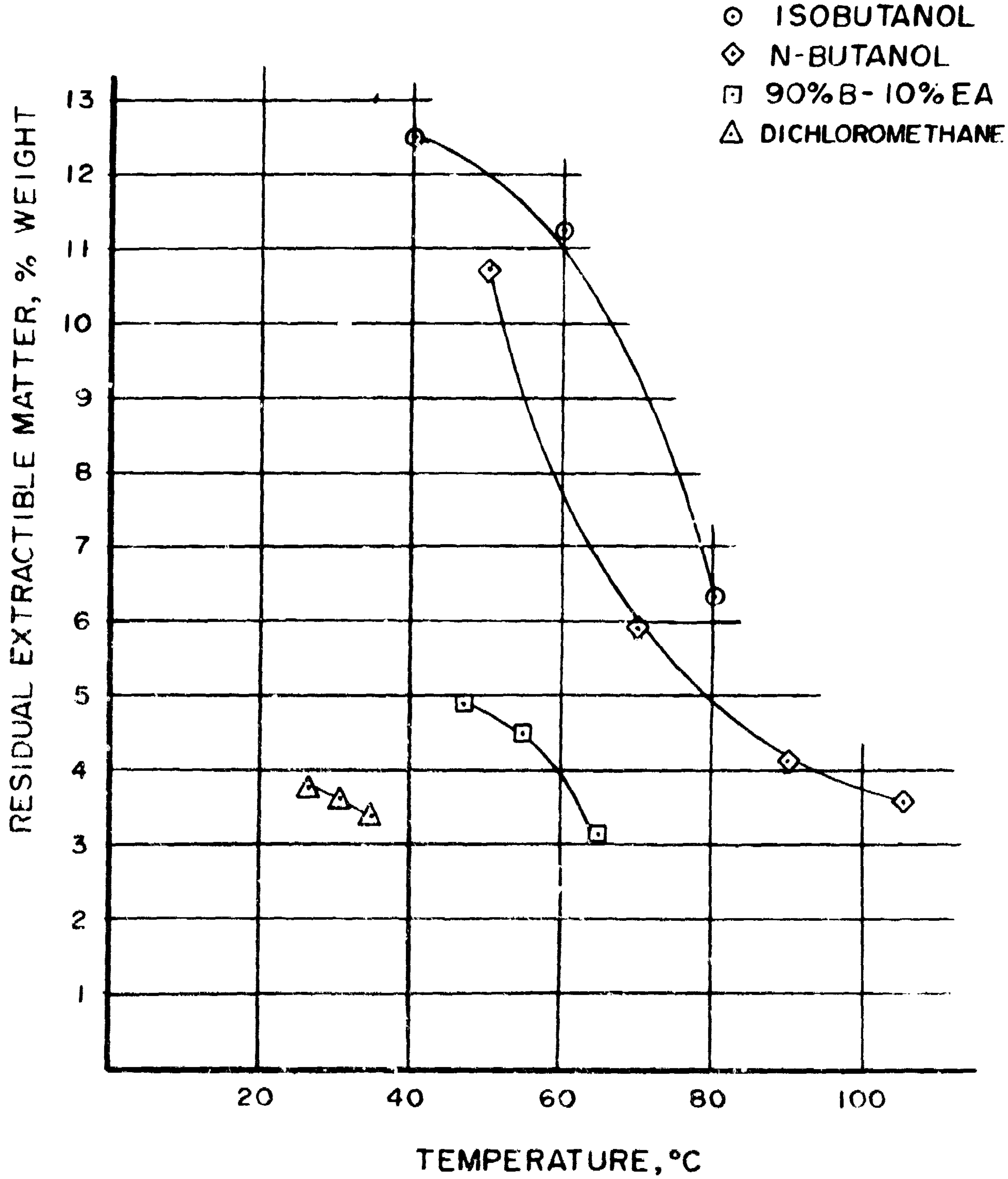

Figure 2. Effect of Temperature on Solvent Power, Comparison of Solvents

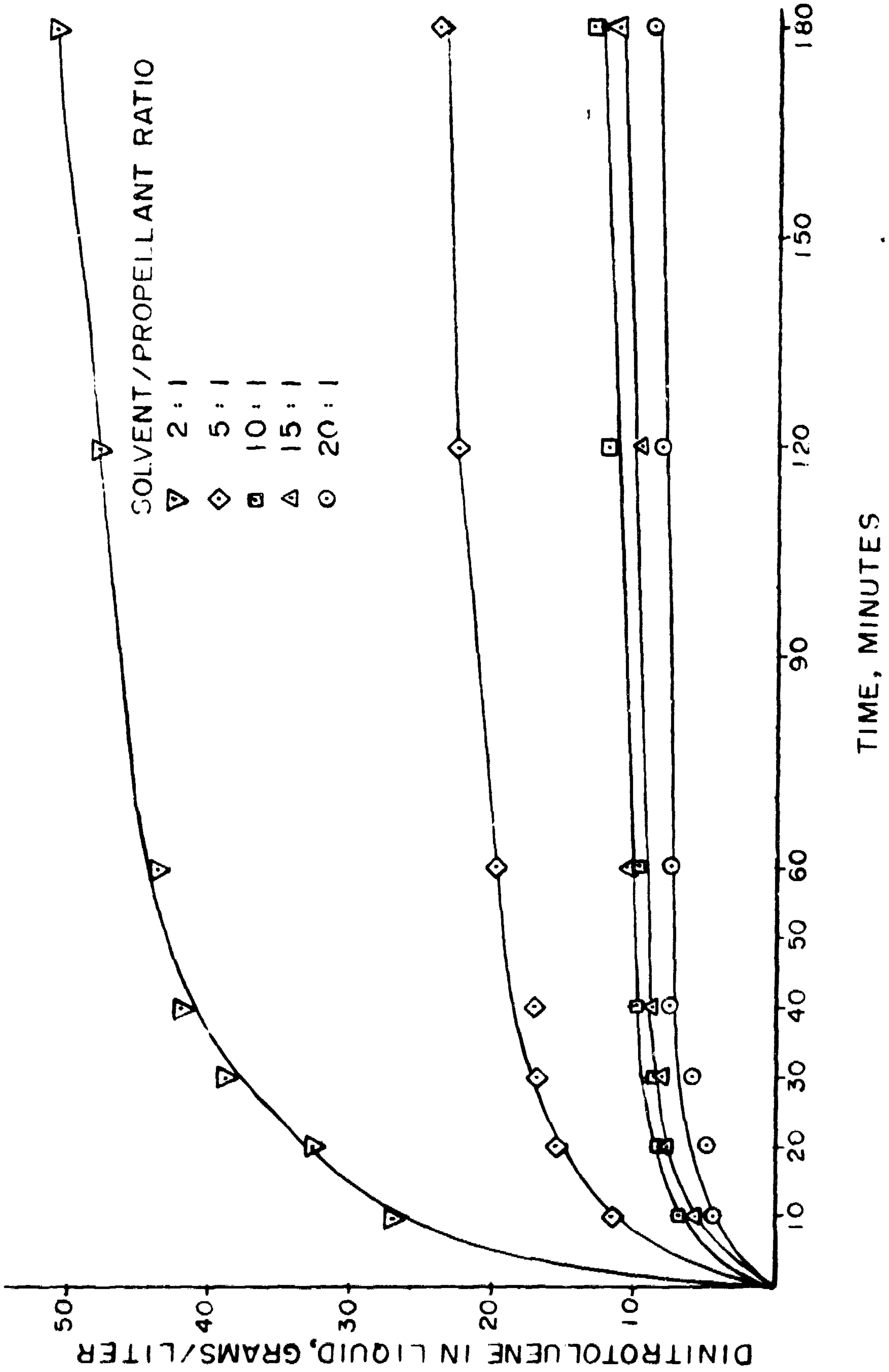

Figure 3. Approach to Equilibrium in Batch Extractions

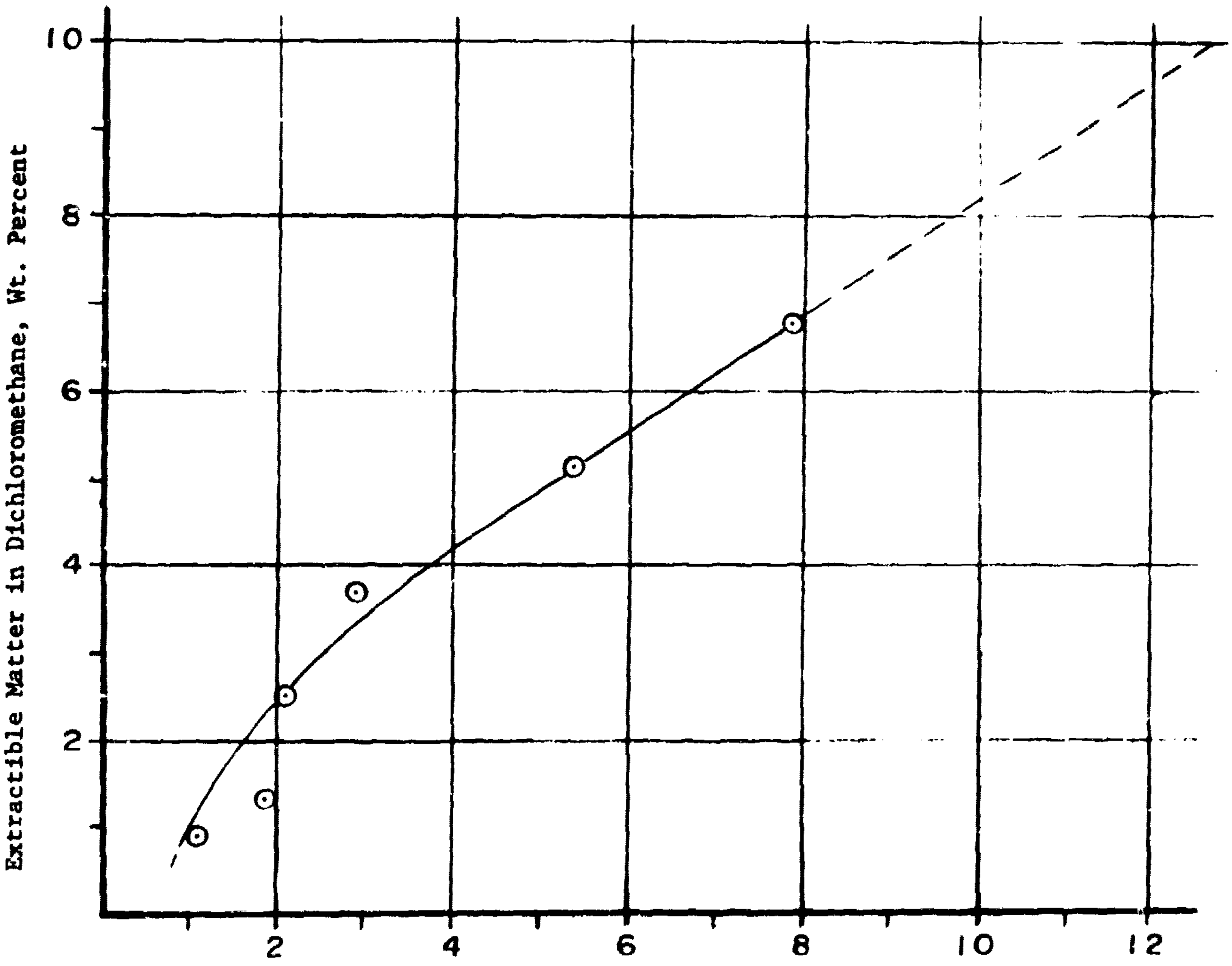

Figure 4. Extractible Matter Equilibrium Relationship

The data above show that dichloromethane can be used without EA, indicating a significant processing simplification. The highest practical operating temperature for using dichloromethane was identified as being 35°C.

Below is discussed the experimentation which has led to a design for the NC recovery operation, using dichloromethane as the selected replacement extraction solvent.

DESIGN OF EXTRACTION SCHEME

Equilibrium and Rate Data

In order to properly design the extraction process, an equilibrium relationship between the modifiers in the liquid and solid phases was required. These data were obtained in a series of batch extractions in which the initial solvent-to-propellant ratios were varied over a wide range (1:1 to 20:1). The extractions were conducted in an agitated, temperature-controlled, 2-liter resin flask. Solvent heat up and propellant addition