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TREATMENT AND DISPOSAL OF HIGH-ENERGY MATERIALS

NATIONAL MATERIALS ADVISORY BOARD (NAS-NAE)

PREPARED FOR
NAVAL ORDNANCE SYSTEMS COMMAND

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This report is intended to provide an overview of naval munitions treatment and disposal, and a delineation of some suggested general and specific avenues of research and development that will enhance future progress in the area. Environmental protection and safety to personnel, as well as the engineering involved in the treatment and disposal of high-energy materials of all the services (Army, Navy and Air Force), are of primary concern. In the past, much of the work in this field has been motivated largely by expedient technological considerations. Therefore, the principal aspects of environmental impact problems underlying the more important treatment and disposal problems are discussed, and the technology of potential processes for solving these problems is reviewed.

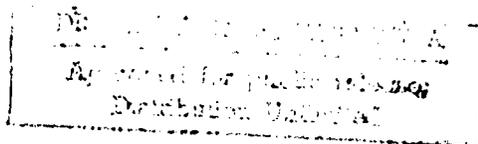
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TREATMENT AND DISPOSAL OF HIGH-ENERGY
MATERIALS AND RELATED COMPONENTS

Report of
The Ad Hoc Committee on
The Treatment and Disposal of High-Energy
Materials and Related Components

National Materials Advisory Board
Division of Engineering - National Research Council



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June 1973

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ABSTRACT

This report is intended to provide an overview of naval munitions treatment and disposal, and a delineation of some suggested general and specific avenues of research and development that will enhance future progress in the area. Environmental protection and safety to personnel, as well as the engineering involved in the treatment and disposal of high-energy materials of all the services (Army, Navy and Air Force), are of primary concern. In the past, much of the work in this field has been motivated largely by expedient technological considerations. Therefore, the principal aspects of environmental impact problems underlying the more important treatment and disposal problems are discussed, and the technology of potential processes for solving these problems are reviewed.

PREFACE

As a result of increased activity and interest in the field of pollution abatement, the U. S. Naval Ordnance Systems Command requested (in January 1972) that the National Research Council initiate an appropriate committee study of the treatment and disposal of obsolete and overage munitions. It was hoped that the study might be helpful in objectively critiquing the Navy's current Propellants, Explosives, Pyrotechnics Pollution Abatement Research and Development (PEPPARD) Program, indicating any fruitful avenues of approach that may have been overlooked.

In this assignment, which was accepted and given to the National Materials Advisory Board (NMAB), the purpose and scope of the Ad Hoc NMAB Committee effort as stated in the original letter of assignment, was, "to study a wide variety of high-energy materials, their treatment and disposal so as to provide a minimum threat to safety in handling and a minimum detriment to the environment. The simplicity, efficiency, and reliability aspects of the disposal operations are to be included as considerations in the study. However, while economics are to be considered, in a general sense, economics are not to be dealt with in terms of any detailed assessment. Examples of items that will come under the purview of the Committee include explosives, mines, ammunition, and missiles. Nuclear, biological, and chemical warfare materials are excluded."

In general, the objectives of the study were "to provide the Navy with evaluations of technical options (suitable and acceptable alternate techniques and procedures) for disposal of a wide variety of high-energy materials, and components and equipment containing such materials, including the probable consequences, advantages, and disadvantages of each, particularly in relation to detriment to the environment, and to recommend appropriate programs of research, testing, and development leading to improved technology in this field..."

Specifically, the Committee was asked to attempt to make:

- "an analysis and categorization of existing items,
- a critical review of current treatment and procedural steps from the storage state to the disposal stage, with identification of problems,
- an assessment of possible disposal techniques, procedures and sites, such as burial (e.g., in deep cavities and worked out mines), recycling as explosives, reprocessing into other useful chemicals, incineration, selective and improved ocean disposal,
- a determination of advantages and disadvantages of the various options, including consequences of their use such as environment contamination, risk of subsequent explosion and damage, risks in handling and transportation,

- identification of areas in which additional research, testing, and/or development is required,
- the postulation of novel approaches (e.g., uses for high explosives in geological test work),
- some definition of such other problems, with approaches to their solution, as might emerge from the above studies, including adequate consideration of the disposal problem during the development stage of the material or component, in order to alleviate subsequent disposal."

With this charter, the National Materials Advisory Board Ad Hoc Committee was established and met for its first meeting in April 1972.

In approaching its task, the Committee realized fully that while its specific assignment originated in the Navy Department, the problem in perspective was common to the three services of the Department of Defense. Thus the Committee in its deliberations endeavored to obtain a detailed insight into the DOD problem by evaluating the state of the art in research and development in U. S. industry and in each of the services.

It is encouraging that research is being actively coordinated within the services, notably by Army and Navy personnel who are concerned with the overwhelming majority of the material involved. However, the search for the best methods to dispose of obsolete-overage munitions economically with a minimal detrimental environmental impact and signi-

ificantly small safety hazard to personnel is still felt to represent a formidable long-term challenge.

The Navy believes that the four most salient current demilitarization problems facing the services are:

- the breakdown of large missile motors
- the development of binders that can be easily degraded in future disposal operations
- the purification of process water
- explosives reclamation.

These, therefore, are the primary subjects discussed in detail in this report.

The Committee held seven formal one to two-day meetings during the period of April 1972 - March 1973, and its deliberations were aided by a number of individuals from various U. S. military agencies. Specifically, in this regard, grateful acknowledgment and thanks are given to the following guests of the Committee who contributed tutorial-type presentations at various meetings:

Captain John Bres, USN, Naval Ordnance System Command, Washington, D. C.

Frank Crist, Army Materiel Command, Tooele Army Depot, Tooele, Utah

R. S. Fey, Hercules, Inc., Wilmington, Delaware

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William McBride, U. S. Naval Weapons Station Yorktown, Virginia

William McQuiston, U. S. Naval Ordnance Station, Indian Head, Maryland.

Any expression of acknowledgement and thanks would be quite incomplete without a special mention of the untiring support and creative contributions of Donald (Don) G. Groves, the professional staff member of the National Academy of Sciences, assigned to this Committee. To him and to all the others who gave their time and energy to the work of the Committee, we are most grateful.

John C. Warner
Chairman, Ad Hoc Committee
on the Treatment and Disposal
of High-Energy Materials and
Related Components

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I.

INTRODUCTION

General

The amounts of high-energy materials for use in ammunition, rocket motors, torpedoes, mines, etc. produced for the U. S. Department of Defense per year and the tonnages of such materials actually used varies widely depending upon military needs. In general, however, for a variety of reasons, such as the need for planned excesses to meet possible contingency requirements, the annual production rate usually exceeds the anticipated usage rate by several kilotons. The tonnage declared obsolete each year is also quite variable depending upon several factors, but primarily on the success of new munition developments (e.g., a new missile motor might replace an older one causing the latter to be declared obsolete). Of course, as the quantities of defective, overage, or otherwise dangerous and non-reclaimable munitions accumulate, the diverse problems of disposal must be faced. Currently, the Navy inventory of such explosive disposables, accumulated over a number of years, totals about 90,000 tons (see Chart No. 1).

CHART No. 1

NAVY AMMUNITION AVAILABLE FOR DISPOSAL (KILOTONS)

(30 October 1972)

Bombs.	2.7
Pyrotechnics	0.2
Depth Charges.	5.8
Demolition Explosives.	0.2
Smokeless Powder	5.0
Mines.	12.8
Rockets.	2.3
Marine Corps Ammunition.	15.0
Bulk Explosives.	0.8
Small Arms Ammunition.	6.4
Gun Ammunition, 20mm to 4 inch	33.1
Gun Ammunition, over 4 inch.	1.9
Torpedos	0.4
Miscellaneous.	2.0
	<hr/>
	88.6

In May of 1971 this figure was 80,000 tons. At that time, in a Navy staff study, "Alternatives to Deep Water Dumping of Ammunition and Explosives," prepared for the Secretary of the Navy, the following pertinent opinions and observations were made:

"The Navy inventory of explosive disposables totals 80,000 tons. At least 50,000 tons are potentially useful and can be either demilitarized for recycling of components or stored and retrieved for processing at a later date. Of the 'hard core' remaining, approximately 25,000 tons consist of certain encased ammunition which, for reasons of safety, cost or infeasibility, cannot now be broken down into inert and active components. Usable explosive surpluses, scraps, tailings and residues from loading and processing plants, approximately 5,000 tons, present less of a problem. The latter can be burned in enclosed incinerators.

"The most available alternative to deep water dumping (DWD) for small encased ammunition (up to about 3 inches in diameter) is controlled incineration and detonation in specially designed plants. Approximately 15,000 tons of the hard core disposables could be destroyed acceptably with this method. Another 10,000 tons, containing ammunition too large for disposal in this way should be considered for deep water dumping or for more elaborate means such as destruction in a deep earth cavity. Some portion of this category may be susceptible to incineration with the Army's new techniques for cutting large diameter ammunition into smaller chunks. A joint service program may be appropriate ..."

It should also be noted that in the past and until February 1971, the U.S. Navy for reasons of safety and economy had customarily disposed of 3,000 tons or less per year of various types of such obsolete munitions by dumping them in carefully selected deep parts of the sea --

a complex chemical-physical vat containing profuse and diverse biota. Although the detailed effects of such a practice upon this environment still are not well understood, it has been postulated and in some cases fairly well established that there are no widespread effects and relatively minor local effects.

However, it is definitely recognized that the oceans are critical to maintaining the world's environment, contributing to the oxygen-carbon dioxide balance in the atmosphere, affecting global climate, providing the basis for the world's hydrologic system, and a base for much of man's necessities such as food and potential minerals. The importance of this reservoir of vital benefits to man raises questions as to the propriety of using it as the receptacle for unwanted waste materials, even in carefully selected sites. On the other hand, some judicious method of ocean disposal of munitions may be possible and may still serve as an alternative to burning them in the open--a practice that is often hazardous, noisy, and a source of air pollution. Among the other alternatives to ocean disposal are: efficient dismantling for recycling and reuse of critical components, mass underground burial or detonation and incineration under controlled conditions.

The U.S. Navy has exhibited an awareness of the above-mentioned general alternative procedures for munitions disposal. Accordingly, the Naval Ordnance Systems Command has, and especially since the suspension of deep water dumping in February 1971, initiated comprehensive research and development programs to determine methods and comparative

costs for implementing such procedures and also has undertaken programs for conceptual design of disposable munitions, new explosives, new means for disposal, etc.

Outline of the Committee Report

Section II of this report contains summary and perspective statements as well as a number of recommendations both of a general and technical nature. Some of these concern further research in various areas which, in the opinion of the Committee, might profitably be pursued in the future. The recommendations should be viewed in the context of the discussion contained in the main body of the report.

Also to assist in the assessment and probable augmentation of the overall research and development program, one section (Section III) of this Committee's report provides a broad review of the Navy's current program and outlines some suggestions for other possible topics to be considered for investigation. In this regard the reader should not expect a comprehensive critique of the program in the sense the term is generally understood by the research community. It can and should be viewed rather as an overview of the objectives of the program with advisory services provided by the Committee as to the relative merits of the various generic and specific approaches now being taken or possibly being overlooked by the U. S. Navy.

The next four sections of the report (Sections IV through VII respectively) are devoted to discussions of the four generic-type methods that may be employed in the treatment and disposal of high-energy materials (HEM). These four methodologies can be broadly classified as:

- Disposal via chemical change and/or recovery of basic ingredients. (Section IV)
- Disposal with no chemical alteration, decomposition, etc. (Section V)
- Disposal after chemical change of the end products of combustion, detonation, etc. (Section VI)
- Other means of disposal and other ways of alleviating the disposal problem. (Section VII)

Section IV of the report constitutes the largest portion of the Committee's discussion. It covers the problems and a state of the art overview in chemical transformation disposal treatment and the recovery of basic ingredients of high energy materials. One such problem which is highlighted in this section of the report is how to degrade and extract polymer binders from propellants.

The problem of disposing of this type of obsolete propellants is an especially difficult one because of legal limitations on burning and dumping. Moreover, the cross-linked nature of the binder makes it extremely difficult to dissolve it in solvents. The encasement of oxidizer and metal particles in the water-insoluble binder also makes it impossible to remove the water-soluble oxidizer by solution in water. Some suggestions for chemically degrading these

binders under conditions which might permit economic recovery of a large portion of the components of the propellant is discussed.

Section IV is also concerned with the fundamental ideas of water use, reuse and/or effluent discharge problems involved in the treatment and disposal of high-energy materials. The judicious use of ground or subsurface water supplies in the manufacture as well as in the treatment, disposal and recovery of munitions is discussed with the objective of achieving maximum environmental protection. A program is recommended for the future.

Section V is addressed to a discussion of the ways to dispose and/or store untreated live munitions and other high-energy materials. The alternatives and merits of such methods both on land and at sea are delineated.

In the next section (VI) the Committee has reviewed procedures for disposing of live munitions and other high energy materials by detonation and burning at sea and various land sites.

Section VII, the final portion of this document, is a brief discussion of some other possible ways of alleviating the disposal problem.

II.

SUMMARY OF RECOMMENDATIONS AND OBSERVATIONS

The Committee has (1) reviewed and studied the magnitude and character of the problem of disposing of obsolete munitions and other high-energy materials; (2) studied disposal methods used in the past and the present; (3) examined methods and processes which are in the development stage; (4) critically reviewed the research and development programs of the Services, especially the Navy's, and as a result documents here in its report a brief summary of recommendations.

