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U. S. NAVAL ORDNANCE TEST STATION ✓

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FOREWORD

In order to give the casual or occasional reader a better understanding of the background and reasons for doing the particular piece of research, one major topic from each branch of chemistry is reviewed. It is hoped that it will also serve to remind the individual researcher of the goal to be attained. In order to prevent the report from becoming stereotyped by the repeated use of the same introduction, new subjects will be treated each reporting period and reference given in topics to the issue giving the background review. In this way it is hoped that each research project will be treated approximately once a year. The background review given this time is:

Reactions of Nitrate Esters	C-3

This is the nineteenth in a series of NAVORD Reports which summarizes the bimonthly progress of research being carried out by the Chemistry Division of the Research Department. The work was carried out under Task Assignments 31001-01, 56017-01, 56019-02, and 63026-04.

This report is transmitted for information purposes only. It does not represent the official views or final judgment of the Naval Ordnance Test Station. It represents information released at the working level that is still subject to modification and withdrawal.

WILLIAM S. McEWAN
Head, Chemistry Division

Released under the
authority of:
JOHN H. SHENK
Head, Research Department

ABSTRACT

This report presents the technical progress of the Chemistry Division of the Research Department in the fields of nitrogen chemistry, physical chemical research, general research, combustion research, and propellant research. The contents cover the period of November - December 1957.

CONTENTS

NITROGEN CHEMISTRY

HIGH-NITROGEN COMPOUNDS[1]

A simplification of the present synthesis of 1- and 2-methyl-5-vinyltetrazoles is greatly desired. Although the yields of mixed 1- and 2-methyl-5-(2-hydroxyethyl)tetrazole are approximately 90% in the current process, the methylation of 5-hydroxyethyltetrazole is done in ethanol solution and considerable manipulation is necessary. A significant improvement in processing time can be achieved without appreciable loss in yield by employing the following procedure: 5-hydroxyethyltetrazole synthesis in dimethyl formamide solution, vacuum evaporation of solvent, solution of residue in aqueous base, sparging with air to remove ammonia, methylation with dimethyl sulfate, and continuous extraction of the methyl hydroxyethyltetrazoles with ethyl acetate or chloroform. An over-all yield of 86% of methylhydroxyethyltetrazoles was obtained in a four-mole reaction. Distillation of the mixture gave 41.8% of the 2-methyl isomer and 44.2% of the 1-methyl isomer. A 92.6% yield of mixed methyl hydroxyethyltetrazoles was obtained in a 0.5-mole reaction, starting, however, with purified 5-hydroxyethyltetrazole. Since the solubilities of the 1- and 2-methyl-5-(2-hydroxyethyl)tetrazoles differ considerably, an effort will be made to extract preferentially one of the isomers and thus achieve a separation of the isomers without resorting to a high vacuum distillation.

Sodium 5-hydroxyethyltetrazole can be quantitatively methylated with an equimolar amount of dimethyl sulfate at 35-40°C in dimethyl formamide; no difficulties were created during the reaction or the work-up by this particular solvent. Normally this methylation is performed in water or ethanol. When one-half mole of dimethyl sulfate was employed per mole of sodium salt, the yield dropped to about 56%, even though the temperature of reaction was increased to 90°C. The difficulty of methylating sodium 5-hydroxyethyltetrazole with potassium methylsulfate in water or ethanol was reported earlier (Ref. 1).

Several attempts to demethoxylate the 1-methyl-5-(2-methoxyethyl) tetrazole have not given the desired 1-methyl-5-vinyltetrazole monomer. Base catalyzed demethoxylations invariably result in partially polymerized products. Acid catalyzed reactions do not proceed at useful rates at temperatures below 180°C. Similar attempts to dehydrate the 1- and 2-methyl-5-(2-hydroxyethyl)tetrazoles using acidic and basic catalysts were equally unsuccessful. Initial efforts to convert

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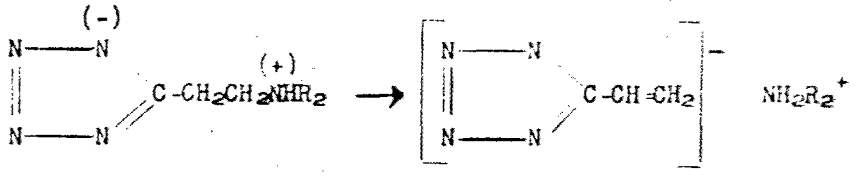
[1] Contributed by W. G. Finnegan and R. A. Henry

sodium 2-(1- and 2-methyl-5-tetrazolyl)ethane sulfonate to 1- and 2-methyl-5-vinyltetrazole by heating in an aqueous sodium hydroxide solution failed. Other methods for effecting a dehydrosulfonation are under consideration.

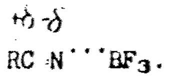
The synthesis of the 1- and 2-methyl-5-vinyltetrazoles would also be greatly simplified if the readily available 2-chloropropionitrile could be converted to 5-(2-chloroethyl)tetrazole. Reaction of this nitrile with ammonium azide, however, did not proceed in the expected manner; hydrazoic acid was evolved.

Apparently, sodium azide and either β-aminopropionitrile hydrobromide or β-dimethylaminopropionitrile hydrochloride react in dimethyl formamide at 125°C to give mainly 5-vinyltetrazole or the corresponding amine salts (cold aqueous solutions of the products rapidly decolorized permanganate and amine was immediately evolved upon the addition of sodium hydroxide). Very little of the desired 5-(β-aminoethyl) or 5-(β-dimethylaminoethyl)tetrazole was isolated. It is suggested that the following isomerization readily occurs and that under the reaction conditions employed ammonia or dimethylamine are lost from the salts by volatization.



where R is CH_3 or H

Some additional experiments have been performed to extend the studies reported previously (Ref. 1) on conditions which favor the conversion of alkyl or aryl nitriles to 5-substituted tetrazoles. In general, the results, which are summarized in the following table, confirm the earlier conclusions; however, three additional points should be noted: (1) Boron trifluoride-diethyl ether complex is about as effective as ammonium chloride in catalyzing the reaction, possibly due to the formation of



$$R\overset{+\delta}{C}\equiv\overset{-\delta}{N}\cdots BF_3.$$

(2) Water is apparently harmful to the reaction. (3) Dimethyl formamide is a much better solvent in which to perform the reaction than certain polyethers.