were accomplished in similar fashion to the prior batch extractions. The duration of propellant-dichloromethane contact was three hours in all cases because it appeared from experimentation that equilibrium had been reached. Liquid samples were withdrawn from the resin flask at regular intervals and analyzed by ultraviolet spectrophotometric methods to determine the approach to equilibrium (See Figure 3). Upon completion of each experiment, the liquid phase was poured off and the solid phase air dried overnight prior to analysis for residual extractible material. In this way, each experiment yielded a solid-liquid equilibrium point and the time interval to achieve equilibrium conditions. Results from the analyses of solid and liquid phases were curve-fitted by the method of least squares. The curve representing the equilibrium relationship is shown in Figure 4. With the equation representing this curve and overall and component (unwanted modifiers) material balances derived around a theoretical countercurrent leaching stage, a computer program was written to assist in the design of the countercurrent extraction process. The results of this design and how they are incorporated in the existing process equipment are discussed below.

Selection of the Number of Stages and the Solvent/Propellant Ratio

With the assistance of a computer simulation, the minimum number of stages and the corresponding solvent-to-propellant ratio could be determined. The simulation was designed to calculate stages proceeding in reverse order. Specifically, the simulation iterated starting with the outlet powder weight fraction of 0.01 extractibles and corresponding pure solvent input. The simulation iterated until the powder feed modifier weight fraction of 0.13860 was exceeded. This value was obtained by analysis of several samples of cannon propellant. The solvent to propellant ratio was specified in the data input along with the propellant feed and product extractibles composition and solvent feed. The data output provided both propellant and solvent inlet and outlet compositions for each stage (See Appendix for sample computer output). The solvent-to-propellant ratio was varied until the minimum number of stages was determined. The results of the calculation for dichloromethane are presented and compared with the current process in Table 3.

