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NAVY DEPARTMENT
BUREAU OF AERONAUTICS
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NAVAL RESEARCH
WASHINGTON, D. C.

13 April 1954
Report No. 807
(Quarterly)
Copy No. _____



RESEARCH IN
NITROPOLYMERS AND
THEIR APPLICATION TO
SOLID SMOKELESS
PROPELLANTS

Contract N7 onr-462 Task Order I
Contract NOas 53-618-c

Aerojet-General CORPORATION
A SUBSIDIARY OF THE GENERAL TIRE & RUBBER COMPANY



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RESEARCH IN NITROPOLYMERS AND THEIR
APPLICATION TO SOLID SMOKELESS PROPELLANTS

Contract N7onr-462, Task Order I
Contract NOas 53-618-c

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No. of Pages: 98

Period Covered:

16 November 1953 through
15 February 1954

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AEROJET-GENERAL CORPORATION

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CONTRACT FULFILLMENT STATEMENT

This quarterly report is submitted in partial fulfillment of Contract N7onr-462, Task Order I, and Contract NOas 53-618-c.

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Report No. 807

I. SUMMARY

A. This quarterly summary covers research conducted in partial fulfillment of Contract N7onr-462, Task Order I, and Contract NOas 53-618-c during the period from 16 November 1953 through 15 February 1954.*

B. The most important results are summarized below:

1. The vinyl polymerization of 2,2-dinitrobutyl acrylate has been further investigated using azo-bis-isobutyronitrile as an initiator. New data have been collected for the establishment of the relationship between the rate of propagation and catalyst concentration.

2. Emulsion polymerization experiments conducted with 2,2-dinitrobutyl acrylate revealed some difficulties in obtaining stable emulsions. Following a formulation based on extensive past experience with this problem, reproducibility of permanent emulsions was achieved.

3. A recently prepared new diisocyanate is 2-nitrazo-1,4-butane diisocyanate. Before polyurethanes were prepared from it the reactivity of the isocyanate function of the new diisocyanate was compared with the reactivities of the diisocyanates reported previously. Using 2-nitro-2-methyl-1,3-propanediol, the rate of reaction with 2-nitrazo-1,4-butane diisocyanate was studied at two catalyst concentrations. The results revealed that at a catalyst concentration of 1×10^{-5} mole ferric acetylacetonate per liter the rate of reactivity of the new diisocyanate was six times greater than that of 3-nitrazo-1,5-pentane diisocyanate and 100 times faster than that of 3,6-dinitrazo-1,8-octane diisocyanate. At a catalyst concentration of 1×10^{-4} mole of ferric acetylacetonate per liter the rates were too fast for an accurate measurement. It is believed that the increased reactivity of the new diisocyanate over the reactivity of those reported previously is caused by the proximity of the nitrazo group to one of the isocyanate groups.

* Previous work on Contract N7onr-462, Task Order I, was covered in Aerojet Reports No. 330, 345, 371, 386, 386A, 404, 417, 417A, 424, 457, 461, 468, 482, 495, 515, 540, 563, 590, 622, 638, 663, 686, 700, 720, 740, and 772.

Previous work on Contract NOas 53-618-c was covered in Aerojet Reports No. 720, 740 and 772.

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I Summary, B (cont.)

Report No. 807

4. The new 2-nitrazo-1,4-butane diisocyanate has been used for preparation of the new polyurethanes listed below. These new polyurethanes have been characterized by elemental analysis, relative viscosity, softening range, and stability tests:

<u>Polymer</u>	<u>Diol</u>
XV-A	2,2-dinitro-1,3-propanediol
XV-H	5,5,5-trinitro-1,2-pentanediol
XV-J	2-nitro-2-methyl-1,3-propanediol

5. In the past, great efforts have been made to obtain high-molecular-weight postnitrated polyurethanes. It was found possible to achieve this by conducting the postnitration under anhydrous conditions. When Polyurethane XV-A, obtained from 2-nitrazo-1,4-butane diisocyanate and 2,2-dinitro-1,3-propanediol, was subjected to postnitration, a product was obtained which did not represent the expected Polyurethane XV-AN. Furthermore, severe chain degradation occurred. Several years ago it was found that polyurethanes made from methylene diisocyanate cannot be postnitrated without extensive chain degradation. Because Polyurethane XV-A upon postnitration yields similar structures to those obtained with methylene diisocyanate polymers, it appears

that the structure $\begin{array}{c} \text{ONO}_2 \text{ NO}_2 \\ | \quad | \\ \text{--CNCH}_2\text{N--} \end{array}$ represents an unstable and readily degraded configuration. Similarly, the postnitration of Polyurethane XV-J also produced a degraded product.