TABLE 1. Further Studies on the Conversion of Benzonitrile to 5-Phenyltetrazole

0.2 mole of benzonitrile, 7 hr at 123-125°C; 100 ml of solvent, and 0.22 mole of sodium azide.

Catalyst	Amount	Kind of Solvent	Yield, %
none	-	DMF	24.9
NH_4Cl	1.07 g (10 mole %)	DMF	59.6; 54.1
$C_6H_5NH_3Cl$	2.6 g (10 mole %)	DMF	73.8
BF_3-Diethyl ether	3.0 g (10 mole %)	DMF	55.6
H_2O	5.0 g	DMF	5.8
none	-	Diglyme	0
BF_3-Diethyl ether	3.0 g (10 mole %)	Diglyme	0
$C_2H_5SO_3H$	2.0 g (8 mole %)	2-Methoxyethanol	16.3

A 91.5% yield of 5-methylmercaptotetrazole was obtained by heating a mixture of methylthiocyanate, sodium azide, and ammonium chloride in dimethyl formamide for 6 hr at 95°C. On the other hand, the yield of 5-benzylmercaptotetrazole was only 22% when benzylthiocyanate was reacted under similar conditions; sulfur was also formed, suggesting the formation of some thiocyanate ion. This result is consistent with the fact that the benzyl group is more readily displaced by a nucleophilic reagent than is the methyl group. With potassium thiocyanate, the only product isolated besides free sulfur, was 5-aminotetrazole (0.8% yield); potassium cyanate gave no tetrazole derivative.

REACTIONS OF NITRATE ESTERS[1]

Background. Studies on the chemistry of nitrate esters are of interest and importance to the subject of rocket propellants for several reasons. The simple esters are prototypes of more complex nitrates such as cellulose nitrate, glycerol trinitrate, and petrin; and investigation of the chemistry of the prototypes provides a foundation for understanding the reaction of more complex systems.

In recent years a number of theories of propellant burning have been conceived. In order to test these theories, it is often necessary to prepare "tailor-made" compounds for use as ingredients in experimental samples of propellant mixtures. Toward this end, certain reactions are being studied which could potentially prove useful as preparative procedures for propellant components.

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[1] Contributed by R. T. Merrow and R. H. Boschan

One example of such a synthesis is the preparation of nitro compounds by the decomposition of acyl nitrates. In particular, fluoropicrin (trifluoronitromethane) has been isolated from the reaction between trifluoroacetic anhydride and nitric acid. In order to test the generality of this procedure, this reaction is being examined with higher molecular weight perfluorinated acid anhydrides, for example perfluorobutyric anhydride. Thus far, fluoropicrin is the only nitro compound that has been prepared by this procedure.

The synthesis of nitrate esters by the reaction of the corresponding chloroformates with silver nitrate has proved to be a fairly useful synthetic procedure. A number of nitrate esters have been produced in fair to good yields by this method. A study of this reaction using hexyl chloroformate enriched with O^{18} in the oxygen atom adjacent to the alkyl group has shown that in this case the reaction goes predominantly without rupture of the C-O bond.

New types of nitrate esters have been prepared, and are being investigated for possible use in mono- and bi- propellant systems. Two esters which have been prepared from fluorinated alcohols, for example, show rather unusual stability toward heat, and may be useful as desensitizers for such materials as nitroglycerin.

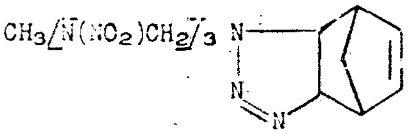
Other investigations (which were carried out and are presently being carried out) are derived either directly or indirectly from problems encountered in processing, storage, or burning of solid propellants: inhibition of grains by chemical means, instability, and unusual burning rates of leaded formulations. A study of the reactions of nitrogen dioxide with stabilizers and ballistic modifiers was recently concluded, and a similar study of reactions of nitrate esters with these compounds is nearly finished. Ramifications of these investigations have led to other research of a more fundamental nature, including the decomposition of nitrate esters in trifluoroacetic acid, and photolysis of nitrate esters in the liquid phase.

Progress. The study of the reactions of nitrate esters with ballistic modifiers and stabilizers in trifluoroacetic acid (TFA) has been essentially completed and the related investigation of the solvolytic decomposition of the nitrates in TFA is continuing. It has been found that the solvolysis is apparently catalyzed by ultraviolet light. Nitrogen dioxide is consumed and reduced by a solution of butyl nitrate in TFA, but not by either the nitrate or the solvent alone. The "induction period" observed when the reaction was followed by ultraviolet spectrometry is not observed when the rate of disappearance of butyl nitrate was measured polarographically. Heptafluorobutyl nitrate does not appear to react with trifluoroacetic acid at room temperature.

Another polyfluorinated nitrate ester was prepared. 2,2,3,3,4,5-Hexafluoropentamethylene glycol dinitrate was obtained in 80% yield by treatment of the glycol with mixed acid.

NITRAMINES[1]

2,4,6-Trinitraza-1-chloroheptane (I) reacts with sodium azide in dimethylformamide at 40°C to give a 79% yield of 2,4,6-trinitraza-1-azidoheptane (II), m.p. 105-108° (dec). Bicycloheptadiene and II react to give a quantitative yield of the triazoline III, m.p. 140°C (dec).



(III)

Dimethyl butynedioate and II in acetone solution at 50°C gave a 95% yield of 1-(2,4,6-trinitrazaheptyl)-4,5-dicarbomethoxy-1,2,3-triazole, m.p. 167-168°C (dec). Propargyl alcohol and II did not give a triazole when heated at 90°C for 30 min. Dimethylcyenamide and II did not react to give a tetrazole after 20 hr at 90°C. In fact, II was recovered unchanged. Sodium azide and 2,4,6-trinitraza-1,7-dichloroheptane react in dimethylformamide to give a 90% yield of 2,4,6-trinitraza-1,7-diazidoheptane, m.p. 135-137°C (dec). This material has a 50% point of 11 cm on a Bureau of Mines impact machine using Type 12 tools and a 2-kg weight.