Table 3. Comparison of Current Benzene-EA and Proposed Dichloromethane Propellant Extraction Schemes

Solvent	Number of Stages	Solvent to Propellant Ratio
Benzene-EA	3	3.8:1
Dichloromethane	2	3.125:1

A proposed scheme of using the current extraction equipment with dichloromethane as the leaching solvent is shown in Figure 5. The duration of each stage was based upon the rate data collected simultaneously with the equilibrium data. Based upon the rate data, it appeared that near-equilibrium conditions could be approximated by extraction durations of less than three hours, the equilibrium interval. Therefore, removal of extractibles for the solvent-to-propellant ratios studied was compared for one and two hour intervals (See Figure 6). It is shown for a one hour interval 82% of the equilibrium value is achieved and, similarly, for a two hour duration 91% of equilibrium is achieved. A two hour duration was selected for each extraction, since that interval adequately represented equilibrium.

Confirmation of Proposed Extraction Scheme

In order to determine the validity of the proposed extraction scheme, a test of the design was conducted in the 2-liter flask. Liquid-side equilibrium values were used for the initial solvent composition for each stage; i.e., for the first stage, the solvent contained 0.754% modifiers and in the second 0.00% modifiers in accordance with the computer simulation. The controlled temperature was 35°C and the duration of each stage was two hours. The solvent-to-propellant ratio was 3.125:1.0, also predicted by the design. The results of this test appear below in Table 4.