6. The introduction of crosslinking and branching in the polyurethane chain results in products with improved physical and mechanical properties. When insoluble Polyurethane I-A, obtained from 3,3-dinitropentane diisocyanate and 2,2-dinitro-1,3-propanediol, was postnitrated, information was obtained on the degree of chain degradation and change of solubility characteristics. This work has now been extended to Polyurethane XIII-A, obtained from 3-nitrazo-1,5-pentane diisocyanate and 2,2-dinitro-1,3-propanediol branched with nib glycerol. From the acetone-insoluble starting material an acetone-soluble postnitrated product was obtained which, judging from the relative-viscosity measurements, was superior to the linear Polyurethane XIII-AN.

7. The recently installed Beken dispersion blade mixer was tested in a run with Polyurethane I-A crosslinked with 0.5% nib glycerol. It was found that higher monomer concentrations could be used than had heretofore been possible. Experiments like this are useful in providing technical data required for the manufacture of polyurethanes on a larger scale.

8. In the preparation of postnitrated polyurethanes a good deal of effort has been expended in developing a method for maximum nitration with a minimum of chain degradation. Although in most instances apparently high molecular weights were retained, a determination of the molecular weight of Polyurethane I-AN osmometrically revealed that more than 30% of the product diffused through the membrane. Therefore, a fractionation of Polyurethane I-AN was conducted with the thought that high-molecular-weight postnitrated polymers might be obtained with thermal stabilities improved over that of the unfractionated material. However, it was found that the thermal stabilities of the fractionated samples bore no relationship to the molecular weights.

9. It has been postulated in these laboratories that the ferric acetylacetonate which catalyzes the formation of polyurethanes also catalyzes the reverse reaction, and therefore the system must be in dynamic equilibrium. In order to confirm this hypothesis, a preparation of Polyurethane I-J, upon being brought to its maximum solution viscosity, was treated with an excess of one of the monomers. Samples were taken before and after this last step and identified by relative viscosities. It was shown that an excess of one of the reagents immediately shifts the equilibrium toward the formation of smaller molecules. Reestablishment of monomer equivalence again shifts the equilibrium to the formation of molecules with a higher molecular weight distribution.

10. The ultimate goal of the nitropolymer program is the successful formulation of a rocket grain. Therefore a good deal of effort has gone into the examination of suitable processes for accomplishing this objective. In previous quarters a definite program was followed in order to accumulate data which would be required in meeting this objective. Thus the effect of branching and crosslinking on polyurethane properties has been studied; as well as the use of excess of the reactants, monomer adjustment and the order and rate of addition of the components. All of these factors are carefully considered and applied in the following three distinct methods of nitropolymer formulation.

a. A single-stage casting of a crosslinked nitropolyurethane in the presence of a high-energy solvent-plasticizer.

b. Preparation of a prepolymer of intermediate molecular weight. Such a material may be stored and later used in a second-stage casting by adjustment of monomer equivalence. This method offers the advantage of lower requirements for heat dissipation and reduced shrinkage.

c. An extrusion process based on prior homogenization of nitropolymer, high-energy plasticizer, and solid oxidizer.

Each of the three processes has advantages, and each has introduced a new series of problems. In the casting procedures problems arise as the result of poor heat dissipation, bubble formation, high viscosity, reproducibility, mold release, etc. In the extrusion process, problems of homogeneity and reproducibility, which have caused some difficulty, have been largely overcome. Samples have been obtained by each of the three procedures and are being evaluated for physical and mechanical properties.

11. A prepolymer has been prepared and isolated from 3,3-dinitro-1,5-pentane diisocyanate and 5,5,5-trinitro-1,2-pentanediol with nib glycerol as the branching agent. The new prepolymer was well characterized by analysis, molecular-weight determination, and stability tests. The prepolymer can be converted into a final formulated product by adjusting to equivalence with diisocyanate.

12. A mixture of plasticized polyurethane and inorganic oxidizers was successfully extruded at 120 to 160°F and a pressure of 15,000 to 20,000 psi to give 3/16-in. rods. These specimens, ranging in specific impulse from 222 to 248 lbf sec/lbm, have high tensile strengths, excellent stabilities, and burning rates from 1.5 to 2.6 in./sec.

13. Up to the present time osmometric determinations of molecular weight have been conducted on nitropolyurethanes, while work on postnitrated polyurethanes was delayed for stability reasons. Unfractionated polyurethanes have given some difficulties because of the diffusion of low-molecular-weight polymers through the osmometer membrane. When low-molecular-weight fractions were removed, diffusion no longer was observed. In this report an attempt to determine the molecular weight of a postnitrated polyurethane is described. It was not successful because more than 30% of the polymer diffused through the membrane. When an isopiestic molecular-weight determination was run on the same polymer in methyl ethyl ketone as a solvent an approximate molecular weight of 26,000 was determined. The significance of these results lies mainly in the recognition that certain structures of polymers are severely degraded during nitration.