GUIDING PRINCIPLES

The Committee has used the following guides in reaching these conclusions and recommendations:

- The United States should assume a position of leadership among the nations of the world in developing processes and practices for the disposal of obsolete munitions and high-energy materials which insure maximum safety to personnel and minimum damage to the environment.
- The potential hazards should include those of a long-range potential as well as those involved in the immediate process of disposal.
- Disposal methods should not be used which create more hazard to personnel or more prospective damage to the environment than would be probable if the obsolete material was simply kept in storage, provided it appears that more satisfactory disposal methods can be developed in the foreseeable future.

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- The Committee goal is to recommend methods which meet reasonable standards without exorbitant expenditures for research, development, or capital investment.

As a minimum such schemes should be developed and put in operation with adequate capacity to handle the volume of obsolete materials expected annually in peace time.

- The Committee favors processes and methods which separate and recover the constituent materials for recycling or for other-purpose use.
- Areas to be used for detonation or burning should be selected on the basis of:
 - a. minimal living populations
 - b. a relatively hostile natural environment
 - c. adequate remoteness from frequently travelled transit routes
 - d. general lack of significantly useful mineral resources
- Although this study was requested by the U. S. Navy, the Committee realizes that the disposal of obsolete/overage high-energy materials and munitions is in reality a Department of Defense problem. Hence, we have considered it proper to inquire into the magnitude of the disposal problem for all the Services, and to learn as much as possible about the schemes for disposal in use or under development by the Army and Air Force as well as the Navy.

The principal observations and recommendations of the Committee are summarized as follows:

1. Recycling

It is recommended that disposal methods involving no chemical change, but involving mechanical and physical processes for the reclamation of the components for recycling, be used whenever they meet standards of safety to personnel, protection to the environment and are reasonably economical.

Although some serious technological problems remain to be solved, the Navy has had considerable success at reclaiming bulk explosives and the constituents from devices such as bombs, mines, depth charges, torpedoes, large caliber shells, etc., by steam and/or hot water washout, melt out, etc. Sophistications and improvements to these methods of recycling should be carried out. Moreover, for devices containing relatively large quantities of high-energy materials, the recovery of materials for reuse might bear a significant portion of the cost of disposal. The major problems remaining in the reclamation of non-plastic bonded munitions are: (a) the development of a process for cleaning up wash and steam-out water; and (b) the purification of recovered high-energy materials for reuse.

2. Controlled Detonation

It is recommended that the controlled detonation of certain types of high-energy materials carried out at or below, but near the ocean surface, over carefully selected

areas (e.g. those continental shelf toe (deep) areas where self-burial of the debris by submarine delta action can take place) continue to be explored. However, the Committee considers this to be a permissible disposal method only when other methods would be too hazardous, uneconomical or more harmful to the environment.

The Committee believes that this lesser desirable method of disposal is nevertheless feasible since it is felt that it would be essentially non-detrimental to the environment and ideally the debris of material would be buried in the deep ocean by submarine delta action. Such a disposal method, however, does require appropriate in-situ experiments to be carried out in carefully selected areas of the ocean to systematically monitor the effects on marine flora and fauna.

3. Controlled Detonation - Underground

It is recommended that controlled detonation of munitions and other high-energy materials in appropriate configured underground cavities be used if recycling is unsafe or uneconomical.

In some cases, high-energy materials have been disposed of in underground vaults by either detonation and/or incineration by U. S. industrial manufacturers (e.g. DuPont). Such a method of deep underground detonation has also been recommended in the Navy's 25 May 1971 report, "Alternatives to Deep Water Dumping of Ammunition and Explosives." Both new excavations and worked-out mines, caverns and other underground openings have been successfully utilized for these kinds (detonation and incineration) of disposal.

4. Gaseous Effluent Clean-up

It is recommended that the search for a reliable and economical process for removing the pollution gases evolved in the disposal process be continued.

Obsolete small arms ammunition can be disposed of by contained detonation or combustion in thick-walled, rotary, kiln-type devices with safety to personnel and with recovery of metal parts. However, a technological problem remains, namely, that of developing a reliable and economical means for removing polluting gases such as CO and NO_x from an explosively surged stream of gaseous effluent.

5. Burning and Disposal of Plastic Bonded Explosives and Propellants

The Committee recommends that the Navy continue its search for a solution to the problems posed in the destruction of plastic bonded explosives and propellants by (a) investigating the feasibility of burning on barges at sea; and (b) developing processes whereby the constituents may be recovered without chemical change for recycle or other use.

Considerable difficulty has been experienced with the disposal of obsolete munitions in which the explosive or propellant is plastic bonded. The need is for developing a disposal or reclamation technology which is safe for personnel and not harmful to the environment. Open pit burning on land of such devices is no longer tolerable. However, the burning and disposal of the residue

products of these burnt materials at sea (see also Recommendations 2, 7, and 8) under properly controlled conditions offers a potential means of disposal as do some recycling processes now under study and development (Recommendation 4).

6. Burial Underground

It is recommended that disposal of live munitions and other high-energy materials by burial underground (e.g., in cavities or worked-out mines) be considered one of the least desirable disposal methods, under most circumstances.

The Committee believes, however, that some high-energy materials can be safely stored temporarily at various underground sites. Locations that can be utilized are:

- (a) those that can be kept safe from human sabotage, accidental explosions and the effects of natural disasters;
- and (b) where contamination to ground water from the stored materials will not take place.

7. Ocean Dumping

It is recommended that disposal of live munitions and other bulk high-energy materials by dumping them onto the ocean floor be prohibited, at least for the foreseeable future.

This method would be hazardous for personnel who in the future might explore the ocean floor for scientific purposes, for natural resource recovery, for cable laying, etc. Moreover, we have no reliable information about the possible effects on marine flora and fauna in the ocean when container corrosion products or the contained high-

energy materials are introduced into this environment. All such questions need to be answered before such disposal can be considered to be carried out even in what may now be deemed a carefully selected location for dumping.

Accordingly, we feel that only a very limited disposal of high-energy materials at sea should be permitted, and then only provided they are burned or detonated in known regions of very low sea life population and in those areas where the resulting solid trash will be buried by relatively rapid geologic processes. (See also Recommendations 2, 5 and 8).

8. Navy R&D Program - General

The Committee recommends that the Navy's (PEPPARD) program be strengthened in its more fundamental and long-range aspects.

The Naval Ordnance Systems Command Research and Development program appears well conceived, appropriately planned, and directed toward the resolution of some of the most important current problems of pollution abatement in the disposal of obsolete munitions and high-energy materials. It should be expanded in speculative areas that show promise of possible technological advances and schemes for disposal by controlled detonation in selected locations underground and at sea. The programs for dealing with plastic bonded explosives and propellants and double based propellants by chemical and physical degradation of the binders seem especially important and deserve increased support.

9. R & D Program Munitions Design

We recommend that a real effort be continued to design munition systems so that when they become obsolete they may be disposed of safely and efficiently.

In this regard the Committee realizes, however, that military effectiveness, reliability in use, and safety to military personnel must have first priority considerations in the design and manufacture of ordnance materiel. Nevertheless, there is a definite need to design munitions so that future disposal problems are alleviated. The design parameters in this regard are not thought to be incompatible on any first principles basis with those affecting military effectiveness, reliability and use in safety.

10. Organization

We endorse the creation of the recently formed permanent organizational device within the Department of Defense for coordinating efforts, eliminating duplication and for solving both short-range and long-range problems concerning the proper disposal of high-energy materials.

The Committee recognizes that the separate Services utilize munitions which are very similar and that the problems of disposal when obsolete are similar. Therefore, the safe and environmentally satisfactory disposal of obsolete high-energy materials is a Department of Defense (DOD) problem. It may be that the entire continuing effort should be a DOD affair; and perhaps even under this arrangement, each Service should undertake responsibility for disposal of certain types of obsolete ordnance for all the Services.

Other Recommendations

Various other recommendations and suggestions are listed in the summary chart contained in Section III ("A Critique of the Navy's PEPPARD Program") of this report. Additionally, other recommended approaches to various specific problems are outlined within the body of the report in Sections IV, V, VI, and VII.

III.

A CRITIQUE OF THE NAVY'S PEPPARD
(PROPELLANTS, EXPLOSIVES, PYROTECHNICS POLLUTION
ABATEMENT RESEARCH AND DEVELOPMENT) PROGRAM

Introduction

Explosive ordnance has a limited storage lifetime due to degradation as well as obsolescence and must be disposed of after the safe operational period has passed. The methods of disposal of ordnance must be safe, economic, and compatible with the environment. Until recently, disposal methods often consisted of dumping at sea, burning, or other means that have unattractive ecological implications. Currently, because dumping of ordnance at sea is no longer permitted, and a number of states have imposed a total ban on burning explosives, a need exists to seek alternative methods of disposal. A research and development program to deal with the problems presented by the inventory of high-energy materials has been defined and funded by the Naval Ordnance Systems Command. The aim of this program is to identify and characterize new, safe, less expensive and ecologically acceptable methods of disposal.

The particular inventory of materials changes with time, reflecting disposal activities, obsolescence and deterioration and the addition of new material. As previously mentioned herein (Chart I) the following is a representative inventory (as of 30 October 1972).

For the purpose of discussion, it is intended to be illustrative of the magnitudes involved, but not precise.

	Amount (kilotons)
Bombs	2.7
Pyrotechnics	0.2
Depth Charges	5.8
Demolition Explosives	0.2
Smokeless Powder	5.0
Mines	12.8
Rockets	2.3
Marine Corps Ammunition	15.0
Bulk Explosives	0.8
Small Arms Ammunition	6.4
Gun Ammunition 20 mm to 4 in.	33.1
Gun Ammunition Over 4 in.	1.9
Torpedoes	0.4
Miscellaneous	2.0
Total	<hr/> 88.6

The Navy's Program

The current DOD Research and Development Planning Summary for the Navy's Pollution Abatement R&D High-Energy Chemistry Program (form DD 1634) states the Objectives and Fiscal Year '73 Plans and Progress.

The Navy's Pollution Abatement R&D Program (form DD 1634)

"Objective:

Significant quantities of waste energetic materials (PEP: propellants, explosives, and pyrotechnics) are generated during manufacture, rework and ultimate disposal of ammunition. Conventional disposal methods degrade the environment (open air burning, land fill, sea disposal, discharge of contaminated process water). This Task Area is intended to develop new methods to reuse or reclaim these waste materials or to eliminate them entirely.

"Approach:

Conduct a survey of PEP ingredients, products and by-products discharged to the environment through NAVORD munitions manufacture, rework and disposal. Develop methods to reclaim or reuse excess explosives. Develop methods to reclaim propellants and pyrotechnics or to convert them into useful materials. Develop weapon design techniques that will facilitate reclamation of the weapon's PEP load. Determine whether there is a Navy chemical agent disposal problem. Determine the extent of pollution unique to the disposal of NAVORD packaging. Investigate microbiological and other means of eliminating PEP contamination from process waters. Determine the feasibility of developing explosives with compositions that have inherent disposal characteristics. Develop technology to minimize undesirable effects from required underwater explosions.

"Plans: FY 73:

Update the survey of NAVORD PEP pollutant materials. Complete the investigation of methods to reclaim and degrade conventional PEP materials. Initiate prototype fabrication using weapon design techniques that favor PEP reclamation. Develop techniques to establish practical biodegradation and nonbiological systems for process water decontamination in the field. Prepare and evaluate explosives ingredients having inherent disposability. FY 74: Update the survey of NAVORD PEP pollutant materials. Develop procedures to reclaim and degrade PEP materials of the most recently developed formulations. Evaluate disposal oriented weapon design techniques under conditions of service use. Fabricate and evaluate field prototype systems for process water decontamination. Formulate and start evaluation of complete explosives compositions using the disposable ingredients previously developed.

"Progress:

Initiated (1) a comprehensive inventory of NAVORD-generated PEP pollutants; (2) development of methods to reprocess Explosive D, Comp A-3 and HBX-1; and (3) an investigation of the separation and recovery of propellant ingredients by solvent extraction.

"Accomplishments:

Developed process used to reclaim 6 million pounds of TNT originally scheduled for deep water dumping (DWD). Developed ultramicro analysis techniques to

measure explosives content of sea water in parts per trillion: (10¹²)² samples from two DWD sites showed no detectable explosives contamination. Published report on physical effects of underwater explosions on ocean environment. Developed separation process that permits recycling magnesium from flare production waste. Conducted tests indicating that biodegradation of TNT occurs naturally."

In further brief summary of the above, and, by generic categories of the high-energy materials to be disposed of, the Navy's current Research and Development program consists of the following:

- Bombs, Depth Charges, Mines and Warheads for Torpedoes and Rockets

Commonly these are filled with TNT, Comp. B (RDX/TNT:60/40), H-6 (RDX/TNT/Al/Wax:29/45/21/5), or Tritonal (TNT/Al:80/20) which can be washed or steamed out of the case and, after appropriate processing, it is reusable. The removal of other explosives, such as plastic bonded explosives, is being investigated. The washout procedure has the disadvantage that it produces large quantities of water contaminated with explosives. This water has to be purified by passing through a bed of charcoal or resin, which in turn must be incinerated or reactivated, in an environmentally acceptable manner. Bench scale tests indicate that biodegradation of the explosives would be more satisfactory than adsorption and the practicality of this approach is being investigated.