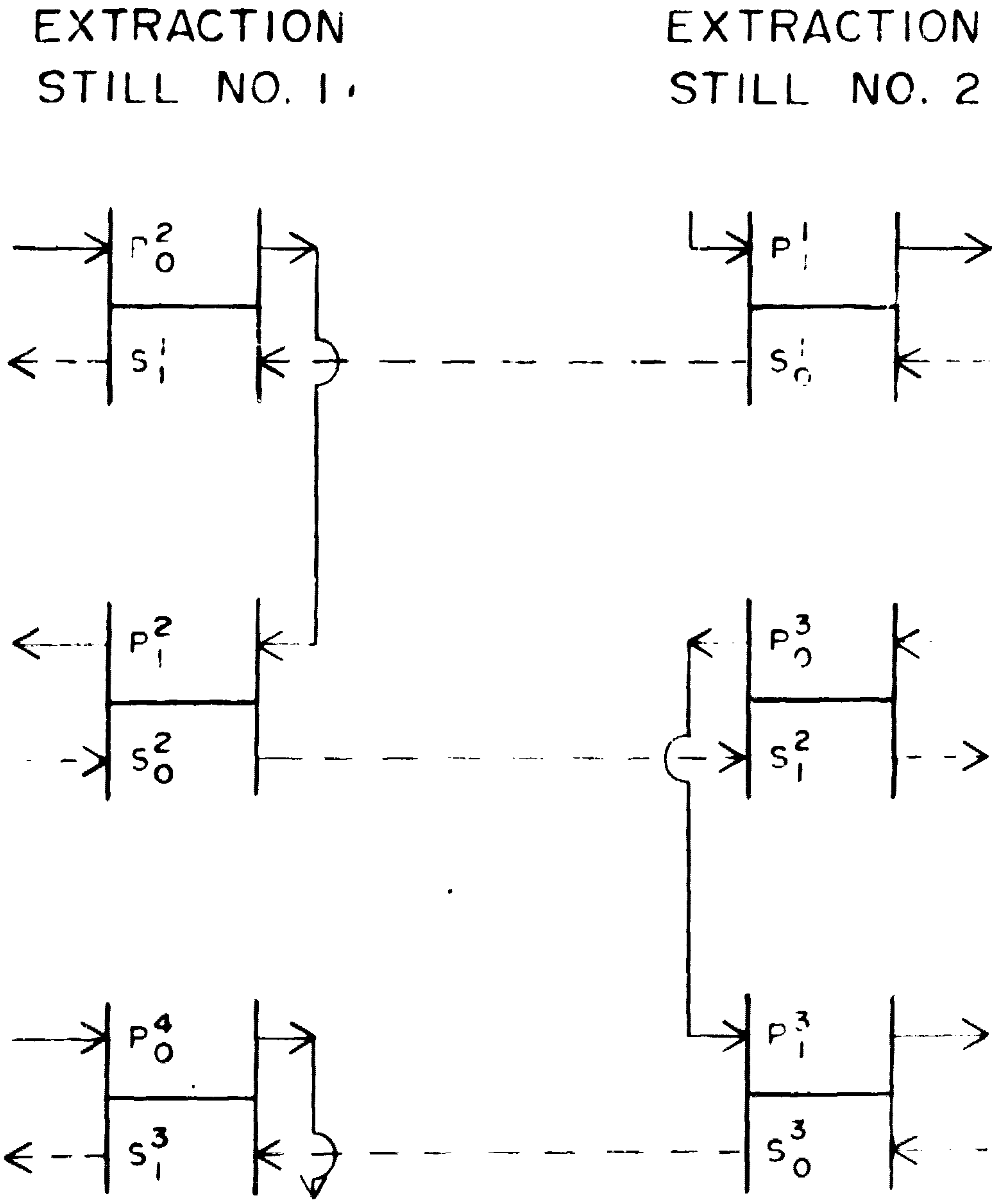

Figure 5. Proposed Extraction Scheme Using Dichloromethane

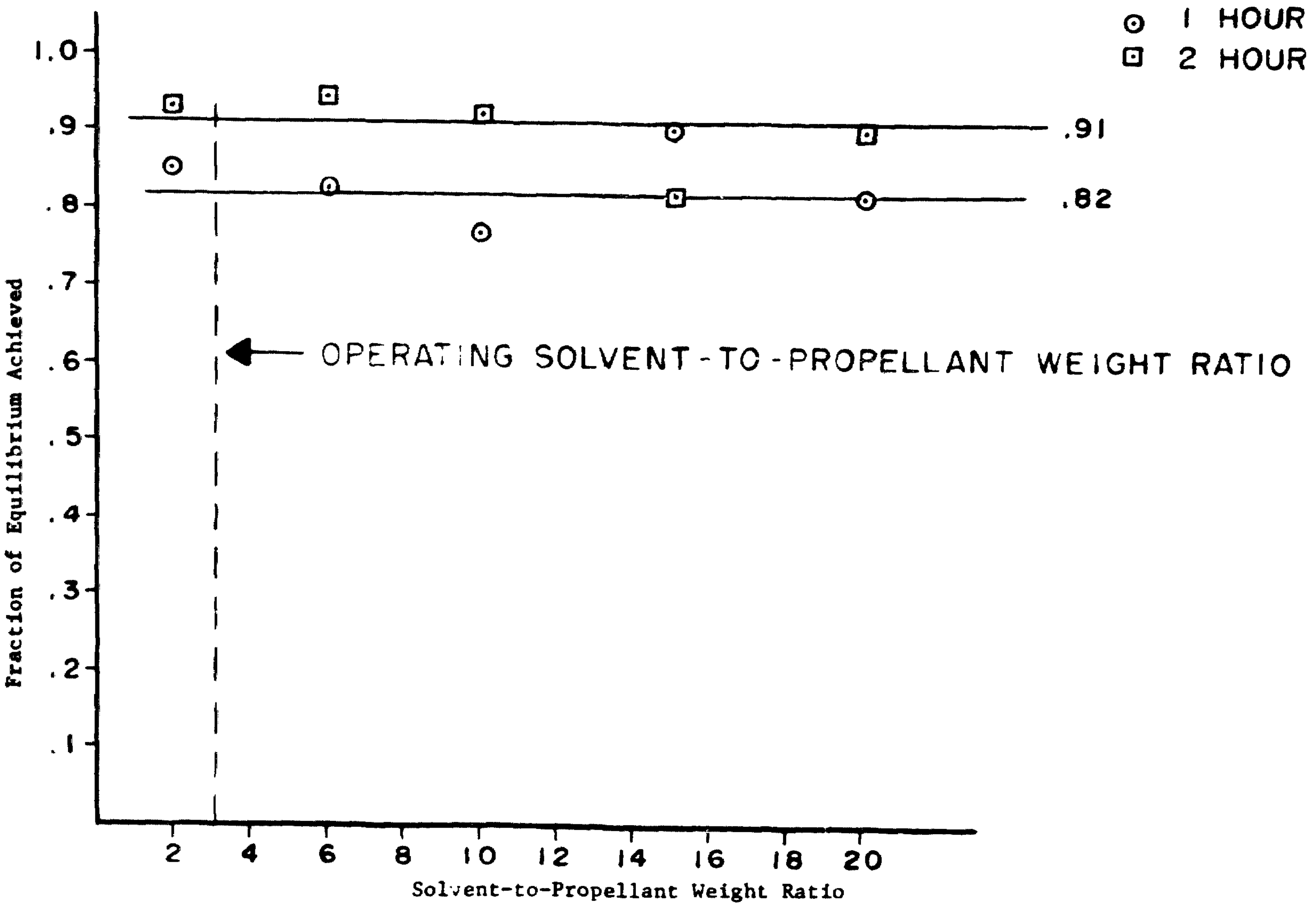

Figure 6. Determination of Stage Cycle Time

Table 4. Results from Confirmatory Test of Proposed Extraction Scheme

Stage	Propellant Residual Extractibles, % Weight	Solvent Residual Extractibles, % Weight
1	3.08	4.25
2	1.12	0.99

The confirmatory test showed that the results were consistent with the equilibrium data considering that the runs were made for a two instead of a three hour duration. It appears that only minor changes in operating conditions will be required in order to produce extracted propellant with less than 1% residual extractibles.