Dimethylcarbamyl chloride reacted with silver nitrate in the presence of nitric oxide in acetonitrile to give a dimethylnitramine-dimethylnitrosamine ratio of 1:1 while in the absence of nitric oxide the ratio is 7:1.

Tri-(N-nitro-N-methylaminomethyl)amine was not cleaved by cyanogen bromide even after refluxing in chloroform for 24 hr.

An attempt to prepare 1,7-dicyano-2,4,6-trinitrazaheptane, a probable precursor of the corresponding dicarboxylic acid, by the treatment of the 1,7-dichloro-2,4,6-trinitrazaheptane (IV) with mercuric cyanide in the solvent dimethylsulfoxide (V) yielded a crystalline precipitate which on the basis of elemental analysis has the probable formula,

$$[Hg(CN)_2]_2[(CH_3)_2SO]_3 .$$

A very small amount of an amorphous solid was also isolated which contained nitramino groups but it could not be purified. Silver

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[1] Contributed by W. P. Norris and R. Reed

cyanide and the dichloro derivative IV did not react in the solvent V, probably because of the insolubility of silver cyanide.

Glycidol, in large excess, failed to react with IV at 50°C; experiments utilizing more severe conditions are underway. The dihalide IV reacted with a large excess of glycerol to form a water soluble crystalline derivative, melting point 100°C, which is believed to be the 1,2,14,15-tetrahydroxy-4,12-dioxa-6,8,10-trinitrazapentadecane. In the concluding phase of the study of the nitrolysis of hexamethylenetetrammonium salts with the mixture trifluoroacetic anhydride-nitric acid in the solvent sulfur dioxide, it was found that the methyl hexamethylenetetrammonium nitrate yielded a crystalline product which afforded 1-acetoxy-2,4,6-trinitrazaheptane upon being crystallized from hot acetic acid. When n-dibutylamine was subjected to the same nitrolyzing conditions n-dibutylammonium trifluoroacetate and N,N-n-dibutyltrifluoroacetamide were obtained; only a small amount of n-dibutylnitramine was isolated.

SYNTHETIC HIGH-ENERGY POLYMERS[1]

Tetrahydrofuran Copolymers

The boron trifluoride-ethylene glycol initiated copolymerization of tetrahydrofuran with ethylene oxide has been found to yield polymeric diols of varying composition and molecular weight. Recently, emphasis has been placed on the task of synthesizing a one-to-one copolymer having a molecular weight, structure, and other physical properties which would be reproducible and which would make the copolymer suitable as an intermediate for polyurethane formation. This goal has now been partially achieved. At an initial 1.0:0.9:0.1 molar ratio of tetrahydrofuran:ethylene oxide:ethylene glycol, 5.0 mole % boron trifluoride gave 90 to 95% yields of crude diol having a molecular weight of about 1200. These reactions were run in ethylene chloride solution (50 wt. %) at 0°C for periods of two to six days. The use of benzene as a solvent resulted in a slight reduction in molecular weight as might be anticipated. Unfortunately, elemental analyses on these copolymers are not yet available and their exact composition is therefore not known. However, it may be predicted that a one-to-one composition will be closely approximated as a result of the high conversions obtained.

A quantitative estimation of the amount of terminal unsaturation in these copolymers has not been made. However, their infrared absorption spectra show no absorption bands in the 6 micron region suggesting that difunctionality approximating 100% has been achieved.

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[1] Contributed by W. J. Murbach and A. Adicoff

Chromatographic grade aluminum oxide (basic) has been routinely used in a slurry technique as a scavenger for boron trifluoride. When used in amounts sufficient to completely remove catalyst fragments from the copolymer only 80 to 85% recoveries of diol are realized. Since this process may lead to composition and/or molecular weight fractionation some other potential scavengers have been investigated. Both calcium hydroxide and calcium fluoride have been tried without success. Other inorganic materials will be evaluated in the future.

Vinyltetrazoles

A technique for the polymerization of 2-methyl-5-vinyltetrazole in solution in such a fashion as to give a suspension of finely divided, filterable particles has been developed. The conditions that have been found necessary to obtain this result are: benzotrifluoride (practical grade), 180 parts; 2-methyl-5-vinyltetrazole, 20 parts; benzoyl peroxide (purified), 0.2 part. The system is flushed with helium for 1 hr with stirring, stirring discontinued, and the system sealed and polymerized at 80°C for 4 hr. Catalyst (benzoyl peroxide) concentrations have been varied as follows: 0.3, 0.2, and 0.1 part. The intrinsic viscosities in dimethylformamide of the polymers produced were 0.570, 0.765, and 1.000 respectively. These values correspond to molecular weights of 500,000, 774,000, and 1,190,000 respectively using the very approximate values for K and α reported previously (Ref. 1). A plot of the reciprocal of the molecular weight against the square root of the catalyst concentration gives points close to that of a straight line. The yields of polymer, however, appeared to drop off sharply as the catalyst concentration was changed from 0.2 to 0.1 part (from a yield somewhat greater than 99% to a yield somewhat greater than 86%). In practice this problem could be overcome by using some additional catalyst toward the end of the polymerization. This would disturb the molecular weight distribution slightly.

In a preliminary experiment a sample of the polymer prepared by the above method was molded into a clear pill. The clarity of the pill indicates that this polymer has molding properties superior to any of the 2-methyl-5 vinyltetrazole polymers previously prepared with respect to molding temperature and pressure.

Attempts have been made to use other high density solvents for the polymerization of 2-methyl-5-vinyltetrazole. None of the solvents used was successful in producing polymers of the desired nature. Apparently factors other than density (probably interfacial tension and solvent cohesive energy density) are important in obtaining the desired polymer.

Attempts to polymerize the monomer in higher concentrations (30 and 50%) were unsuccessful giving masses of polymer rather than discrete particles although some material of discrete particle nature was obtained.

Experiments have been conducted reusing the benzotrifluoride without redistillation. The solvent has been recycled four times. The polymerization seems to take place without any serious difficulties. The cycling data is given in the following table.