■ Pyrotechnics

At the present time excess/obsolete pyrotechnic materials are burned; however, laboratory results show that the active ingredients of illuminating flares can be separated into their major constituents: powdered magnesium and sodium nitrate for reuse in pyrotechnics. A pilot plant for this process will be built in the near future. Signal flare compositions are being investigated for possible recovery of the phosphorus that they contain.

■ Demolition Explosives, Smokeless Powder and Bulk Explosives

Most of these are presently being burnt. The Navy is now investigating the problems of reclaiming for reuse, Comp. A-3 (RDX/wax: 91/9) and Explosive D (ammonium picrate). As mentioned above, Comp. B, Tritonal and TNT are being recycled. The capability exists to reprocess single base smokeless powder.

■ Rocket Motors

Small rocket motors are cut apart and fed into incinerators. The difficulty is that of scrubbing the exhaust gas, and various techniques are being investigated by the Army. The Navy is investigating alternatives to conventional incinerators: wet air oxidation, combustion in fused salt baths, and fluidized bed incinerators.

At the present time large motors are burnt in the open. The Navy is investigating means to degrade binders so that in

the future, propellant and explosive compositions might be reprocessed. In addition, easily degradable binders are being sought for use in future explosives and rocket propellants.

- Small Arms Ammunition

In some instances this ammunition is incinerated, and in others, it is pulled apart to recover the propellant. In both instances the metal parts are recovered and sold as scrap.

- Gun Ammunition, 20mm and larger

These 20mm rounds which have explosive warheads are detonated, usually in a closed furnace. Although the explosive could be removed for reuse, this is considered uneconomical for small rounds. With larger rounds, such explosive recovery is sensible and the safe recovery and reuse of the explosives are being investigated.

The current Naval Ordnance Systems Command Pollution Abatement Research and Development work was reviewed and the comments of the Committee are given in the following Table I:

TABLE I NSIC Pollution Abatement and Research and Development Program - Comments

<u>Current Program</u>	<u>Committee Comments</u>
<p>I. <u>Review and Survey</u> Determination of pollution problems and formulation of solutions for Navy activities in disposal of propellants, explosives and pyrotechnic materials.</p>	<p>I. Special emphasis should be placed on identifying suggestions for future R&D. This should be a continuing program with a view toward updating all phases of the R&D program in the light of progress in the field.</p>
<p>II. <u>Reclamation</u> (a) <u>Explosives</u> - conduct exploratory and advanced developments on chemical processes involved in the reclamation and reprocessing of solid explosives. (b) <u>Pyrotechnics</u> - conduct exploratory and advanced developments on the physical and chemical processes involved in the disposition and decomposition of flares, igniters and pyrotechnics. (c) <u>Rocket Motors</u> - conduct exploratory and advanced developments on the physical and chemical degradation of propellant binders.</p>	<p>II. The Committee commends the Navy on its long-range approach to reclamation of high-energy materials. Funding of such projects should be continued.</p> <p>It is recommended that R&D be continued to develop the technology necessary to dispose of obsolete pyrotechnics by reclamation of their components without polluting the environment. Generally, pyrotechnics for disposal can be kept in temporary storage until the necessary reclamation technology is developed. If obsolete pyrotechnics cannot be kept in storage awaiting the development of reclamation technology, it may be possible to dispose of these materials by burning on specially constructed barges towed out to selected locations at sea.</p>
<p>III. <u>Prevention of Pollution</u> (a) <u>Biodegradation</u> - develop an efficient biological process for destroying HEM in waste water. (b) <u>Effects of Underwater Explosives</u> - study the effects of underwater explosions on living organisms and develop methods of minimizing undesirable effects.</p>	<p>III. The Committee believes that the study of biodegradation of HEM is excellent but of limited scope. It is only the first step in the development of a total systems approach for possible application of biodegradation to the removal of these materials from pollutant waters. The complete resolution of the problem will require considerable R&D effort--perhaps even new and novel approaches. The results of the underwater explosion program are prerequisite to any decision relating to marine disposal by detonation.</p>

TABLE 1 NOSC Pollution Abatement and Research and Development Program - Comments

IV. Disposal of Waste

(a) Study the feasibility of disposing of explosives in molten salts.

(b) Making Copper Azide Inert - Copper azide is an especially hazardous material often formed during storage of HEM. Its presence interferes with safe disposal of HEM. A method of eliminating this problem will be studied.

IV. (a) Disposal of explosives in molten salt is speculative but promising on the basis of preliminary results. The Committee favors continuing this program.

(b) The elimination of copper azide formation is also considered necessary and Committee endorses R&D program.

(c) Research and development on reclamation of certain munitions is underway and should be encouraged and expanded. The Committee suggests a general broad-scale R&D program on the waste water problem which is very similar to the waste water problem encountered in munitions manufacture. Attention is called to the significant progress being made by the Army in disassembly of large caliber shells by remote control machining.

V. Future Materials

(a) Soluble or Thermally Degradable Binders - develop explosive compositions which are readily disposable.

(b) New Explosive Compounds - determine the suitability of polynitroaliphatic substitutes for standard military explosives.

V. The degradable binder program is an excellent approach to one of the pressing problems of propellant systems. Degradation by thermal means may be more appropriate.

New explosive compounds should be investigated and the Committee believes the Navy's program should be expanded beyond the proposed study of polynitroaliphatic substitutes.

General Comment

The Committee feels the NAVORDSYS COM R&D program is well conceived, appropriately planned and directed towards the resolution of some of the most important current problems of pollution abatement. It would appear equally important, however, that with the NAVORDSYS COM strengthening of its program of R&D significant technological breakthroughs could be forthcoming.

The program does not include any effort directed at developing a reliable and economical technology for removing polluting gases such as CO and NO_x from the products of detonation or combustion. Much effort is being devoted to this problem by academic institutions, industry and other government agencies because of the ubiquity of this problem. The Navy should be encouraged to maintain close contact with developments in this field.

IV.

DISPOSAL BY CHEMICAL TRANSFORMATION AND/OR RECOVERY
OF BASIC INGREDIENTS

Introduction.

High-energy materials (HEM) may be processed by physical means such as cutting, crushing or melting, to allow disposal or recovery as particles, or by physical-chemical means involving more or less complex solvent-non-solvent reagent treatments to separate HEM from metal parts, etc., to transform the mixed systems into separate ingredients or to perform chemical reactions to destroy, desensitize or convert to useful derivatives. The broad range of chemistry covered by the variety of HEM compositions and containment devices, etc., will often require highly specialized attention. Thus, it would be expected that development of a complex physical-chemical disposal or recovery routine would be justified only for large volumes of material or consideration of special value or unusual hazard.

State of Art

Individual ingredients and operational systems of HEM are well defined in the as-manufactured state as to physical and/or chemical properties and permissible stresses of either or both kinds. Materials for disposal, however, may have deteriorated in any of many ways, through contamination, decomposition, melting, separation, freezing, etc.; such would often be deemed unsuitable

for chemical treatment of any kind. In the case of a pure material used as such (cast TNT, pressed tetryl, granular diazo), the physical and chemical properties will generally dictate appropriate recovery and/or treatment methods, assuming preliminary testing results are satisfactory. Compound systems, however, (minol, amatol, pentolite, composition C, smokeless powder, etc.) will require more sophisticated physical treatments and/or chemical processing operations to separate the ingredients to even an impure state. To qualify as recovered material for reuse, it must meet the appropriate quality specifications, and hence extensive purification may be required, which could make the cost of recovery too expensive for consideration as a means of disposal.

In some instances an ingredient, relatively expensive in its original-use state with stringent purity and quality standards, may be usable as recovered, though in a less-pure state, in a less demanding application. Thus, recovered rocket propellant aluminum powder or HMX or a mixture of the two might serve in certain demolition explosive systems. On the other hand, HMX is relatively easy to separate from aluminum and is relatively easily purified, so that it might readily be restored to virgin grade specification and reused in basic formulations.

Obviously, the recovery of ingredients from a complex system such as a double base rocket propellant

will require a correspondingly complex sequence of physical and/or chemical processing operations to recover the basic ingredients--either in the recovery of the ingredients in their original purity and state or as a chemically transformed species. Fundamentally, one is concerned with the development of a suitable chemical processing operation containing all the attendant problems of research and development, process engineering and design, cost evaluation, and finally construction and operation of the processing sequence. The simplest type of process envisioned would require the dissolution of the entire solid base material followed by the selective precipitation or crystallization of the basic ingredients in their original basic purity and state. At the other end of the spectrum is a complex sequence of physico-chemical operations and transformations that may or may not yield the basic ingredients in their original state and purity, or perhaps an entire differing species of chemical products that may either be more readily disposed of or have by-product value in the chemical market place. As with any physical/chemical processing complex, due regard must be given to the attendant problems of air and/or water pollution and environmental impact. In fact, this could be the overriding factor in reaching a decision regarding the feasibility of a particular recovery operation.

Ingredient recovery for reuse corresponds, in a sense, to transformation to useful by-products. In some instances the useful by-product will be the (chemically) unchanged material adapted in physical form; i.e., an original military explosive or propellant reformulated and repackaged for a differing civilian use. Actual chemical transformation to a new product would, generally, only rarely be feasible; the frequency of production will probably be discontinuous or the cost of alteration to the new-product market specifications will be prohibitive. Thus military nitrocellulose is normally outside the civilian range of viscosity or nitrogen content or both, though the purified material might be digested to bring it within commercial range. However, the cost of the necessary alteration would be prohibitive when compared to other methods of disposal. Similarly, to go so far as to denitrate NC to cellulose for reconversion lacquer grade NC, CA, CAB, or viscose would seem likely to be quite costly.

Water soluble salts can in many instances be leached from HEM--nitrates, chlorates, perchlorates, etc. --and then crystallized for recovery or converted into other salts more readily usable. Thus, lead nitrate, if not usable as such, might be converted to sodium nitrate and lead oxide or hydroxide. Ammonium perchlorate might go to $KClO_4$ and NH_4Cl or NH_4NO_3 . Chlorates are useful as such in herbicides, etc. Lead azide can be converted to non-explosive lead compounds, recovering the expensive azide ion as sodium or potassium salt.

It is to be expected that the recovery and reuse or sale of the more basic complex constituents of a high-energy material will be more financially rewarding, require a lesser expenditure of energy, and cause less possibility of damage to the ecology than would recovery of chemically transformed or converted less complex constituents or materials resulting from a physico-chemical processing sequence. For example, recovery of TNT from an explosive HEM material would probably be more desirable than chemical conversion and recovery of nitric acid and toluene. A sustained effort should be made to find safe and economically feasible means of recovering and recycling or selling constituents of high-energy materials and related components. Only, if no safe and economically feasible means of recovery and reuse are available should destruction and/or dumping of high-energy materials and components be contemplated. A wide variety of high-energy materials are recovered and sold by both the U. S. Army and Navy.

Metal constituents of the high-energy materials and components can also generally be recovered and sold as scrap or secondary metal. In this case it probably will be financially rewarding to segregate constituents made from different metals or alloys from each other, because segregated metallic scrap has a higher market value than unsegregated scrap.

The most appropriate means of recovering constituents of high-energy materials and components will depend on the types and expected average annual volumes of the various materials and components to be processed. Recovery will be greatly facilitated if the original design incorporates features to assist in safe and simple disassembly and recovery and if subsequent storage conditions are adequate to prevent deterioration.

As a general rule, physical or mechanical means of recovery are more desirable and economical than physico-chemical means, including chemical transformations, which result in side or by-product streams of liquids and/or gases that must be further processed to minimize ecological damage. In general, there are three generic types of product (HEM) states that results from the consideration of possible recovery operations. These are:

- Recovery of the basic ingredients in their original state and purity specifications;
- Recovery of the basic ingredients in an altered state of purity or combination but in the same basic chemical form;
- Recovery of the basic ingredients following transformation to other chemical species for subsequent use/dispersal.

There are basically also three functional processing operational schemes that are generally used to effect the above:

- Physical separation techniques (solution, crystallization, precipitation, etc.)
- Physico-chemical transport processes (distillation, absorption, extraction, leaching, etc.)
- Chemical reaction transformation systems (chemical reaction, complex formations, transformation, etc.)

Although not specifically included above, it should be recognized that ecological and environmental constraints and considerations are a mandatory part of any chemical process scheme considered for the recovery/disposal of high-energy materials. (A discussion of the water use or reuse problem is contained in a subsequent portion of this section of the report.)

Some Recycling Work Being Done by the Navy

Some of the current recycling engineering methods now being utilized, should be discussed under the general heading of the section. In this regard, for example, the Naval Explosives Development Engineering Department (NEDED), located in Yorktown, Virginia, is engaged in the development processes for demilitarization of explosive loaded Naval ordnance. The inventory consists of many types of weapons loaded with a variety of explosives--each with different processing problems and difficulties.

Recycling is the prime objective for:

- Weapons that will be unloaded and reloaded for Fleet issue.
- Obsolete or surplus weapons that contain large weights of explosive and in large enough quantities as to seriously jeopardize the Navy's magazine storage capability.

In the first case, they are concerned with unloading of rejected explosive D and Comp A-3 loaded projectiles. After removal of the explosive the projectile bodies are reloaded for reissue to the Fleet, thus saving the cost of procuring new bodies.