DESIGN OF SOLVENT RECOVERY

For the proposed extraction process, the candidate solvent must be easily recovered and recycled to the system. The ease with which dichloromethane can be removed from the extracted propellant and separated from modifier enriched solvent from the 2-stage extraction process was determined. The experimentation conducted in order to define the required processing for solvent stripping and solvent recovery is discussed below.

Solvent Stripping

A technique similar to that used for removing residual B-EA co-solvent from extracted propellant in the current production operation was employed for reclaiming dichloromethane. The recovery of dichloromethane differed in that no vacuum was required to achieve acceptable removal.

In the stripping of dichloromethane from the extracted propellant, advantage was taken of the formation of a dichloromethane-water azeotrope at 38.1°C. To the extracted propellant was added 1-liter of water. With agitation, the temperature was raised under controlled heat input in order to allow the rate of diffusion of dichloromethane from the propellant to be sufficient to permit azeotropic distillation. The temperature was then permitted to rise to 99°C and held for five minutes at which time the solvent strip was considered completed. Analysis of the stripped propellant showed 0.40% residual dichloromethane. The duration of the solvent strip was approximately eight hours. In Table 5 are compared the residual solvent levels and stripping times for both the current and proposed production schemes.

Table 5. Comparison of Current and Proposed Solvent Stripping Processes

Stripping Method	Residual Solvent,% Weight	Processing Time, Hr.
Current	3.00	15-17
Proposed	0.40	8-9

In developing the stripping process in conjunction with the use of dichloromethane, it was noticed that when applying heat for the distillation of the dichloromethane it must be applied under strict control. When heat was applied at too high a rate, the rate of distillation exceeded the rate of dichloromethane diffusion and azeotropic distillation was not achieved as evidenced by the temperature trace in Figure 7. At a lower rate of heat input, the leveling of the temperature indicates that azeotropic distillation is occurring, also shown in Figure 7. The importance of azeotropic distillation is that by this method 162 ml of dichloromethane were recovered as compared to 52.5 ml when heat was applied at an excessive rate.

Solvent Recovery

Dichloromethane which has become modifier-laden from being used in two prior extraction stages and which would be ineffectual in leaching modifiers from propellant because it is at equilibrium with the propellant was batch distilled in order to determine the conditions and ease with which pure dichloromethane could be recovered. A volume of 250 ml dichloromethane containing 2.34% modifiers, from the end of the first stage of the confirmatory test, was placed in a 2-liter flask. The temperature was raised at constant heat input until insufficient liquid remained in the flask for analysis. This coincided with a temperature of 93°C. The results of this batch distillation appear in Figure 8. In Figure 8 it is shown that dichloromethane can be recovered with less than 0.012% contaminants while the bulk fluid contains greater than 70% modifiers. Based upon these results it is anticipated that the recovery of dichloromethane can be accomplished with a minimum of solvent loss while the recovered dichloromethane will be virtually free of contaminants. In order to achieve this in a distillation column, the operating temperature would be somewhat higher than 93°C.

IMPLICATIONS OF USING DICHLOROMETHANE IN NITROCELLULOSE RECOVERY

The proposed scheme for extracting unwanted modifiers from single-base cannon propellants with dichloromethane indicates significant potential advantages over the current processing technique. The higher specific gravity of dichloromethane allows more solvent in a batch and therefore, a 55.5% increase in propellant processed per batch. Combined