Cycle	Time, hrs	Yield, %
1	4	99
2	1	90
3	2	86
4	4	123

These results can be explained as follows. In each of the cycles listed 30 g of monomer were used in 270 g of solvent. In cycles 2 and 3 which were polymerized for less than 4 hr, some monomer was unpolymerized. In the fourth cycle the polymerization was conducted for 4 hr so that all of the initial charge was polymerized as well as the previously unpolymerized monomer giving a yield greater than 100% by about 7 g. These results indicate that a 4 hr polymerization at 80°C is necessary to convert all of the monomer to polymer. The intrinsic viscosities obtained in each of these runs will be determined.

Copolymers of 1-methyl-5-vinyltetrazole (1M5VTz) and 2-methyl-5-vinyltetrazole (2M5VTz) have been prepared from monomer solutions having ratios of 1M5VTz to 2M5VTz of 3:1, 1:1, and 1:3. The 3:1 and 1:1 samples were chloroform insoluble but were dimethylformamide soluble. There was some indication that some polymer had formed heterogeneously. The 1:3 polymer was dimethylformamide insoluble and 2M5VTz homopolymer was chloroform insoluble after two weeks agitation in these solvents. The polymers are probably insoluble because at the time of the polymerization experiment only an inferior grade of 2M5VTz was available. It has been observed in the past that monomer of low quality may give crosslinked and insoluble polymers.

ALKYLHYDRAZINES[1]

Solution Oxidation

Elucidation of the mechanism in the solution oxidation of 1,1-dialkylhydrazines is of importance because of a series of new organic reactions of the ionic intermediates ($R_2N{=}NH^+$) formed from the two-electron oxidation of 1,1-dialkylhydrazines in acidic solution as well as the formation of polymeric tetrazenes. Little is known about the stability of these intermediates, their basic character, their reactivity, and mechanism of the coupling reaction. Previously it was demonstrated that oxidation of mixtures of 1,1-dimethylhydrazine and 1,1-diethylhydrazine resulted in the formation of 1,1-diethyl-4,4-dimethyltetrazene in addition to the expected products of tetramethyltetrazene and tetraethyltetrazene. Isolation and purification of the pure unsymmetrical tetrazene was not attempted at that time.

Recently work has been initiated on the separation of mixtures of tetrazenes utilizing gas chromatography. During the past reporting period a Perkin-Elmer Model 154 Vapor Fractometer was used to resolve mixtures of tetramethyltetrazene, 1,1-diethyl-4,4-dimethyltetrazene, and tetraethyltetrazene at 90°C by the use of a "K" column which contains polyethylene glycol of average molecular weight of 1,500 on an inert media. With optimum conditions repetitive runs could be reproduced within ± 3% on known mixtures of tetramethyltetrazene and tetraethyltetrazene. It is estimated that in analyses, any component of a mixture could be determined within at least ± 5% of its true amount. The separation of the pyrolysis products of tetramethyltetrazene on the same column was possible along with a partial identification of the resolved components. For higher boiling tetrazenes the "F" column which contains a stationary phase of tetraethylene glycol dimethyl ether may have some application.

Solution oxidation of N,N'-diaminopiperazine with iodine in a neutral to basic aqueous solvent buffered with a sodium carbonate-sodium bicarbonate system gives rise to a solid polymeric tetrazene. The polymer could not be purified by recrystallization because of its low solubility in the various solvents investigated. Efforts were directed toward enhancing the solubility of the polymer by attempting to terminate the polymer by the introduction of other molecules which contain only one reactive hydrazine group. 1,1-Dimethylhydrazine and 1,1-di-n-butylhydrazine did not give successful chain termination. It is believed that this result arises from the

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[1] Contributed by W. R. McBride, N. N. Ogimachi, E. M. Bens and H. W. Kruse

differences in oxidation potential between the diaminopiperazine and the 1,1-disubstituted hydrazines.

Work has continued on the preparation of substituted hydrazines which could subsequently be used in chain termination studies and in hydrazine oxidation studies. Nitrosation of piperidine gave N-nitrosopiperidine (b.p. 96.2-98°C/10 mm) in 84% yield. Subsequent reduction with $LiAlH_4$ gave N-aminopiperidine (45-48°C/10 mm) in 45.5% yield. The poor yield in the reduction is partially due to accidental ignition of the reaction mixture and to difficulties in removal of aluminum and lithium ethylates which are formed in the decomposition of the reduction complex. A portion of the N-aminopiperidine was oxidized with iodine to give dicyclopentamethylenetetrazene (m.p. 44.8-46°C yield 87.5%. Anal. Calculated: C, 61.0; H, 10.1; N, 28.9. Found: C, 61.2; H, 10.3; N, 28.6).

N-methylpiperazine was prepared by treating piperazine with formaldehyde and reducing the polymer which is formed with powdered zinc and hydrochloric acid (crude yield 73%). Nitrosation of the crude product gave N-methyl-N'-nitrosopiperazine (b.p. 93-98°C/3-6 mm yield 19.1%). Subsequent reduction with $LiAlH_4$ gave N-methyl-N'-aminopiperazine (b.p. 76-78/12 mm yield 25.6%. Anal. Calculated: C, 52.2; H, 11.4; N, 36.5. Found: C, 51.8; H, 10.8; N, 35.5).

Two other substituted hydrazines were prepared but the yields were poor and purification of the final product has not been accomplished. The compounds are 1,1-diethanolhydrazine and N-(β-hydroxyethyl)-N'-aminopiperazine.

Work is in progress to test the effectiveness of the above mentioned compounds as chain terminators in the oxidation of N,N'-diaminopiperazine. Efforts have also been initiated on the preparation of N-aminopiperazine.

PHYSICAL CHEMICAL RESEARCH

COORDINATION COMPLEX STUDIES[1,2]

The supposedly simple cobaltous azide has been under study. The nature of the material produced by the reaction of ethereal HN_3 with cobaltous carbonate is uncertain. It does not appear to be simply $Co(N_3)_2$, since there is some evidence of aquation. Its thermal decomposition at 140°C differs markedly from that of the complex hexamminecobalt(III) azide in that all runs to date have terminated in violent explosions with very little evolution of gas prior to ignition.