Most of the explosive is removed from the projectiles by contour drilling and the residue removed by high pressure water erosion. The pressure used is 8,000 psi and at 90° F.

The explosive removed can either be sold on the commercial market or reworked to meet Navy standards. CIL, Canada has expressed an interest in buying both explosive D and Comp A-3 in an "as is" condition. However, processes have been developed by NEDED for rework. Both materials are in the form of fine face powder. The explosive D is recrystallized by a well-known and accepted process with the fine A-3 powder being reagglomerated into nodules in a heated water slurry.

Processes have also been developed for recycling of the water used in the high pressure washout of the residue. In these, water is conserved and other neighboring

natural water sources are not contaminated with the effluent.

In the second case mentioned -- that of removal of explosive from large obsolete and surplus weapons -- the Navy is developing processes that will allow the explosive to be recycled into new weapons and the metal cases sold for scrap.

In the area of underwater mines alone, this material totals about 16,200 tons. About 10,000 tons of this is explosive (TNT or HBX), the remainder is metal parts.

A melt-out process for the TNT was first developed. Here, the material can be reclaimed in either a small flake or granular form.

NEDED is also currently working on processes for the HBX loaded mines. They have demonstrated that this material can be removed in an uncontaminated form that is readily reusable in the compounding of H-6 explosive for bombs and torpedoes.

The process used is a hot water jet erosion. After washout, the water/explosive flows into a vacuum kettle where the water is removed. The dried material is then dispensed through a multiported dispenser to an endless stainless steel belt where it solidifies and is broken into flakes as it flows off the belts. This material can be easily remelted in standard batch kettles and the composition adjusted with new materials to form other HBX types or H-6.

All the HBX work is being done on a make-shift pilot plant basis where it was not feasible to conduct production rate studies. However, a modification of an existing building at Yorktown is being designed into a pilot production plant where this information can be developed.

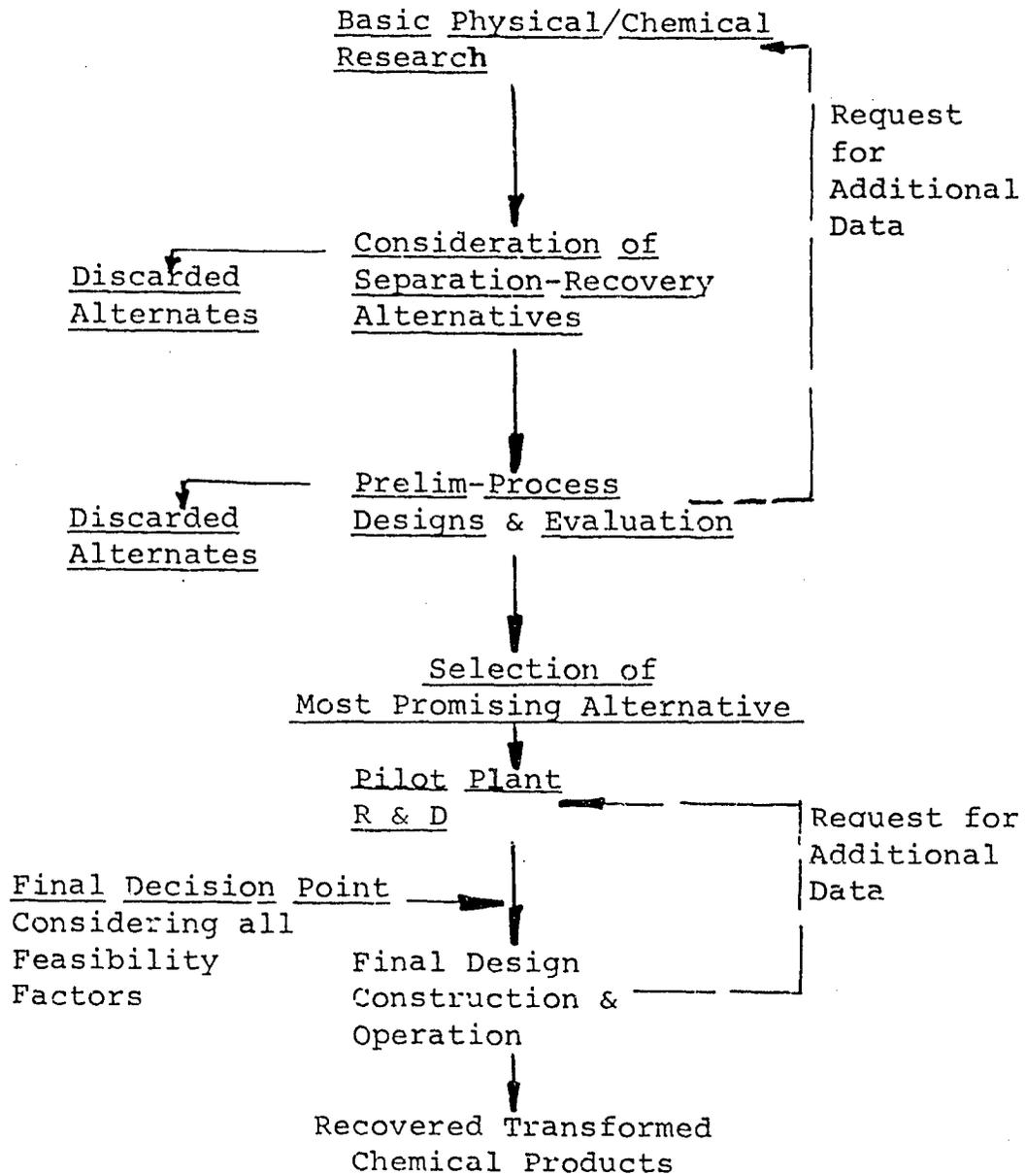
The plant will be based upon the recycle concept for the washout water also. From the data generated in the plant, design criteria will be established for proposed East and West Coast production plants.

Conclusion and Recommendations

Specific recommendations regarding the general feasibility of chemical transformation for the recovery/disposal of high-energy materials by the NAVORDSYCOM are quite difficult to make because of the myriad of material types of concern and the multitude of processing options available. However, chemical transformation for disposal/recovery certainly should be viewed as a viable alternate to be explored. This is particularly true from those complex material systems not amenable to the simpler disposal systems discussed elsewhere in this report.

The consideration of chemical transformation systems for the recovery/disposal of the basic ingredients of high-energy material systems should be approached in the classic chemical and chemical engineering sense of (A) basic research for the complete characterization of the raw material (HEM) followed by (B) a review of possible separation alternates (i.e., physical separation techniques,

Physico-chemical transport possibilities, and/or chemical transformation techniques that might convert to more readily disposable/recoverable forms), and (C) preliminary process design and economic evaluation. At this point, decision can be made concerning possible alternate processing schemes and possibly the need for more fundamental physical/chemical information. Selection of the most promising alternate will then lead to (D) pilot scale research and development to establish engineering parameters and optimum operation considerations and ultimately the final state (E) the design, construction and operation of the chemical process plant. This is illustrated in the following block diagram:



A schematic and logistical approach such as depicted above affords a minimum of three basic decision points along the route to a final decision. It should also be kept in mind that new developments in the science and engineering technology may introduce a hitherto not considered processing alternate or a discarded alternate may suddenly become the most promising; hence a continuing science/engineering review and awareness will be needed.

Two examples may be cited to illustrate some of the facets delineated above. One is the R&D experiences and recent funded work (on the Polaris A-3) relating to physico-chemical transport processes for propellant solution, plus separation and ingredient recovery. The other relates to the following possible alternative approach.

Polymer Binders - Their Removal and Recovery From Propellants*

Polymer binders in propellants usually constitute from 16 to 20 percent of the total weight of the propellant. The remaining 80 to 84 percent is generally made up of oxidizer, usually (in Polaris motors) ammonium perchlorate (AP) 60 to 82 percent, aluminum metal, 2 to 18 percent, and stabilizers 0 to 1 percent.¹⁻⁵ The binders of chief concern, at present, appear to be of two types: 1) polyurethanes and 2) cured polybutadiene prepolymers in Polaris and Minuteman motors respectively.

The problem of disposing of obsolete propellants is a formidable one because of legal limitations on burning and dumping. The product gases from burning would cause serious pollution of the atmosphere and other possible means of disposal also present problems.

The most desirable means of disposal would involve separation of the binder, oxidizer and metal by suitable physical or mechanical processes which would permit their reuse. Such a procedure may also offer important economic advantages, particularly if recovery of each component could be accomplished in reasonable purity. The problems associated with processes directed toward mechanical separation of the components are many. The polymeric binder is a cross-linked material so that it is not soluble in most solvents, making it impossible to remove the binder

*The complete report, from which this portion is taken, can be found in the Appendix of this report.

simply by normal solvent extraction. The properties of the binder are similar to those of vulcanized rubber. Furthermore, the finely divided metal and oxidizer particles are intimately coated with the binder, which is impervious to water, making separation extremely difficult.

Due to the chemical nature of the binder, a reasonable removal approach, and one that appears to offer considerable probability of success, is a chemical one. Here the chemical approach would involve cleavage of the polymeric cross-links leaving binder fragments which would be soluble in a suitable solvent. This would permit the binder to be removed from oxidizer and metal by a simple extraction-filtration procedure. However, it should be emphasized that adequate consideration should be given to the potential hazards which exist in bringing organic solvents in contact with large quantities of oxidizer.

Properties of Ammonium Perchlorate Which May be Useful in Economic Recovery

Ammonium perchlorate is reported to absorb sufficient ammonia at room temperature to liquify,⁶ giving solutions resembling Diver's solution. This property of AP suggests that liquid ammonia could be a useful solvent in a recovery method of this component of propellants. The possible hazards of the system must be considered carefully, and some laboratory studies conducted before any large-scale attempts to utilize this concept are made.

Important Factor to Consider in Planning Potential Research and Development on Recovery and Reuse of Propellant Components

Since propellants may have been stored with little control under rather wide extremes of temperature, aging may have occurred. Aging is defined as the sum of the changes the propellant undergoes in the interval between curing or casting and firing in a rocket chamber. The outward manifestations of aging are changes in the physical and mechanical properties. These outward changes are symptomatic of physico-chemical changes on the molecular scale and the latter must be identified and measured, if possible, in order to apply the appropriate recovery methods effectively and safely. Possible types of molecular-scale changes include depolymerizations or scissions of binder molecules, decompositions, crystallization of binder, phase changes, and various changes associated with minor components.

Ideally, binders would not have been found satisfactory unless it had been shown with considerable confidence that they do not undergo spontaneous crystallization during storage at any temperature, that they dissolve little or no oxidizer, and that they are chemically stable for long periods in close contact with the oxidizer. To the extent that these considerations may be relied upon, it may be assumed that most of the above possible physico-chemical changes will be minor. However, some method of monitoring these possible changes should be developed before chemical degradations are undertaken.

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THE WATER USE, REUSE, AND/OR EFFLUENT DISCHARGE

Introduction

Most of the difficulty related to the use of ground water supplies in the manufacture, treatment, disposal, and/or recovery of ordnance materials are industrial waste water treatment problems. Solving such water treatment is not a matter of finding the most economical water-use cost only, but also to determine the most efficient and economical total processing cost. Consequently, this requirement includes the attendant costs of meeting environmental water quality standards and a total systems approach must be used:

Each industrial manufacturing operation is unique in its total energy and raw materials requirements, the physical and/or chemical transformation steps required to produce the final products of commercial value, and the production of a variety of waste or effluent streams. It should also be borne in mind that few (if any) industrial waste water treatment systems that meet the criteria and constraints of Federal, State, and/or local community water quality legislation involve a single unit operation or unit processing step. Generally, a multi-purpose series of processing operations is involved to produce the effluent of desired quality.

Therefore, in essence, the approach this Committee recommends to the Naval Ordnance Systems Command (NAVORDSYSCOM) is to view the water use-reuse-effluent discharge problem of each manufacturing and/or treatment process plant as a unique chemical-industrial processing operation. For example, the raw materials are the virgin water and the recycle water supplies, and the products are the residual by-products and effluent returned to the environment.

A General Operational Type Resolution of the Problem

To accurately predict the resolution of the myriad problems--technical, administrative, and socio-political--that face the Naval Ordnance Systems Command for efficient and economical resolution of the water quality problems in ordnance manufacture, treatment, and/or disposal missions, would require the design of a chemical processing operation with minimum operating cost and capital investment. Nonetheless, a systematic approach can be envisioned that will enable the Naval Ordnance Systems Command to develop a program of research, development, engineering design and operation, while knowing only the product to be produced but little or nothing about the available raw materials or the operational constraints to be imposed upon the system.

The program suggested is composed of three basic informational development (documentation) steps to be followed by a comprehensive plan of analysis, evaluation

and projection for the future. The basic information development/documentation are as follows:

Raw Materials (Water) Supply Inventories

A complete chemical, physical, and biological inventory should be developed, on a continuing basis, relative to the quality of the surface and/or subsurface water supplies utilized in processing operations at each installation involved in ordnance manufacture, treatment, disposal, and/or component recovery.

Catalog of Current Operating Practice

Relatively complete process operational details should be documented on the current operational practices related to water purification and reuse. This would include chemical/physical pretreatment steps to prepare raw material water supplies for use as well as the subsequent processing steps preparatory to reuse or disposal. In brief, a process flow chart for each water supply system attendant to each plant and/or processing operation, with component physical and chemical characterization at intermediate processing points should be formulated. Operational difficulties and problems related to water use and/or recovery should be noted.