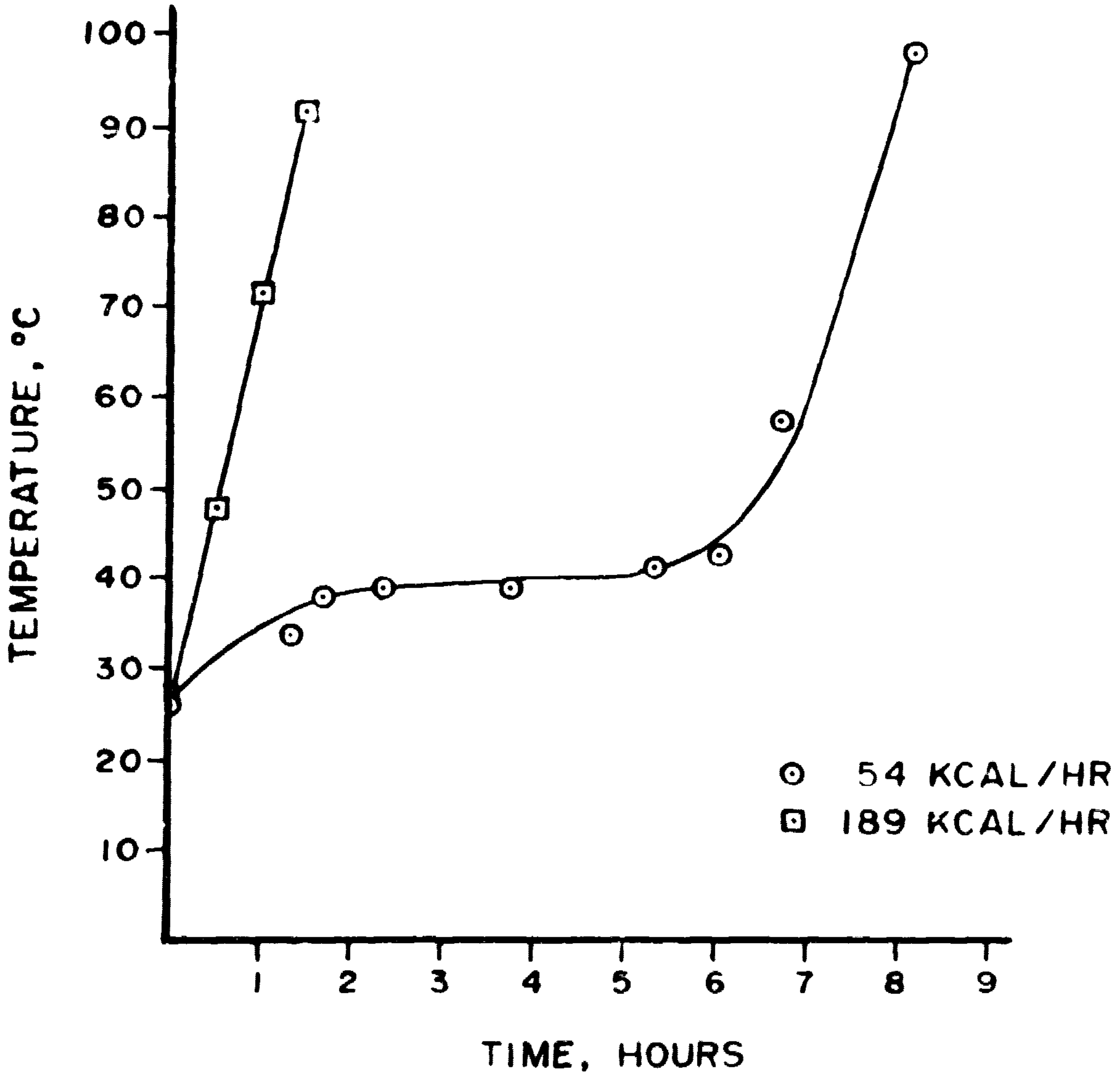

Figure 7. Effect of Heat Input on Stripping

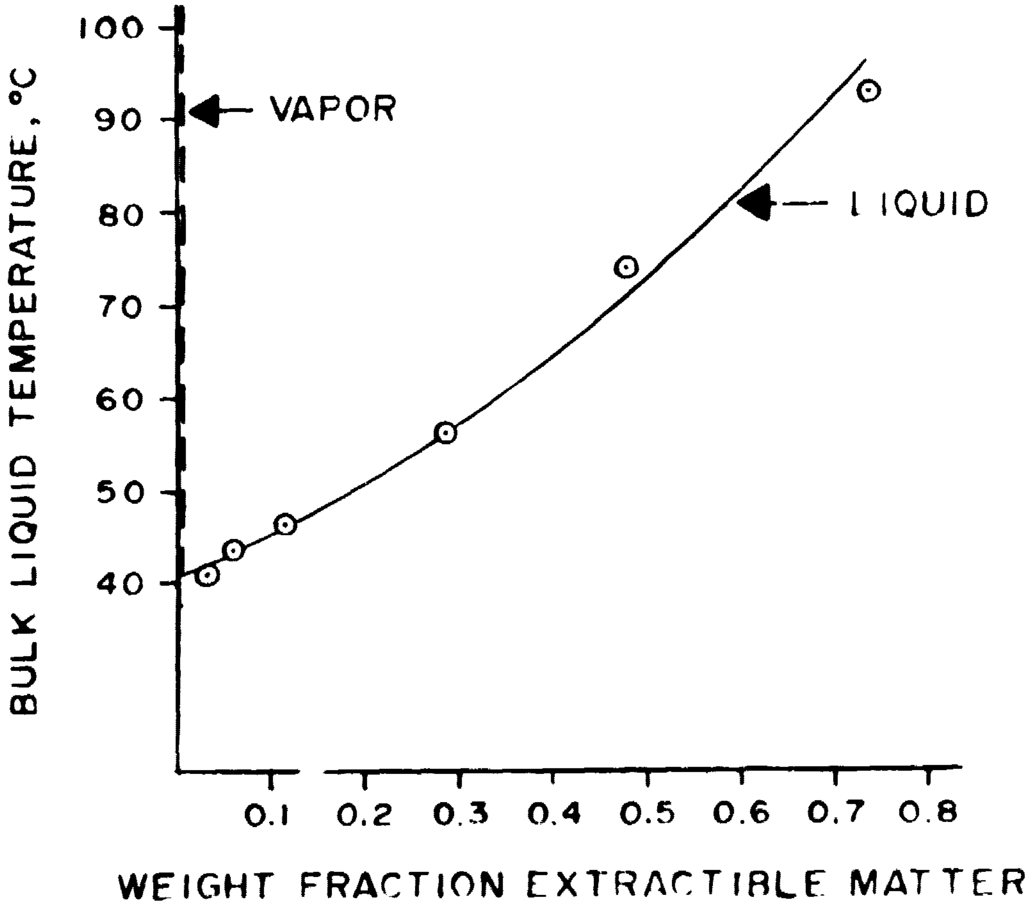

Figure 8. **Vapor-Liquid Data for Recovery of Dichloromethane**

with the reduction in stages from 3 to 2, resulting in a 30% shorter processing time for 2 batches, a 123% increase in production rate can be effected.

Less significant than increased capacity or reduced processing time, although still important, are reduced steam requirements because of the lower extraction temperature, 35°C, and the lower specific and latent heats associated with dichloromethane. Energy requirements associated with the current and proposed extraction solvents are presented in Table 6.

Table 6. Comparison of Energy Requirements for the Current and Proposed Extraction Schemes

Solvent	Extraction Cal/g Solvent	Stripping Cal/g Solvent
Benzene-EA	16.8	117.7
Dichloromethane	2.8	79.2

A further advantage of using dichloromethane is processing simplification. The reduction in stages from 3 to 2 means less handling of each batch of solvent. The ability to use dichloromethane as the sole extraction solvent makes the recovery operation more easily accomplished.

Finally, all the processing efficiencies discussed above have been accomplished as a by-product of the effort to make the NC recovery operation a safer one. The total elimination of a fire hazard attributed to the extraction solvent is achieved when using dichloromethane. The high TLV of 500ppm combined with the reduced toxicity of dichloromethane makes the extraction environment significantly easier to manage.

CONCLUSIONS

Dichloromethane is the most effective candidate solvent replacement for the nitrocellulose recovery operation.

1. Dichloromethane will improve the operating environment because of its reduced toxicity, higher O.S.H.A. threshold limit value, and non-flammability.