ULTRAVIOLET STUDIES[3]

In addition to the previously reported results, the transmission characteristics of alpha-nickel sulfate hexahydrate at liquid nitrogen temperatures were determined in the visible and ultraviolet region. All necessary information for consideration of this crystalline compound for filter application is now available. However, several factors defer its acceptance pending the completion of the feasibility study of a sample of nickel fluoride which was prepared by Pennsylvania Salt Manufacturing Company in amounts sufficient for the growth of single crystals by the Naval Research Laboratory.

Several additional inorganic compounds were prepared at this Laboratory. Nickel fluoride tetrahydrate was obtained by evaporation over sulfuric acid of a solution of the amorphous compound in 48% hydrofluoric acid. Cobalt (II) fluoride tetrahydrate was prepared by the action of hydrofluoric acid on cobalt (II) carbonate followed by evaporation of the resulting solution over sulfuric acid. Transmission measurements of pressed windows of these materials confirmed the opinion that the absorption of the nickel (II) ion is not attributed solely to its association with six water molecules either in aqueous solution or in alpha-nickel sulfate hexahydrate. Qualitative information was obtained on the transparency of crystalline nickel fluoride, its color and index of refraction.

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[1] Contributed by Taylor B. Joyner

[2] This portion of the report is UNCLASSIFIED

[3] Contributed by J. A. Happe and W. R. McBride

GENERAL RESEARCH

COMPOSITE PROPELLANTS

Analysis of Propellant Mixes for NH_3 and MTDA[1]

Isopropanol, methylethyl ketone, methylisobutyl ketone and toluene, were investigated for suitability as solvents in the sparging method for determining NH_3 and MTDA in composite propellant mixes. These were all used directly from stock, without drying, and suitability in terms of ammonia blank appeared to be chiefly dependent upon their water content as determined by the Karl Fischer technique.

Solvent	Water content Gram/100 ml	Blank, in terms of N/1 acid consumed
Isopropanol	0.41	1.26
MEK	0.31	[illegible]
MIBK	0.08	0.03
Toluene	0.01	0.00

The toluene result for "blank" was surprising because visual comparisons gave the impression that this solvent would dissolve an appreciable amount of ammonium perchlorate.

COMBUSTION PRODUCTS FROM RARE[2]

Construction is almost completed upon a device to sample solid rocket exhaust material from experimental designs of RARE. The equipment consists of a piston and related equipment to inject a probe laterally into the rocket flame in a reproducible manner. The probe is constructed similarly to one previously described (Ref. 2). It consists of twenty-five 1/8-in. diameter holes 1/4-in. apart in a bar of steel which serves as the sample holder. A 1/4- x 1/4-in. stainless steel bar with matching holes serves as

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[1] Contributed by R. H. Pierson

[2] Contributed by A. N. Fletcher, L. A. Burkardt, and G. W. Leonard

a guard to prevent sampling while the probe is being brought into position. Appropriate stops align the holes of the guard and the sample holder when the probe is in its desired location in the flame. A microswitch will be attached in order to measure the length of time the probe is in the flame.

MILLICOULOMETRIC INVESTIGATIONS[1],[2]

The millicoulometric investigations previously presented have been completed and are to be published as NavOrd Report 5367. This report presents, in detail, a method by which n-values in polarography may be accurately and repeatably obtained. The method is designed to be employed with a Sargent Model XXI Recording Polarograph. The investigations have shown that accurate millicoulometric results will be obtained if current flow, as recorded by the polarograph, is measured with no electrical damping introduced into the circuit. A rapid technique of integration of the strip-chart trace has afforded a convenient means of obtaining the coulomb passage during the test. Various parameters such as temperature variation, oxygen contamination, and vibration effects have been evaluated and eliminated, when necessary, by careful design of the apparatus involved. The resulting method has yielded results with the standard compound, p-nitroaniline, whose n-value is 6, of 6.15 with an estimated standard deviation of 0.17.

This method was applied to members of the guanidine family with repeatable results. The results obtained indicated odd-numbered n-values for some of the reductions under the conditions of the tests. Full understanding of these results must await further investigation of the chemistry of the reductions of the guanidines.

A portion of this paper, presented by Gerald C. Whitnack at the Symposium of Modern Methods of Electrochemical Analysis connected with the Congress of Pure and Applied Chemistry at Paris, France, was well received by the audience. This report is to be published with David N. Hume and Guy William Leonard as reviewers of technical accuracy.

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[1] Contributed by R. D. Weaver

[2] This portion of the report is UNCLASSIFIED

ELEMENTAL ANALYSIS

Carbon, Hydrogen and Nitrogen Determination[1,2]

During the spectrophotometric study of complexes of tetraalkyltetrazenes with iodine in inert solvents such as carbon tetrachloride, a solid product could be isolated from the reaction of tetramethyltetrazene with iodine in reasonably pure form. Since this material spontaneously decomposed with the liberation of iodine within 5-12 min after preparation, a drastic limitation was placed on the microanalytical procedure. In all cases it was necessary to weigh the material on the microbalance, to place the boat in the combustion train, to sweep the air from the combustion train, and to begin the analysis prior to the decomposition of the material. Iodine was determined semi-quantitatively as iodide by a spectrophotometric technique. Analysis was C, 9.93, 10.02; H, 2.29, 2.35; N, 11.28, and I, ca. 75.9%. The weight loss on decomposition as well as the analysis of the decomposed material was determined. These analyses indicate the adaptability of the micro methods for the safe analysis of materials inherently unstable.

Elemental Analysis by Gas Chromatography[2,3]

Attempts at elemental analysis have been carried out in the past on an oxidizing system. Considerable difficulty has arisen with this system as water and nitrogen dioxide combine to react with the column material. The molecular seive column may absorb carbon dioxide irreversibly unless the column material is nearly anhydrous. The elution time of the carbon dioxide varies with the moisture content of the column material, also, making a quantitative method difficult at best.