Basic Research

Basic research studies should be directed, insofar as water pollution is concerned, to those specific types (TNT, RDX, Binders, etc.) unique to the ordnance of concern.

In addition to evaluating standard procedures, methods, and materials for their adaptability to NAVORDSYSCOM's unique pollution problems, new and novel procedures that might be unique for the pollutant in question should not be overlooked.

Inasmuch as practically all of the waste water treatment systems generally in use at the present time involve, in addition to possible chemical treatments, particulate solids removal, adsorption and a final degradation step (bacteriological or non-bacteriological), NAVORDSYSCOM should have a continuing basic research program to characterize various adsorbents and degradation media (bacteriological and non-bacteriological) for applicability to the unique chemicals of concern. The Navy's present R&D (PEPPARD) program includes some work in this area. Because of the unique nature (molecular structure, etc.) of the chemical species involved in NAVORDSYSCOM's pollution problems, departure from or alteration of the usual processing sequences might yield unexpected improvements. For example, a partial bacteriological degradation prior to an adsorption step might improve the adsorptive capacity of the adsorbent and, at the same time, provide a more amenable environment for a final degradation step. Means of catalyzing the biodegradation process should not be overlooked.

Engineering Research and Development

Engineering research and process development will, of course, be directed to a large degree by the results achieved by the basic research program. However, a significant amount of engineering research and development effort

should be directed towards the improvement and/or resolution of pollution problems arising through current processing operations.

Consideration might be given to the provision of separate collection-treatment systems for wash waters, steaming-out condensates, floor washings, etc., where practical. This would enable primary and/or secondary treatments at the basic processing unit and possibly provide less diluent and interaction effects that result in large collection systems resulting from a number of processing steps. Also, it might alleviate some of the problems associated with large waste treatment systems due to size alone. Another possibility is the use of closed circuit systems, wherever feasible, with only slip stream purification to maintain higher system inventories of contaminants, but (hopefully) lowering the effluent quantities to be treated.

V.

THE DISPOSAL OF HIGH-ENERGY MATERIALS (HEM)
WITH NO CHEMICAL ALTERATION

Introduction

As this Committee has stressed in Chapter II (Summary of Recommendations) of this report, the disposal, burial and/or storage of bulk untreated (viz. with no prior chemical alteration) high-energy materials is a method in some cases to be prohibited, and, in other cases, to be used only as a last resort. If it is used at all in these latter occasions, it must be most carefully researched prior to use so as to insure that no detrimental effects to the environment or personnel are incurred. Such occasions where this least desirable method of disposal might be considered are in those situations where the materials cannot be safely and economically recycled, modified for an alternate use or otherwise degraded with an acceptable generation of additional pollution to the environment. Also there may be cases where it is highly desirable to store certain types of munitions temporarily for some future operational contingency or for future processing methods of reclamation.

While we feel that no high-energy materials should be abandoned in an unmodified form in the ocean, we suggest that with the proper investigation there may be distinct possibilities for this kind of disposal at such candidate locations as:

- In deep, worked-out mines or cavities created by mechanical excavation or by nuclear explosions, located in geologically stable areas that are essentially impervious and do not afford ground water percolation.
- Near the surface in remote environmentally-hostile areas, such as the geologically suitable playa deposits of the deserts and thick beds of clay stone and "dry" rocks.
- In the craters of active volcanos.

In this chapter each of these disposal and/or storage methods, plus the ocean disposal situation are discussed.

Ocean Disposal

Historically some types of obsolete munitions, for which reclaiming processes are not yet applicable or which for reasons of safety, cost, or infeasibility cannot be applied, have been disposed of by dumping them in selected deep parts of the ocean. This has been felt by the Navy to be the most economical, safest, and most pollution-free means of disposal available. While the 2,000 - 3,000 gross tons of such materials disposed of annually in this way has represented only a small fraction of the total inventory amounts of overage and obsolete munitions, the deep water dumping procedure has represented a cost-effective way of disposing of some "problem" materials.

However, on October 18, 1972, the 92nd Congress of the U. S. enacted Public Law 92-500 which amended the Federal Water Pollution Control Act to read in part as follows:

"Sec. 101 (a) The objective of this Act is to restore and maintain the chemical, physical, and biological integrity of the Nation's waters. In order to achieve this objective it is hereby declared that, consistent with the provisions of this Act -- it is the national goal that:

"(1) The discharge of pollutants into navigable waters be eliminated by 1985;

"(2) Wherever attainable, an interim goal of water quality which provides for the protection and propagation of fish, shellfish, and wildlife and provides for recreation in and on the water be achieved by July 1, 1983;

"(3) The discharge of toxic pollutants in toxic amounts be prohibited;

"(4) Federal financial assistance be provided to construct publicly owned waste treatment works;

"(5) Area-wide waste treatment management planning processes be developed and implemented to assure adequate control of sources of pollutants in each State; and

"(6) A major research and demonstration effort be made to develop technology necessary to eliminate the discharge of pollutants into the navigable waters, waters of the contiguous zone, and the oceans."

This new Act reflects an unprecedented ecological awareness and increased interest in the protection of the total environment, both on a national and international level. Moreover, this interest is based on the rapidly proliferating uses to which the sea is being put. These include:

- fishing by deep water trawls
- cable laying (all depths)
- oil exploration (shallow)
- mineral mining on sea floor (moderate and shallow)
- sand and gravel mining (shallow)
- chemical extraction (shores)
- more ocean exploration and engineering activities (all depths but very limited areas)

There is another type of basis for the prohibition of deep water dumping (DWD) of munitions stated in "Alternatives to Deep Water Dumping of Ammunition and Explosives, Staff Study for the Secretary of the Navy, 25 May 1971:"

" . . . a possible unfavorable interpretation of DWD with regard to international freedom of the seas. If dumping munitions can be construed to threaten life, it violates a prime canon of international law. The U. S. does not own a private deep ocean. The relationship of solute concentration to toxicity levels of marine life in the immediate vicinity of the dumps also needs clarification. Although no clear evidence of hazard has been uncovered, the burden may very well rest with the government to prove that none indeed is created by DWD. However, the problem of innocence is not unique to DWD; other means of disposal may be similarly encumbered . . . "

However, with proper research it may be quite possible to prove conclusively that some modified forms of munitions disposal on a limited scale in the ocean are not only technically feasible and desirable, but also within the specific requirements of the law. (Some of these possible permissible practices such as the burning and detonation of high-energy materials on and within the ocean environment are discussed elsewhere in this report).

With the full realization that both in principle and in fact, the oceans are really nature's disposal plant since a variety of solid and suspended solid wastes from land, sea and air sources naturally and inescapably are desposited in this environment, some people argue that untreated high-energy materials could be placed in active submarine deltas of the ocean where-self burial by geologic action would take place in a matter of months. However, this Committee feels that inclusion of bulk munitions to this solids burden of the ocean is highly undesirable. For one thing, the detailed effects of such pollution upon the flora and fauna of the ocean are essentially unknown at present. Moreover, we feel that no high-energy materials should be abandoned unburied in an unmodified form in the sea since such a procedure contains the very real risk of some future accidental detonation. Moreover, it is not sufficient to require the recording of the location at which such materials are left -- where shiploads of ammunition are sunk -- since in the course of time records will be lost or

destroyed. Unfortunately, "out of sight" is "out of mind" but not out of danger, and danger is not a desired legacy to the future.

In conclusion, therefore, it is felt that actually only a very limited disposal of high-energy materials at sea should be permitted, and then only provided they are burned or detonated in known regions of very low sea life population and ideally (but not essentially) in those areas where the resulting solid trash will be buried by relatively rapid geologic processes (self-burial in submarine deltas). Additionally, materials disposed of by this procedure should only be those that cannot safely and economically be recycled, modified for alternative use, or otherwise degraded, with an acceptable generation of additional pollution. With such an attitude adopted the Navy can assert its leadership in assuming a sensitive and sensible long-range and more sophisticated attitude toward man's best use of the ocean for his own welfare.

Land Disposal

Introduction

The storing or disposal of wastes in underground vaults and/or near surface burial has been used for many types of materials over the years. In some cases, high-energy materials have also been disposed of in underground vaults by either detonation and/or incineration by industrial manufacturers (e.g., DuPont). Such a procedure as deep underground storage and detonation has also been recommended in the Navy's 25 May 1971 report,

"Alternatives to Deep Water Dumping of Ammunition and Explosives." New excavations, worked-out mines, caverns and other underground openings have been successfully utilized for both kinds of disposal. New excavations in selected areas which possess the appropriate geologic conditions are usually the most economic and environmentally suitable sites for storage and/or burial of the critical materials generated by the disposal of obsolete and overage munitions (particularly some 20 percent of the inventory today that primarily consists of: (a) bulk propellants; and (b) rocket motors.)

Worked-out mines in limestone, gypsum, salt and sandstone are the most desirable for subterranean storage and/or burial, and at present there are several hundred million square feet of usable space available in such mines. However, except for these particular non-metallic mines, most existing subsurface openings can be considered as generally unfit for underground storage or burial. This is due to many factors, such as: many mines are located in structurally weak rock or areas weakened by mineral alterations; the waste materials may react adversely with the mineralized wallrock; cavities are not designed for long-term stress resistance; the cross-sectional size of opening is too large or too small; the water table is too high and the environment would be contaminated by ground water pollution; and the plan of underground workings do not conform to an efficient storage or assembly line for "backfilling".

Some caves may be found to meet burial requirements, but most will require much remodeling. Commonly, caves do not have a uniform floor level, the rooms are irregularly aligned due to origin by solutioning action, and they invariably have a high humidity. Generally, an entirely new system of openings excavated by mechanized methods, compare favorably in overall cost to the expensive modifying of a worked-out or abandoned mine or cave.

The major engineering and geologic needs for planning a successful underground burial program (assuming land rights) include: (1) ease of surface accessibility; (2) a regional geologic reconnaissance followed by a detailed area study as a basis for selecting the site; (3) adequate subsurface investigations followed by an evaluation of the three-dimensional geologic conditions; and (4) an assessment of any impact on the environment and regional geological conditions of the disposal materials, particularly the ground water regime.

Many investigators consider storage and/or burial underground as only an interim solution to the high-energy materials disposal problem because of the long-range potential hazard that man may eventually detonate the explosives by "mistake" or by sabotage. However, underground storage-burial or detonation/incineration underground with burial of the residue offer major short-term advantages, and guidelines for such disposal are therefore included in this report.

Strategy for Underground Burial

- Insures no contamination of biosphere. A complete isolation of the waste materials from man's environment.
- Utilizes a natural environment that is poor and/or hostile with respect to man's future needs and plans. Such locations are largely governed by the geologic conditions.
- The choice between deep or shallow burial is a function of safety--that is, could the material conceivably explode or is it a non-explosive inert waste only. (Shallow burial is within 10's to a few 100 feet of the surface, while deep burial is many 100's to 1000's of feet at depth.)

Environmental Factors Critical to Feasibility for Burial

Rock caverns or open-cut excavations to be used must be "dry" and impermeable so that no water can migrate through the burial site and thus act as a contaminant of either the ground water reservoirs or surface flow. The area should also be of such a nature that waste materials will not interact with the wall rocks of the cavern or excavation to form gases or generate explosive materials. Such sites are to be located outside regions of potentially strong seismic events.

Therefore, such sites would include the following features:

- A thick section of "dry", essentially impermeable rock for the host burial material. The burial is located within such rocks as a mudstone, fine-grained sandstone, claystone and shale, or in intact massive bodies of hard rocks.

- The floor of the shallow cavity or burial site is located tens of feet above the regional ground water table and there is no circulation between the waste area and the ground water reservoir at greater depth. Where burial is deep--the site is located below the zone of water bearing rocks and within a "dry" rock mass; there is no accumulation of ground water to the near surface reservoir.
- There are no through-flowing surface water streams nearby the site.
- The site is located in a non-seismic area.

With the site selection properly carried out with the above factors in mind, underground storage is advantageous since:

- The waste materials will not generate a high-heat that affects the cavern wall rock adversely (such as cause spalling and collapse or open up the fractures by removing the mineral filling and enhance ground water flow).
- Any gases generated by waste/rock interaction cannot be released to the biosphere-- or if this occurs, the gases can be controlled and dissipated and cause no pollution of the environment.
- Under a catastrophic change in natural conditions (although unforeseen on selection) the waste materials could be retrieved-- likely an unnecessary precaution due to the short term required for deterioration of the waste.

- Similarly, there may be a future shift in the environmental attitude towards burial or a chemical change taking place during decay, and the new policy would require retrieval of the wastes.

Geological Setting of Potentially Impermeable Sites for Burial - Geographic

- Sites on Military Bases in U.S.A.
 - Burial at shallow depths, such as in open-cut excavations, inclined shafts or adits in steep terrain. This category includes:
 - (a) the Savannah River type of surface burial in clayey deposits; (b) the self-burial type possible in an active river delta such as the Mississippi region; (c) the playa deposits type common in arid sectors of western states where thick "dry" impermeable beds occur at the surface; and (d) the Triassic basins type of deposits.
 - Burial at deep depths, such as in pre-existing tunnels and worked-out mines, solution wells and cavities in salt beds and salt domes, and new, pre-designed underground cavities. This category includes:
 - (a) many of the locations currently utilized for deep waste-injection of industrial materials; (b) the Triassic basins type of deposit common throughout the eastern Piedmont and Coastal Plain regions with burial via shafts in these isolated, "dry" rock masses; and (c) the numerous worked-out salt mines and solution cavities in the salt dome deposits of the Gulf Coast region, or the thick salt beds of New York, Pennsylvania, Michigan, Kansas, etc.