2. Dichloromethane will permit a 2-stage operation without the need for a cosolvent thereby greatly simplifying material handling and solvent recovery.

3. The low operating temperature and low specific and latent heats associated with dichloromethane will result in reduced energy requirements for the nitrocellulose recovery step.

4. Dichloromethane can be recovered from the extracted propellant more easily than the current extraction cosolvent resulting in lower solvent losses.

RECOMMENDATIONS

It is recommended that pilot plant extraction and stripping of surplus cannon propellant be conducted using dichloromethane in order to validate the results of the laboratory studies. Furthermore, it is recommended that an economic analysis be performed in order to assess the quantitative impact of the change to dichloromethane on the cost of NC recovery operations.

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1. Federal Register, Volume 36, Number 157, August 13, 1971
2. Sax, N. Irving, Dangerous Properties of Industrial Materials, 1968
3. Durrans, Thomas H., Solvents, 1957
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5. Mellan, Ibert, Industrial Solvents, 1950
6. Doolittle, Arthur K., The Technology of Solvents and Plasticizers, 1954

APPENDIX

Computer Output

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PROPELLANT/SOLVENT = .32000
FEED PROPELLANT EXTRACTABLES = .13860 WT. FRACTION
FEED SOLVENT EXTRACTABLES = 0.00000 WT. FRACTION
EXIT PROPELLANT EXTRACTABLES = .01000 WT. FRACTION

STAGE    PROPELLANT IN    PROPELLANT OUT    SOLVENT IN    SOLVENT OUT
  1         .14424            .03418          0.00754        .03948
  2         .03418            .01000          0.00000        .00754
```