Since the Unterzaucher method for the direct determination of oxygen utilized a reducing atmosphere, the pyrolysis product usually consisted of carbon monoxide. The accepted methods for the determination of the carbon monoxide rely upon its oxidation; measuring the carbon dioxide produced or the amount of oxidizing agent consumed. If all of the oxygen is not reacted to form carbon monoxide, this amount escapes detection. The direct measurement of the carbon monoxide produced and the residual carbon dioxide in the system can be made using solid adsorption chromatography utilizing a silica gel column. A recirculating system is used during the pyrolysis which is then all introduced on the column at the same time. Difficulties have been experienced with leaks but preliminary results indicate the analysis of nitrogen and oxygen is possible on the same sample.

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[1] Contributed by E. M. Bens and W. R. McBride
[2] This portion of the report is UNCLASSIFIED
[3] Contributed by E. M. Bens

INFRARED SPECTROSCOPY[1]

Approximately 100 spectra on gases, liquids, and solids have served to identify structure, to determine impurities in materials, and to characterize mechanisms of reactions. Of interest and added to the catalog of reference spectra are the following: guanylurea perchlorate, hexaminemononitrate and hexafluoropentamethylenedinitrate.

Transmittance measurements on IA Irdomes have been made on Corning 0160 glass, calcium aluminate, and arsenic trisulfide. A study of reflection losses of various dome compositions and geometric configurations has been initiated. The drop in transmittance as the curved surface of a dome is passed through the beam at 2 microns is due to asymmetries in the transmitted beam. Cylindrical strip lenses are capable of refocusing the beam on the entrance part of the instrument.

ELECTROCHEMICAL STUDIES

Polarographic Determination of Fe(AA) in Polyurethane Propellants[2]

Polarographic studies indicate the possibility of directly determining the ferric acetylacetonate (FeAA) content of a sample of POLARIS propellant (Aerojet ANP 2622AF) from an ethanolic extract of the propellant constituents. The ammonium perchlorate (NH_4ClO_4) in the sample serves as the supporting electrolyte. The FeAA in the extract gives a well-defined wave at approximately 0.55 v (vs. Hg-pool). The presence of N-2-hydroxyethyl-N,N',N'-tris(2-hydroxypropyl)ethylenediamine (MTDA) tends to shift the half-wave potential to more positive values. Small variations in NH_4ClO_4 content apparently do not affect the FeAA wave.

A standard curve was prepared by transferring the weighed constituents to a volumetric flask containing 95% ethanol (EtOH), shaking to dissolve the soluble constituents, and diluting to the mark with more EtOH. A stock solution of FeAA was prepared in the same manner. FeAA stock (1-5 ml) was added to 5 ml of the propellant extract and the resultant 10-ml solution flushed with nitrogen and polarographed. The wave heights obtained were approximately 0.38 ua per mg of FeAA in the 10-ml polarographic solution.

A series of standard samples (prepared at a later date) was used to check the standard curve. The samples contained the expected weight % (based on a 10-g sample weight) of all the propellant

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[1] Contributed by A. L. Olsen
[2] Contributed by W. M. Ayres

constituents. Preliminary results indicate the method is applicable under the conditions imposed. Further studies with actual batch samples of the propellant will be made and optimum conditions determined.

THERMOMETRIC STUDIES

Differential Thermal Analysis[1,2]

Studies on cellulose, cellulose acetate (C.A.), cellulose nitrate (N.C.), pentaerythritol trinitrate (PETriN), pentaerythritol tetranitrate (PETN), and 3,3-Bis (nitratomethyl)-oxetane were continued and a method of identification with thermograms is presently being developed.

Approximately 10 - 15 mg of material is mixed with 0.6 g of aluminum oxide in a 10- x 75-mm test tube and placed in the furnace for heating. The heating rate is controlled at 2°C per minute in most cases. The thermograms thus produced are compared for identifying marks which characterizes that compound.

A second test tube (10 x 75 mm), containing approximately the same amount of material as the above test tube, is fitted to an evacuated glass tube (2.5 ml) for gas sampling. Work is now in progress for determining the constituents in the gases expelled during a thermal decomposition with a Perkin-Elmer Vapor Fractometer.

JANAF-PANEL ON ANALYTICAL CHEMISTRY OF SOLID PROPELLANTS[2,3]

The thirteenth meeting of the JANAF-PACSP was held at Frankford Arsenal, Philadelphia, Pa., on 19-22 Nov. 1957. Only one representative (the Panel Chairman) from NOTS was present. In spite of some obvious absences due to curtailment of travel at many military establishments, the attendance was good; there were about 43 visitors and 27 Frankford employees, making a total of 70. The three talks by special guests, Gallant, Gordon, and Spurlin, were very interesting and generated a large number of questions. Round Robin No. 16 on % N in nitrocellulose by the NOTS titrimetric procedure has been completed and was profitably discussed at the meeting. The Composite Group will embark upon a cooperative test program regarding particle size distribution as determined by Micromerograph. Three representatives visited the nearby office of

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[1] Contributed by J. M. Pakulak

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[3] Contributed by R. H. Pierson

the manufacturer of the equipment, obtained much valuable information and made arrangements for a supply of standard samples suitable for such a program. A collective report of the first 12 round robins of the Panel has now been completed through the rough draft stage at NOTS. Plans were made in the Composite Group and also the General Panel to begin compilation of "Panel" methods, to take the place of or to supplement the program formerly directed toward review of Mil-P-11960B or its revisions. The next meeting of the Panel is tentatively scheduled for June 1958 at Longhorn Ordnance Works, Marshall, Texas.

CHELATION STUDIES[1,2]

Work has been started on the purification of some diamines which will be used in studies of the chelating abilities of these materials with certain cations. Commercial N(2-hydroxyethyl)N,N',N'-tris(2-hydroxypropyl)ethylenediamine (MTDA), N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine (Quadrol), and N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine (TEDA), have been distilled in the falling film molecular still after degassing at 70°C for a period of 16 hr. The materials found in the liquid nitrogen traps are mostly water with evidence of carbon dioxide and a ketone which has not been identified. The quantity recovered in the traps was very small, amounting to less than 1% of the total charge.