■ Sites off Military Bases - U.S.A.

• Burial at deep depths

Another Potential Disposal Site

It has been suggested that the craters of active volcanos, such as those in Alaska, Hawaii, and the South Pacific region might be utilized as sites for the disposal of certain types of high-energy materials. This Committee, because of its limited time involved in the study of various other more primary candidate Treatment and Disposal Methodologies, has not addressed this particular subject of disposal in active volcano craters. However, we tend to endorse such a suggestion, with the reservation that the idea be carefully further investigated to determine whether it is environmentally sound and one consistent with the national interests. On a preliminary basis and to support our qualified endorsement, it appears that such geologic settings and features do offer a reasonable disposal solution. The natural environment around an active volcano is indeed hostile, and a region where man will not be attempting to clean-up or change the environmental conditions. The matter of access for dumping poses a transport and handling problem for the engineer.

VI.

DISPOSAL (AFTER CHEMICAL CHANGE) TO THE END PRODUCT OF
COMBUSTION AND DETONATION

Introduction

The use of combustion in open pits on land or detonation in open pits for the disposal of explosives, munitions of various kinds, propellant charges, etc., has been standard procedure employed by the military for many years.

In such a procedure, pits or trenches are dug to depths of from six or seven to ten feet and the explosives or propellant charges loaded into them. Waste oil or similar material is added to promote combustion when needed and the pit contents set on fire. The end products of these operations are smokes of varying particulate concentration and the expected gaseous combustion products CO₂, CO, and NO_x all of which are released to the atmosphere without any attempt at containment or processing.

In earlier years such burning was carried out with relatively little attention being paid to prevailing wind and weather conditions at the site of the burn. The major burn sites are generally located in rather sparsely populated localities such as the desert southwest of Great Salt Lake in Utah where the Dugway Proving Ground facility of the Army is located. However, such burns are also carried out in a number of instances in more populated areas.

In recent years, in recognition of the general concern over atmospheric pollution, care is usually taken to limit the magnitude of a combustion operation. Furthermore, it is usually only carried out when the wind and weather conditions at and near the site are favorable for the production of a high plume which will disperse the combustion products widely and dilute them effectively.

Thus in such open pit burns, involving explosive compounds or propellant charges, the end products of the combustion are dispersed as gases in the atmosphere or as particulate matter fall-out.

Where the disposal of munitions of various types, such as small arms rounds, artillery shells, rockets, small bombs, pyrotechnics, mines, fuses, and detonators, is carried out in open pit burning, provision is made to prevent scattering of the burn and ejection of projectiles or other material from the pit by an overlay of a heavy woven steel wire blanket on top of which logs or dunnage are piled. In addition a very hot combustion zone is developed through the mixing of wood crate waste or similar material directly in with the munition items and through the use of larger quantities of waste oil or some similar fuel.

Generally speaking, combustion combined with detonation in pits, as just described, can be safely and successfully carried out for small munitions items. The

level of energy involved in the case of detonation of the large amounts of H.E. (high explosive) in large bombs or rockets or the larger caliber artillery shells is such that containment of the explosion within the pit is difficult if not impossible and the open pit technique cannot safely be employed in these cases.

The gaseous and particulate end products of this combustion-detonation procedure are essentially the same in burns involving munitions items as in those involving explosives and propellants, though the particulate matter in the fall-out in the case of the munitions may include a small metal and metal oxide content along with the carbonaceous particulate matter.

At the conclusion of the burn of the munitions items there will be mixed with the ashes of the organic matter (usually wood) a scrap metal residue which will either have to be sold, buried, sea dumped, or otherwise disposed of. The nature of this metallic scrap residue may vary widely. Depending on the particular item of munitions being burned, it may contain iron, lead, copper, zinc, or aluminum, or mixtures of these.

Open pit burning operations on land, which pollute the atmosphere with smoke and toxic gases such CO and NO_x will be restricted more and more as efforts to control environmental contaminants are increased. However, there should be little basis for objection to such burning type operations if these were carried out at sea for example, under properly planned and controlled conditions.

Continuous or Controlled Incineration

In the past disposal by combustion or controlled burning of some items as a whole or of their disassembled parts has been carried out in rotating cylindrical retorts with heavy steel walls. The retort is fed either batch-wise or on a continuous basis, and the pieces in the feed stream are kept small enough in size so that the explosion of one of them is contained by the strength of the rotating retort.

The gases, mainly CO, CO₂, and NO_x plus any particulate matter (metal oxides, carbon, etc.) have been allowed to escape to pollute the atmosphere. Considerable research still needs to be done to design scrubbers and/or precipitators to reduce the extent of atmospheric pollution from these retort furnaces.

Both the Navy and the Army have used this method for disposal of small arms ammunition, fuses, boosters, and similar items. Presently this procedure is used by the Navy only for small arms ammunition through 20 mm. However, if the disposal of explosives, propellants, and munitions items in any large quantities is to be carried out at locations on land, it will be necessary to develop an operation for doing this with a minimum of hazard and the least possible atmospheric contamination.

Some of the necessary elements for such an operation are currently being studied at the Tooele Army Depot, Utah. The principles involved are as follows: the complex munition is broken down into

relatively small pieces and those containing propellant or explosive are burned in a deactivation furnace; the effluent gases from this furnace are trapped and the CO₂ and NO_x produced are taken out in scrubbers which contain solutions of alkali. The aim is ultimately to convert them to solutions of calcium carbonate and nitrate, or solutions of the corresponding sodium salts; the salts would then be recovered from these solutions by spray drying and then sold or otherwise disposed of as in the case of the scrap metal involved.

While this system still needs considerable further development and improvement, it would certainly appear in principle to provide a safe method of handling munitions and one which could be completely automated and governed by remote control while it was being appropriately monitored through closed circuit television.

Disposal at Sea by Burning and Detonation

In the burning of bulk explosives or propellants at sea, the products of combustion would be smoke or gases and the operation could be carried out anywhere at a sufficient distance from land to avoid any atmospheric contamination over land areas. It seems likely that in such an operation, if properly carried out, the gases developed would be dissolved or greatly diluted by large volumes of air.

This statement is certainly misleading in that the damage criterion used is probably in error for such large explosions and it completely ignores the tremendous variation in animal or fish population with location.

Unclassified information from the classified naval "Operation Wigwam" experiment of 1955 indicates that following the detonation of a 30KT device at 2,000 feet in very deep water, air and surface searches for fish-kill resulted in the observation of a single dead fish. It is very probable that the careful selection of the detonation site and the size of the explosion were both contributing factors in this phenomenally small observed kill, which, in accordance with the prediction quoted above, should have included all the marine animals in 50 cubic miles of ocean and all the swim bladder fish in 1,300 cubic miles of ocean.

Actually the precise depth at which detonation occurs does not appear to be very significant, except that a controlled detonation would appear to be much preferred to an uncontrolled one, and this should be more readily achieved at shallow rather than in deep water.

The geographic location should preferably be in the deep ocean along the toe of the continental shelf, in the deltaic region (the mouth) of an active submarine canyon. Here the solid debris should be buried by

sedimentation in a minimum time and there should be a minimum probability of interference with future manganese nodule or other mining efforts, since it would be most unlikely that economical quantities of ores would concentrate in such regions.

While initiation of an explosion would be easier with the material at the water surface, completion of the detonation process throughout the mass of materials is more apt to be insured if the detonation were to be accomplished with the confinement provided by a moderate depth of water above the explosion. This would also markedly reduce the area over which scrap metal would be distributed by the event. If the depth of the explosion were kept at less than about $2W^{1/3}$ where depth is in meters and W in long or metric tons, most of the gaseous products of the explosion would escape to the air.

In conclusion, we feel that disposal at sea should be used as a recommended method and that:

- Special care must be taken to insure that ammunition is truly deactivated and not partly scattered in an active state; and
- The site selection at a suitable distance from land should be optimized without too much regard for the distance the barges are to be towed, because once ammunition is loaded for sea, the cost of towing the "extra mile" is probably nominal.

Disposal Underground by Burning and Detonation

This subject is directly related to the considerations mentioned in the previous section of this report where we have discussed the use of worked-out mines and cavities as candidate sites for the storage and/or burial of bulk ordnance. Using the same criteria for site selection as mentioned in this regard, it is felt that various subterranean locations could be well utilized for explosive detonation and burning.

Other Suggestions

The suggestion is often made that waste high-energy materials might be disposed of by sending them out into space. Obviously, this suggestion is unrealistic. It would take the burning of at least 20 pounds of propellant in the rocket motor for each pound of material lifted into space. Such a burning would produce 20 times more atmospheric pollution than simply burning the waste material.

Another recurrent suggestion for the use of explosive materials is to burn them as fuel. The problem here is that explosives are generally very poor sources of energy. The heat of combustion of TNT is variously quoted at values between 800 and 1,000 calories per gram, while most common solid or liquid fuels yield between 6,000 and 11,000 calories per gram. One gallon of gasoline is thus equivalent to 80 pounds of TNT.

A General Comment

Since much of the explosive ammunition employed by the Navy and Army is similar in many respects, it would seem wise to concentrate disposal operations in one of the Services as a Department of Defense operation.

VII.

SOME OTHER POSSIBLE WAYS OF
ALLEVIATING THE DISPOSAL PROBLEM

Introduction

The chemistry of explosives is one of the oldest branches of applied chemical science and a great deal of research has been done on the synthesis of new molecular combinations which would have explosive properties. Related work of this nature has been supported in the past by the Advanced Research Projects Agency (ARPA) to the extent of about twenty-five million dollars without very encouraging results.

While it is conceivable that new multi-component combinations of existing explosives and oxidizing agents might lead to some improved combinations, it appears dubious that investigations of new molecular combinations would be worthwhile. While some of these combinations have been found to be highly energetic in various compounds containing nitrogen fluorine bonds, they have at the same time proved to be so sensitive that they could not be used because of the lack of the stability which a good explosive must have to be employed in munitions.

On the other hand, there is probably considerable need to investigate new and improved synthetic methods for manufacturing existing explosives both from the standpoint of the development of more efficient and economical methods as well as ones which will produce less objectionable wastes to affect the environment.

For example, most military propellants and explosives are more refractory than one would like for ready recycle from munitions. An exception to these are the so-called "water gels," employed in a few categories of bombs. Unfortunately, water gels, as a family, do not have the very high detonation velocities required for weapons where fragmentation is an important factor. Relatively recently, a novel explosive type has been developed that approaches more closely the detonation velocity required in many military applications.

The explosive type is a stable water-in-oil emulsion gel patented by Atlas Division, I.C.I. America (U.S. 3,447,978, June 5, 1969). A typical composition might be:

oil	6 percent
water	15 percent
sodium nitrate	15 percent
ammonium nitrate	63 percent
emulsifier	1 percent

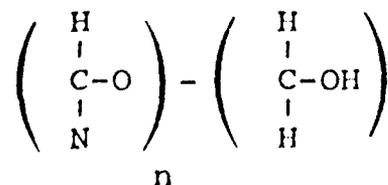
The oil is the continuous emulsion phase, and in it are dispersed micron-sized droplets containing saturated salt solution and solid salts. Because of the intimacy of mixture, detonation characteristics are excellent, with velocities in excess of 6,000 meters per second. In contrast, conventional water gels, in which the aqueous phase is continuous,

have detonation velocities of about 4,500 meters per second and, hence, much lower brisance in weapons applications. In addition, the performance of conventional water gels deteriorates rapidly as temperatures fall below 40°F and crystal growth occurs in the aqueous phase, reducing the intimacy of the fuel/oxidizer mixture. In the emulsion gels, the oil film around the aqueous droplets limits crystal growth to a few microns; fuel/oxidizer intimacy is maintained; and good performance persists at low temperatures.

One might postulate that compositions of this sort might easily be broken down by a simple steam distillation into an oil fraction containing most of the emulsifying agent and an aqueous phase containing the inorganic oxidizing salts and residual emulsifier. Recycle to new production would be simple.

The R&D task to be accomplished is to modify the basic emulsion gel formulation to achieve the desired levels of sensitivity and detonation velocity.

In plastic bonded explosives, it is difficult to separate high explosive (HMX, RDX) from polymeric binder. Conceptually, what we would like is a binder that reverts to its monomeric state at some temperature above the specified use temperature of the munition but below the temperature at which the high explosive begins to react. As an example, polyformaldehyde



unzips rapidly under the influence of heat because of the presence of the mobile alcoholic hydrogen. In DuPont's "Delrin," this unzipping tendency is minimized by replacing the hydrogen with a tightly bound group or element.

The R&D task to be accomplished is the development of a polymer that will revert to a low molecular weight compound at some elevated temperature.

Other Possibilities

- A continuing problem in the training of military personnel is the provision of realistic experience with weapon performance. Simulated training is no real substitute for the real thing. The planned expenditure of munitions stores should be encouraged as a logical means of disposal during the nominal lifetime of the materials. This would markedly improve the true readiness of our armed forces, while at the same time reducing the problems of disposal of obsolete ordnance.