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[1] Contributed by E. M. Bens and G. W. Leonard

[2] This portion of the report is UNCLASSIFIED

COMBUSTION RESEARCH

BURNING-RATE STUDIES[1,2]

Treatment of Teflon or Kel-F with solutions of alkali metals in liquid ammonia results in a rapid attack that is visible to the eye as a darkening of the surface. This surface treatment results in a material which is capable of being bonded. A milder and more controllable reaction can be obtained by using solutions of alkaline earth materials such as calcium, or alkali metal amides in liquid ammonia. This also results in a surface capable of being bonded by adhesives. The exact nature of these reactions is not known, although attempts have been made to study them by infrared spectroscopy and by analysis for nitrogen to determine if amide groups had been added to the polymer. The use of these treated polymer powders in propellant applications appears to offer advantages over untreated materials. Accordingly, various compositions are being prepared using the treated polymers with oxidizers and metals. These mixtures are pressed into pellets and burned in a nitrogen atmosphere to determine the burning rates. Burning rates of these compositions vary widely. The fastest and slowest rates obtained thus far are shown in the examples below.

Kel-F; B; NH_4ClO_4 $d = 1.92$; $S_i = 100$ cm.; at 1,000 psig, B.R. = 1.4 cm/sec

Kel-F; B; NH_4NO_3 $d = 1.86$; $S_i = > 180$ cm; at 1,000 psig, B.R. = 0.26 cm/sec

(d = density, S_i = impact sensitivity, B.R. = burning rate)

At present an investigation is underway to find a better vehicle to suspend the solid materials. Attempts are also being made to find other methods of treatment of the fluorocarbon polymers that could result in improved propellants.

NITRIC ACID STUDIES[2,3]

Chemical shifts produced in the position of the proton resonance by the addition of nitronium perchlorate and potassium perchlorate to nitric acid have been measured. The data have been

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[1] Contributed by H. Williams and C. D. Stanifer

[2] This portion of the report is UNCLASSIFIED

[3] Contributed by J. A. Happe and H. F. Cordes

plotted as observed shift versus moles of solute per mole of nitric acid. For both salts the plots are linear with the shifts being toward lower field strength. The slope of the nitronium perchlorate curve was 144 cps per mole of solute per mole of nitric acid over the range of zero to 0.07 moles of solute per mole of nitric acid. None of the points deviated by more than 0.5 cps from the linear plot. The potassium perchlorate data could be represented by a straight line of slope 191 cps per mole of solute per mole of nitric acid up to a solute concentration of 0.0075 moles per mole of nitric acid. The maximum deviation of an individual point from the linear plot was 0.2 cps.

Accurate measurements have also been made of chemical shifts produced by the addition of sodium perchlorate, an inert salt, to water at 25°C. These experiments have been carried to a solute concentration of 0.22-moles sodium perchlorate per mole of water. The data when plotted as described for the nitric acid system do not result in a linear plot but lie on a smooth curve with an initial slope of 280 cps per mole of solute per mole of water. A shift relative to pure water of 32 cps toward higher field strength was observed at the highest solute concentration investigated.

Several experiments have been carried out in order to determine the effect of dilution on the proton resonance position for nitric acid. Carbon tetrachloride and chloroform have been used as solvents for the anhydrous acid. Dilution of nitric acid with these solvents shifts the resonance position to higher fields as might be expected for a decrease in hydrogen bonding caused by dilution. A shift of 235 cps relative to water was observed for a 0.05-mole fraction solution of nitric acid in carbon tetrachloride as compared to a shift of 265 cps for the pure acid.

BORON-NITROGEN COMPOUNDS[1,2]

Studies have been started on two types of compounds involving boron-nitrogen bonds. The first of these is the reaction of decaborane with several hydrazines and amines and the second is the attempt to form polymers of four membered boron-nitrogen ring systems employing hydrazines and boron trihalides as starting materials.

Although the nature of the reaction and products formed is not known with certainty, it has been found that a number of alkyl hydrazines will react with decaborane to form polymer-like materials

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[1] Contributed by N. R. Fetter

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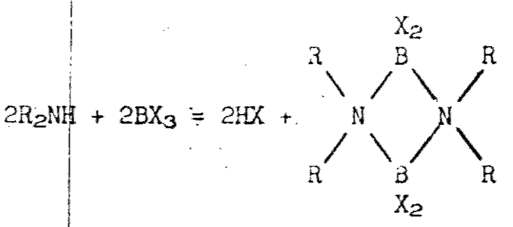
varying in consistency from thick fluids to stiff solids. These materials are easily combustible, simple to prepare, insensitive to impact, soluble in acetone, and are available in a wide range of consistencies, depending upon the hydrazine or amine used. As an example of a typical preparation, approximately 0.05 moles of 1,1-dimethylhydrazine are dissolved in 50 ml of benzene and 0.05 moles of decaborane are added slowly under nitrogen at room temperature. The product, which is insoluble in benzene, is a light yellow tacky fluid which becomes stiffer when the benzene and excess hydrazine are removed in a vacuum oven. Further experiments are planned to determine the nature of the reaction and its products.

Other investigators have found that secondary amines of the type R_2NH ($R = CF_3$ or C_2H_5) will react with BCl_3 or BBr_3 to form compounds with a four-membered boron-nitrogen ring



where X = Cl or Br.

It was thought that long chain polymers might be formed if 1,2-dimethylhydrazine and similar compounds were employed because they are essentially two secondary amines bonded through the nitrogen atoms of the molecule. It seemed feasible to use these hydrazines to make molecules in which the four-membered ring shown above could be repeated many times.

Experiments with hydrazine, methylhydrazine, 1,2-diformylhydrazine, and 1,2-dimethylhydrazine have been conducted using only BBr_3. So far no polymeric product has been observed, although a vigorous reaction always occurs. The exact composition of the products is unknown, but studies have been initiated to determine their character. In a typical preparation, 0.1 moles of 1,2-dimethylhydrazine are dissolved in 50 ml of anhydrous benzene. BBr_3 (0.1 moles) dissolved in 50 ml of benzene is added dropwise to the solution. The reaction mixture is maintained at 0°C and it is stirred continuously. At this point 0.1 moles of either pyridine or triethylamine are added to take up any HBr formed. The solid material in the reaction vessel is recovered by vacuum filtration and is recrystallized from absolute ethanol. The benzene is stripped from the filtrate by distillation to recover any soluble, non-volatile products.

USE OF THE IBM ELECTRONIC DATA PROCESSING MACHINE FOR QUANTUM MECHANICAL CALCULATIONS[1,2]

During the present reporting period two subroutines which were written as parts of Nesbet's integral transformation program have been debugged. After Professor Nesbet has had a chance to check them, they will be relativized and incorporated into the integral transformation program. In the meanwhile, coding of the simultaneous integration of three of the four 2-electron integrals (exception: the exchange integral) is well under way.

MECHANISM OF ACETYLENE PYROLYSIS[2,3]

As part of the program in the study of acetylenic type fuels, acetylene has been pyrolyzed in a flow system at 700°C. The products were mostly benzene with traces of methane, ethane, ethylene and butene, plus an undetermined amount of hydrogen. Conversions were held to 5% or less. The disappearance of acetylene obeyed second order kinetics. Deuterium was added to the acetylene in equal amounts in order to detect free radical intermediates. Exchange with the acetylene prevented accurate data on deuterium addition to the products; however, the amount of benzene-d_1 formed was low enough to rule out benzene formation via a phenyl radical process exclusively.

A 1:1 mixture of acetylene and acetone was photolyzed at 350°C for 5 min. at a pressure of about 200 mm Hg. Benzene again was a major product and propylene was obtained as a new product. When the reaction was carried out with acetone-d_6 very little deuteration was observed in the benzene. The propylene was a mixture $CD_3C_2H_3$ and $CD_3C_2H_2D$ in about the same ratio of CD_3H and CD_4 observed in the methane produced respectively.

This suggests that benzene is formed by a radical addition process which is initiated in pyrolysis by the bimolecular reaction of acetylene to form a bi-radical which adds to a third molecule then forming benzene. When CD_3 radicals are present the process could be initiated by methyl radical addition to one molecule of acetone forming $CD_3\text{-}CH{=}CH$. This can abstract hydrogen to form the propylene observed or add to another molecule of acetylene forming $CD_3\text{-}CH{=}CH\text{-}CH{=}\dot{C}H$ which then adds to a third acetylene forming $CD_3\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CH{=}\dot{C}H$. The latter can by ring closure and beta elimination form benzene and regenerate the original CD_3 radical. The pentadiene and toluene intermediates have not been found; however, an effort is being made to find them by mass spectrometer analysis.

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[1] Contributed by D. S. Villars

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[3] Contributed by C. M. Drew

UNSTEADY BURNING OF PROPELLANTS[1]

A window bomb with a volume of about 3.5 cu. in. for propellant combustion studies has been designed. It is hoped that with this bomb it will be possible to observe the behavior of propellants under the conditions of rapidly varying pressures such as occur in unsteady burning. It is intended that the bombs shall be used in conjunction with a motor driven rotating valve capable of producing cyclic pressure variations of frequencies up to 330 cps. Amplitudes will be inversely proportional to frequency, but it is expected that amplitudes of the order of 20% of mean pressure will be attainable at 100 cps.

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[4] Contributed by M. H. Hunt

PROPELLANT RESEARCH

SOLID PROPELLANTS[1]

Formulations

Several lots of propellant formulations, consisting of poly 2-methyl-5-vinyltetrazole (PMVT) (20% by weight) and micro-pulverized NH_4ClO_4 (80%) have been prepared. This formulation (referred to as TAP 2080) is mixed in a sigma blade mixer, using acetonitrile as a solvent for the polymer (1.3 part of solvent for part of polymer). The mixture is then dried in a warm blower oven either as chopped extruded strands or small chunks directly from the mixer. The dried material is finally ground in a Wiley Mill. (The friction sensitivity[2] is 30.8 kg - cm and the impact sensitivity 35 cm with a 2-kg hammer.) Much of the material prepared to date has been used in propellant and ignitor compositions by the Propellant and Explosives Department and the Weapons Development Department.

Compression Molding

Due to an inability to obtain high density, extruded strands on the 20 PMVT-80 ammonium perchlorate formulations, extensive burning rate measurements are not yet available. Attempts to extrude plasticized compositions also failed to give high-density products. In order to get satisfactory strands for the burning-rate studies, and effort is being made to prepare them by compression molding. The Wiley-milled material compression molds very nicely. Since the thermal stability of this composition appears to be adequate (no spontaneous detonation at 250°C; 1-sec temperature of explosion, 450°C; Taliani stability, slope = 0.35 at 110°C), a wider latitude in temperature is permitted during pressure molding. As the following figures show, and as one would expect, the optimum temperature and pressure depends upon the nature of the polymer and the particular conditions employed during its preparation. Polymer, which contains methyl cellulose (1.3% entrained during a suspension polymerization in water) and which probably possessed some cross-links, required both higher temperature and pressure to obtain plastic flow. For example, 115°C and 35,000 psi are the average minimum conditions required with several lots of polymer made at the Naval Powder Factory; whereas polymer prepared locally without methyl cellulose and under more favorable

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[1] Contributed by M. M. Williams

[2] PETN has a friction sensitivity of 37.1 kg - cm; tetryl, 460.6; and tetracene, 6.68.

conditions in non-aqueous systems has been molded at temperatures and pressures as low as 95°C and 20,000 psi, respectively. On a TAP 2080 formulation, using NPF polymer, molding conditions of 115°C and 60,000 psi gave a product with the same appearance and density as one obtained at 122°C and 50,000 psi. Densities of 1.79 g/cc versus a theoretical value of 1.80 g/cc have been realized. Thermal stability tests would seem to indicate that the molding temperature may be further increased if a reduction in molding pressure is desired.

Three samples of essentially pure polymer of known intrinsic viscosity have been obtained. Although the quantity is limited, it is hoped that both flow properties and tensile strength can be measured as a function of molecular weight on these samples.

Heats of Explosion

A round robin for standardization of calorimeters for heat of explosion determinations, sponsored by Picatinny Arsenal, included this facility. The tests have been completed and results submitted. A study of the effect of metal additives on the heat of explosion of composite propellant formulations has been initiated. X-ray diffraction patterns of the solid residues which remain after burning are being taken in order to characterize definitely the nature of the end-products.

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