- Depth charges and bombs have been used effectively in studies of the structure and properties of the atmosphere and the earth, and such use of excess quantities of these weapons could be encouraged. Seismic study programs may be expected to continue for many years and these can use large quantities of explosives if they are made readily available. Control of firing sites and conditions would be required.

- It is considered that a close collaboration among the professionals in such disparate disciplines as marine biology, chemical oceanography, marine geology,

Explosive design and disposal engineering will be essential to progress toward environmental protection. For example, such an active collaboration is urgently required as soon as possible to carry out many needed controlled oceanic experiments. These experiments, properly designed, could furnish a meaningful decision-making basis for some future regulations in the matter of disposal, detonation and burning of high-energy materials in the ocean environment.

The results of such experiments might form the foundation for the setting of standards at an effective international dumping convention or forum. Such standards could turn out to be obligatory or merely recommendatory.

The formulation and use of international standards as guide or rules for oceanic environmental protection would be of great significance.

■ The Committee recommends that the Navy and the DOD consider sponsoring, on a continuing basis, national meetings whose theme would be addressed to some appropriate facet(s) of the subject of the treatment and disposal of high-energy materials. This logical and significant step would seem to have many obvious advantages as well as some more subtle benefits arising from the exposure of the problem to the general public with the hope of generating public support of programs being directed toward the problem's solution.

VIII.

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APPENDIX

POLYMER BINDERS -- THEIR REMOVAL
AND RECOVERY FROM PROPELLANTS

Introduction

Polymer binders in propellants usually constitute from 16 to 20 percent of the total weight of the propellant. The remaining 84 to 80 percent is generally made up of oxidizer, usually (in Polaris motors) ammonium perchlorate (AP) 60 to 82 percent, aluminum metal, 2 to 18 percent, and stabilizers, 0 to 1 percent.¹⁻⁵ The binders of chief concern at present (in Polaris motors) appear to be one of two types: (1) polyurethanes or (2) cured polybutadiene pre-polymers. The problem of disposing of obsolete propellants is a formidable one because of legal limitations on burning and dumping. The product gases from burning would cause serious pollution of the atmosphere and other possible means of disposal also present problems.

The most desirable means of disposal would involve separation of the binder, oxidizer and metal by suitable physical or mechanical processes which would permit their reuse. Such a procedure may also offer important economic advantages, particularly if recovery of each component could be accomplished in reasonable purity. The problems associated with processes directed toward mechanical separation of the components are many. The polymeric binder is a cross-linked material so that it is not soluble in solvents, making it impossible to remove the binder simply by solvent extraction. The properties of the binder are

similar to those of vulcanized rubber. Furthermore, the finely divided metal and oxidizer particles are intimately coated with the binder, which is impervious to water, making it impossible to remove the water-soluble oxidizer from the metal binder.

Due to the chemical nature of the binder, a reasonable removal approach, and one that appears to offer considerable probability of success, is a chemical one. Here the chemical approach would involve cleavage of the polymeric cross-links leaving binder fragments which would be soluble in a suitable solvent. This would permit the binder to be removed from oxidizer and metal by a simple extraction-filtration procedure. However, it should be emphasized that adequate consideration should be given to the potential hazards which exist in bringing organic solvents in contact with large quantities of oxidizer.

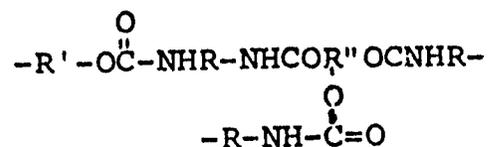
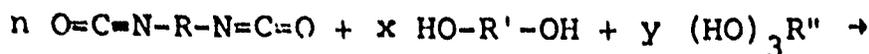
Background Information and Present Status of Problem

As previously mentioned, the binders of chief concern appear to be either polyurethanes or cured polybutadiene prepolymers. The cross-links are of the ester type and should be susceptible to cleavage by several chemical approaches.

In order to justify some of the proposals for degradation which follow, a brief summary of the chemistry of of these two binder systems will be presented.

A. Polyurethanes

The polyurethane binders are produced according to the following generalized reaction:



cross-linked polyurethane

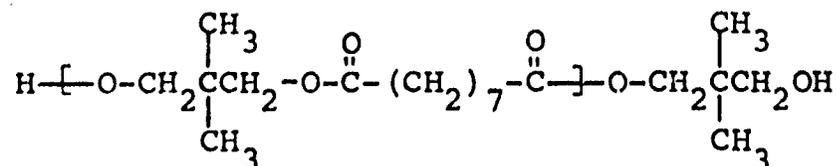
$$n + x + 2/3y$$

Cross-link density is a function of y/x , since the trifunctional molecule is the cross-linking agent. If y/x is large, cross-link density will be high. If y/x is low, cross-link density will be low. Since the polyurethanes are cross-linked polymers, they are not expected to be soluble in any solvent unless degradation of the cross-links is accomplished first. The remaining linear polymer should then be soluble in a number of organic solvents.

1. Dihydroxy Compounds

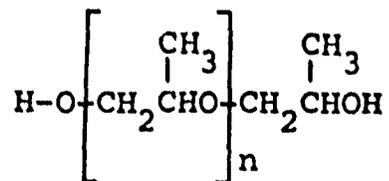
- Polyesters which are hydroxyl-terminated

Apparently, polyesters are now seldom used in propellant binders. An example of one which may have been used in some of the motors under consideration is neopentylglycol azelate (NPGA) of about 2,000 molecular weight:



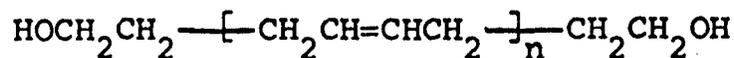
- Hydroxy-terminated polyesters

Perhaps the most commonly used polyether was poly-(1,2-oxypropylene)-diol (PPG) of about 2,000 molecular weight:



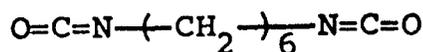
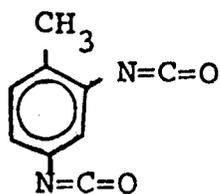
■ Hydroxy-terminated polybutadiene

This was a relatively recent development based upon lithium initiated polymerization of butadiene followed by termination of the anionic chain ends with ethylene oxide.



2. Isocyanates

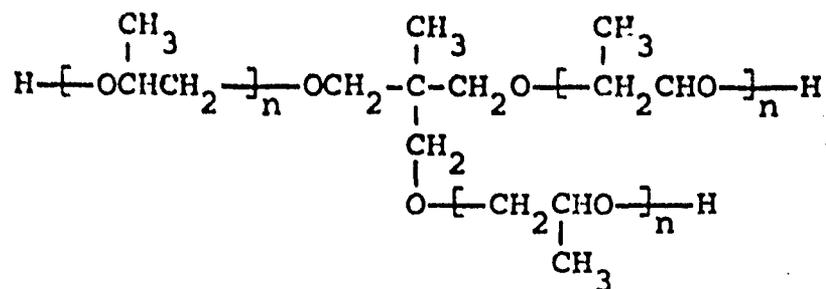
The isocyanate used must be at least difunctional. The most commonly used diisocyanates are the following:



2,4-Toluenediisocyanate (TDI) Hexamethylene diisocyanate (HDI)

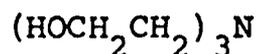
3. Trifunctional Hydroxyl Components (cross-linkers)

The cross-linking component must have a functionality of at least three. Trifunctional alcohols were mainly used. The following example of a trifunctional alcohol derived from use of trimethylolpropane as an initiator for propylene oxide polymerization is typical of the cross-linkers used:



4. Bonding Agents

Certain problems which arose in processing required the use of bonding agents. These are highly polar organic diols or triols which accumulate on the surface of the oxidizer particle yielding a dense layer of hydroxyl groups for the initial reaction with the isocyanate.



B. Polybutadiene Binders

Butadiene prepolymers containing carboxyl groups along with a curing or cross-linking agent have been used widely to make the binder matrix for solid composite propellants and very probably many of the new Polaris motors utilized this material. These systems provided 2-3 seconds higher specific impulse and permitted manufacture of composites containing 82 to 88 percent solids.

1. Polybutadiene Prepolymer

The prepolymers most extensively used were:

- Copolymer of Butadiene and Acrylic acid of molecular weight 2000-4000 (PBAA)

These were random copolymers and, dependent upon the method of synthesis, varied from zero functionality to

polyfunctionality and many problems resulted.

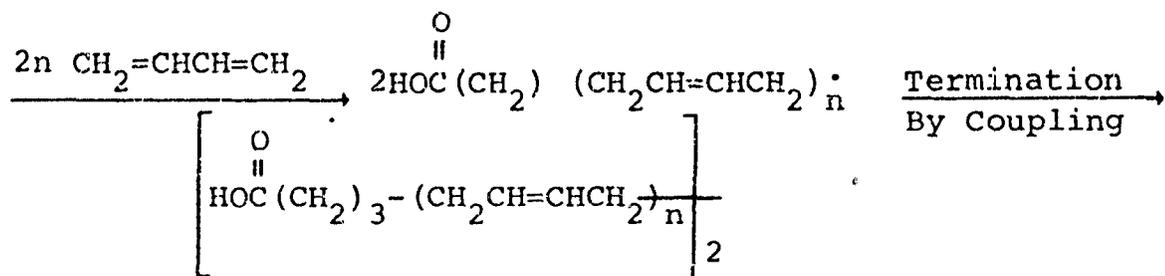
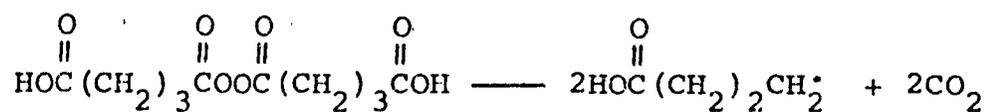
- Terpolymers of Butadiene, Acrylic Acid and Acrylonitrile of molecular weight 2000-4000 (PBAN)

Perhaps more solid propellant has been produced from this material than from any other single prepolymer. However, even though the use of this material overcame many of the problems associated with PBAA, the problem of controlling the functionality per prepolymer molecule still existed. Prepolymer functionality should be exactly two, i.e., every molecule should contain two and only two carboxyl groups.

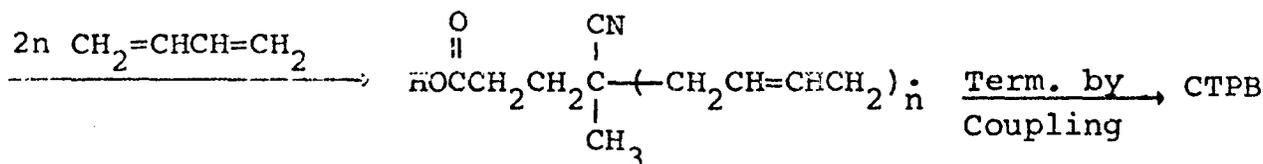
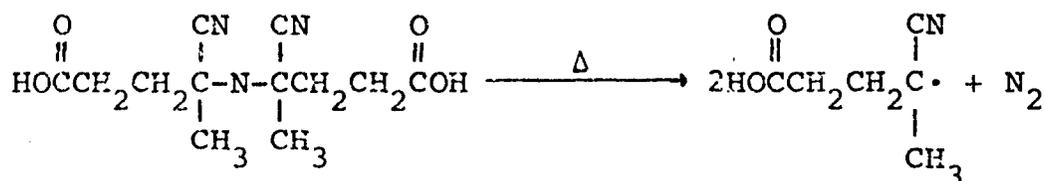
- Carboxyl Terminated Polybutadiene of molecular weight 2000-4000 (CTPB)

The problem of functionality was so important to reproducibility of butadiene based propellants that an extensive research program was undertaken both by industry and government to provide means of controlling the functionality. The following methods were developed to produce carboxyl-terminated polybutadiene.

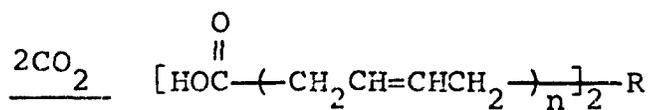
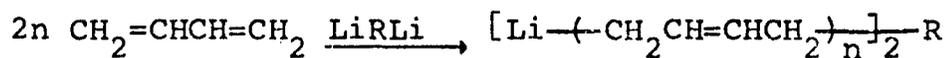
- Free-radical Initiated using Glutaric Acid Peroxide⁶



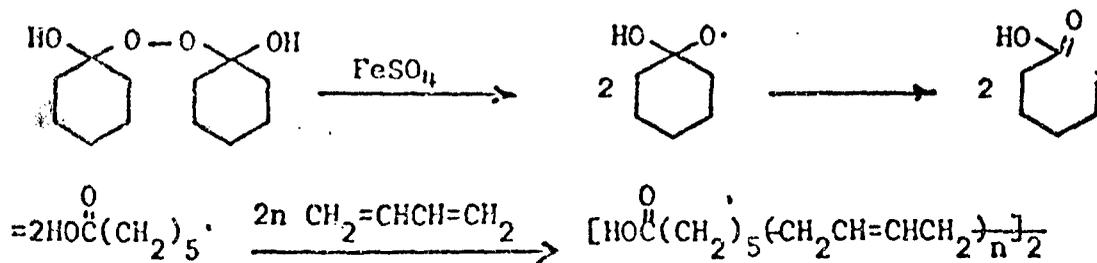
■ Free-radical Initiated using 4,4'-Azobis-4-cyanopentanoic Acid⁷



■ Anionic Initiated using Lithium⁸



■ Free-radical Initiated using Cyclohexanone Peroxide⁹

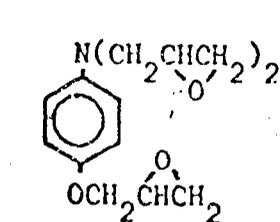


2. Curing Agents or Cross-linking Agents

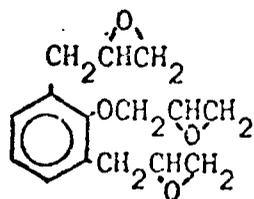
Curing agents used were di- or trifunctional compounds in the range of 0.2-1.0 percent of total which reacted with the carboxyl groups of the prepolymer to produce the binder matrix. The following chemical types were most often used:

■ Epoxides

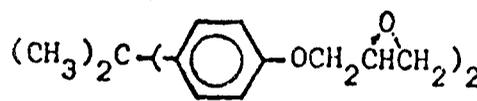
The following structures are typical of the polyfunctional epoxides used:



ERLA-0510

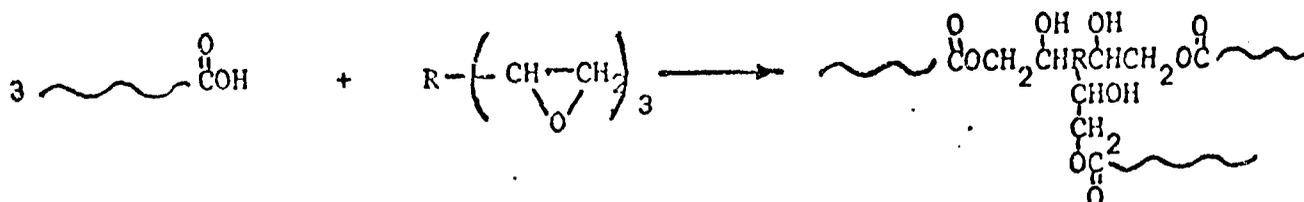


Epon X-801



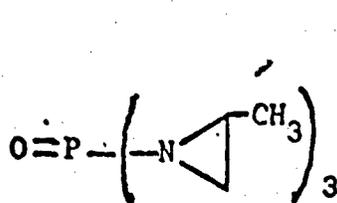
DER-332

The nature of the curing or cross-linking reaction can be represented as follows:

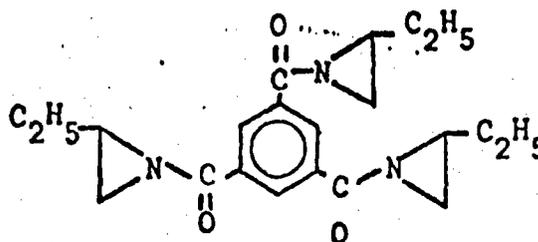


■ Aziridines

The following structures are typical of the polyfunctional aziridines used:

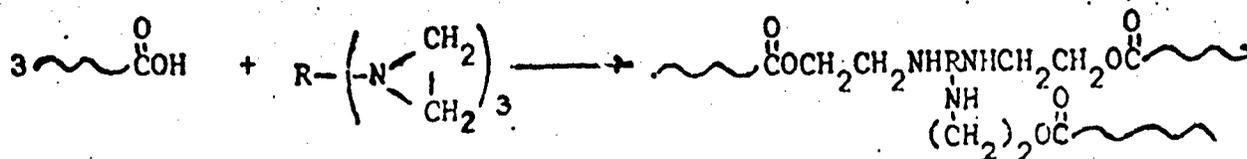


MAPO



BITA

The nature of the cross-linking reaction of polybutadiene prepolymer with aziridines can be represented as follows:



Suggestions for Chemical Degradation and Possible Recovery of Components

The possibility of chemically degrading the polymeric binders used in propellants should be investigated and an attempt made to devise a practical method of separation of the binder from metal and oxidizer. The chemical nature of the cross-links in both major types of binder under consideration indicates that it may be possible to develop a method which will be applicable to both types.

Properties of Polyurethanes and Possibilities for Degradation

■ Hydrolytic cleavage

Although the urethane link is an ester-like link, it is more stable to hydrolysis than esters; however, it is

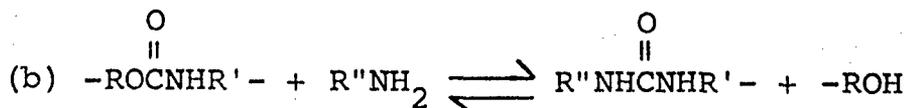
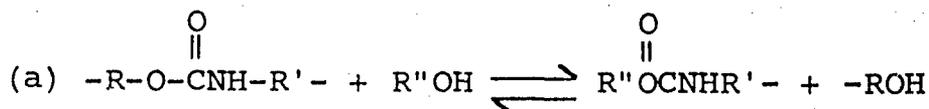
subject to both acidic and basic hydrolysis. Generally, strong acid or strong base is necessary to accomplish hydrolysis at a reasonable rate. Unfortunately, AP is converted to free ammonia and perchlorate ion in presence of strong acid. This limits the use of a hydrolytic reaction for degradation, particularly if recovery of AP is a prime objective.

■ Thermal degradation

Polyurethanes derived from primary and secondary alcohols generally require temperatures above 200°C before thermal degradation occurs at an appreciable rate. Those derived from tertiary alcohols and phenols undergo thermal degradation at a lower temperature, as low as 50°C;¹⁰ however, it appears that the latter are seldom used in the binders under consideration. Thermal means of degradation, therefore, appear to be impractical, particularly in presence of the large amount of oxidizer

■ Solvolytic cleavage

The urethane link is cleaved by (a) alcohols and (b) amines (ammonia may also be used):



Since polyurethane binders are synthesized from a mixture of dihydroxy and trihydroxy compounds, use of a monohydric alcohol, e.g. methyl alcohol or n-butyl alcohol, or of a monofunctional amine, e.g. ethyl amine or n-butyl amine, would accomplish a chain cleavage for each molecule which reacts. Sufficient reaction would cleave all cross-links and the remaining linear polymer would then be soluble in a suitable solvent.

The reactant alcohol or amine may be introduced as a solution in a suitable solvent to swell the matrix to permit more rapid penetration of the reactant to the cross-links.

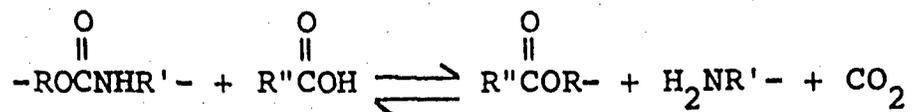
The reactions are equilibrium reactions and a large excess of the monohydric alcohol or monofunctional amine would, of course, favor the desired degradative reaction, and may also function as a solvent for the fragments.

These degradative reactions can also be catalyzed. The effective catalysts are generally the same as those which favor the polymerization reaction, i.e., the reaction of the alcohol with the isocyanate.

Catalysts suggested¹¹

Boron trifluoride etherates, pyridine or other tertiary amines, ferric acetylacetonate, and cobalt naphthenate have been shown to be effective catalysts for urethane formation. The latter has been shown to increase the rate of urethane formation by ten-fold. Ferric acetylacetonate has been shown to accelerate the reaction of an isocyanate with an alcohol up to 10^7 times.

It should also be possible to accomplish chain cleavage (and cross-link cleavage) by reaction of the urethane link with a monobasic organic acid:



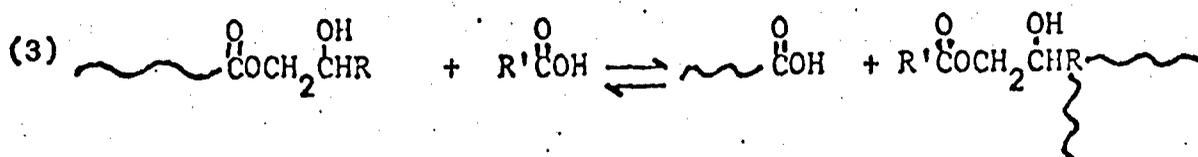
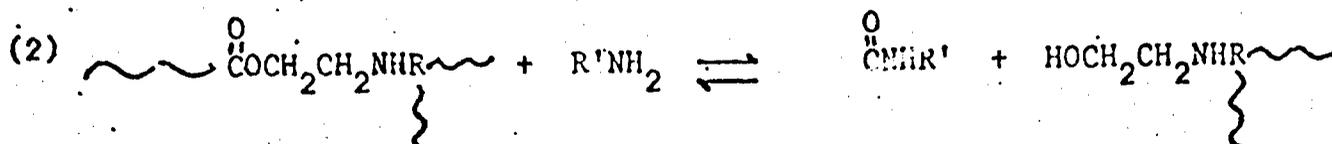
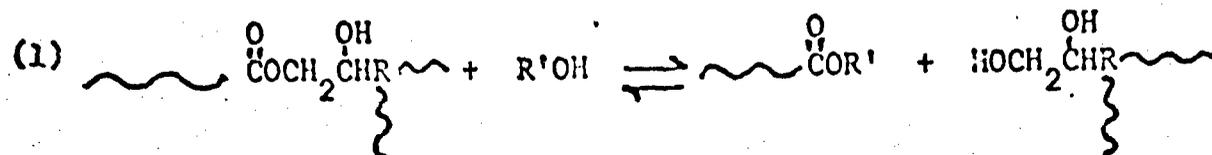
This equilibrium would favor the desired degradative effect if a large excess of the monobasic organic acid is used. The reaction should also be susceptible to catalysis.

Properties of Cured Polybutadiene Binders and Proposals for Degradation

Since the polybutadiene based binder matrices are extensively cross-linked, there is little possibility that solvents alone could be used to remove them from the oxidizer and metal. The most vulnerable link in this matrix is the ester link which is known to be hydrolyzable through either acid or base catalysis to the corresponding alcohol and carboxyl group. Such hydrolytic reactions would also cleave the cross-links and leave the liquid prepolymer of 2000-4000 molecular weight. (Some cross-linking may have occurred between these prepolymer chains through oxidation processes on the carbon-carbon double bonds of the chain). However, the problem of recovery of AP almost precludes the use of strong acid or strong base to hydrolyze the matrix. Thermal degradation of these matrices also appear not to be feasible in the propellant form due to potential hazard from rapid oxidation.

The most feasible method of degradation, similar to that of the polyurethanes, appears to be based upon a depolymerization-termination reaction utilizing monofunctional

alcohols, ammonia amines or carboxylic acids. These equilibria are shown in the following equations:



These reactions could also be catalyzed to possibly lower the activation energy of the process. A large excess of the monofunctional reactant would favor the degradative or depolymerization process, and could also function as a diluent or solvent. However, it may be necessary to use a solvent as well which will dissolve the liquid prepolymer and aid in separation of the binder matrix from the oxidizer (AP) and metal.

The catalyzed degradative reaction should also be studied with the hope that the catalyzed reactions will show the magnitude of rate enhancement that has been observed in certain of the catalyzed urethane-formation reactions. These suggestions are based upon the principal that a true catalyst does not change the ratio of products to reactants at equilibrium but merely changes the activation energy for the process which would change the rate. The principal of microscopic reversibility is relied upon

to make the assumption that the mechanism for the reverse degradative reaction would be the same as that for the forward reaction which led to the cross-links.

Properties of Ammonium Perchlorate Which May Be Useful in Economic Recovery

Ammonium perchlorate is reported to absorb sufficient ammonia at room temperature to liquify,¹² giving solutions resembling Diver's solution (NH_4NO_3 , NH_3). Although the salt (AP) forms no known hydrates, it is reported to form a triammine,^{13,14} $\text{NH}_4\text{ClO}_4 \cdot 3\text{NH}_3$, which is unstable at room temperature. The solubility of AP in liquid ammonia is 137.93 g/100g NH_3 at 25°C.¹³ Its water solubility at the same temperature is only 25.5g/100 g H_2O .¹³ This property of AP suggests that liquid ammonia could be used as a useful solvent in a recovery method of this component of composite propellants. The possible hazard of hazards of the system must be considered carefully, and some laboratory studies conducted before any large-scale attempts to utilize this concept are made.

Important Factors to Consider in Planning Potential Research and Development on Recovery and Reuse of Propellant Components

Propellants may have been stored with little control under rather wide extremes of temperature and aging may have occurred. Aging is defined as the sum of the changes the propellant undergoes in the interval between curing or casting and firing in a rocket chamber. The outward manifestations of aging are changes in the physical and mechanical properties. These outward changes are symptomatic of physico-chemical changes on the molecular scale and the

latter must be identified and measured, if possible, in order to apply the appropriate recovery methods effectively and safely. Possible types of molecular-scale changes include depolymerizations or scissions of binder molecules, decompositions, crystallization of binder, phase changes, and various changes associated with minor components.

Ideally, binders would not have been found satisfactory unless it had been shown with considerable confidence that they do not undergo spontaneous crystallization during storage at any temperature, that they dissolve little or no oxidizer, and that they are chemically stable for long periods in close contact with the oxidizer. To the extent that these considerations may be relied upon, it may be assumed that most of the above possible physico-chemical changes will be minor. However, some method of monitoring these possible changes should be developed before chemical degradations are undertaken.

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