14. In order to confirm the isopiestic method for the determination of low-molecular-weight polymers, a comparative study was run with polymers whose molecular weight was determined by an alternative method. As comparison three samples of liquid polysulfide polymer furnished by Thiokol Chem. Corp. were checked and good agreement was found. In addition, the molecular weight of a sample of Polyurethane I-J characterized by an osmometric molecular-weight determination was determined by an isopiestic determination and good agreement was also observed. Thus, for the first time it has become possible to obtain molecular weights by two independent methods in the intermediate molecular-weight region of 20,000 to 40,000.

15. Diisocyanates containing the nitramino group have become very important intermediates for the preparation of polyurethanes. A number of them have been reported in the past. This work was continued with the synthesis of three new diisocyanates, the 2-nitrazo-1,4-butane diisocyanate, 3,7-dinitrazo-1,9-nonane diisocyanate, and 3,6,9-trinitrazo-1,11-undecane diisocyanate. Furthermore the work has been extended to the preparation of diols containing the nitramino group. 4-Nitrazo-1,2-pentanediol was prepared and characterized by a crystalline dibenzoate.

16. Stress-Relaxation

a. Stress relaxation data at six different temperatures were obtained on a plasticized polycrystalline propellant, N-4 double-base. The shape of the master curve and its temperature dependence reveal that this material is characterized by an extremely broad distribution of relaxation times (ca. 12 cycles) and has a distinctive relaxation time of 3200 sec at a distinctive temperature of 45°F.

b. Stress-relaxation data at three different temperatures were obtained on a plasticized crosslinked nitropolymer, XIII-A-10X-40D. The shape of the master curve and its temperature dependence reveal that this material is characterized by extreme rubberiness with a distinctive relaxation time of 0.03 sec at a distinctive temperature of 40°F.

c. An Aminco modulumeter has been used to measure the "rubbery" moduli of various crosslinked nitropolymers. Data show that 2% branching agent is sufficient to convert the linear polymer to a gel structure, whereas 25 wt% plasticizer is already sufficient to impart a rubbery character to the nitropolymer.

d. Tensile tests on Nitropolymer I-J at 75°F at a rate of strain of roughly 5 in./min characterize this material as extremely tough. The post-yield properties are as follows:

Ultimate Strain	9%
Maximum Stress	9000 psi
Work to Rupture	700 in.-lb/in. ³

II. TECHNICAL PROGRESS: NITROPOLYMERS (Contract N7onr-462, Task Order I)

A. VINYL POLYMERIZATION

1. Bulk Polymerization of 2,2-Dinitrobutyl Acrylate

a. Discussion

(1) Earlier studies of the kinetics of bulk polymerization of 2,2-dinitrobutyl acrylate catalyzed with azo-bis-isobutyronitrile* were continued, using a reaction temperature of 50°C. The present work made use of the "polymer precipitation method," in which several portions of each catalyzed monomer were sealed in glass tubes and permitted to react for a series of timed intervals, and the extents of reaction were determined by precipitating the polymer formed. A consistent body of results was obtained, providing useful guidance for process work.

* Aerojet Reports 686, pp. 6,7 and 712, pp. 4,5.

(2) Each catalyst concentration yielded a reasonably well-defined rate of polymerization (Figure 1). The usual correlations were attempted by observing the variations of rate with catalyst concentration and with molecular weight of product. These showed:

(a) A plot of rate squared vs catalyst concentration gave a smooth curve, not linear but bowing downward steadily.

(b) A plot of reciprocal of the degree of polymerization (estimated from viscometric measurements) vs rate was a horizontal line. No slight trend upward or downward was detectable.

(3) These observations may be discussed with reference to a mechanism applied by Tobolsky and Baysal to the bulk polymerizations of styrene and methyl methacrylate.* These authors consider a scheme of reactions in which there is no chain transfer to monomer (this postulate has been verified experimentally for this catalyst) and in which initiation occurs exclusively from mono-radicals. Under these conditions, the rate of polymerization, R_p , is expressed by

$$R_p^2 = R_{p,th}^2 + K^2[M]^2[Cat]$$

In which $R_{p,th}$ is the rate for the purely thermal reaction

K is a constant function of rate constants

$[Cat]$ is catalyst concentration
 $[M]$ is monomer concentration.

Thus, for the early stages of polymerization, in which $[M]$ has not changed greatly, R_p^2 should be a linear function of catalyst concentration.

(4) The fact that the actual line (Figure 2) is not straight but bows downward indicates that the system does not completely follow this mechanism. A similar, but much more pronounced, bowing was observed with trinitroethyl methacrylate catalyzed with methyl amyl ketone peroxide.** As yet, this effect has not been satisfactorily explained.

* J. Polymer Sci. VIII, 529-541 (1952) and XI 471-486 (1953).

** Aerojet Report No. 700, Figure 10.

Conversions in Bulk Polymerization of
2,2-Dinitrobutyl Acrylate at 50°C. Azo-bis-isobutyronitrile Catalyst.

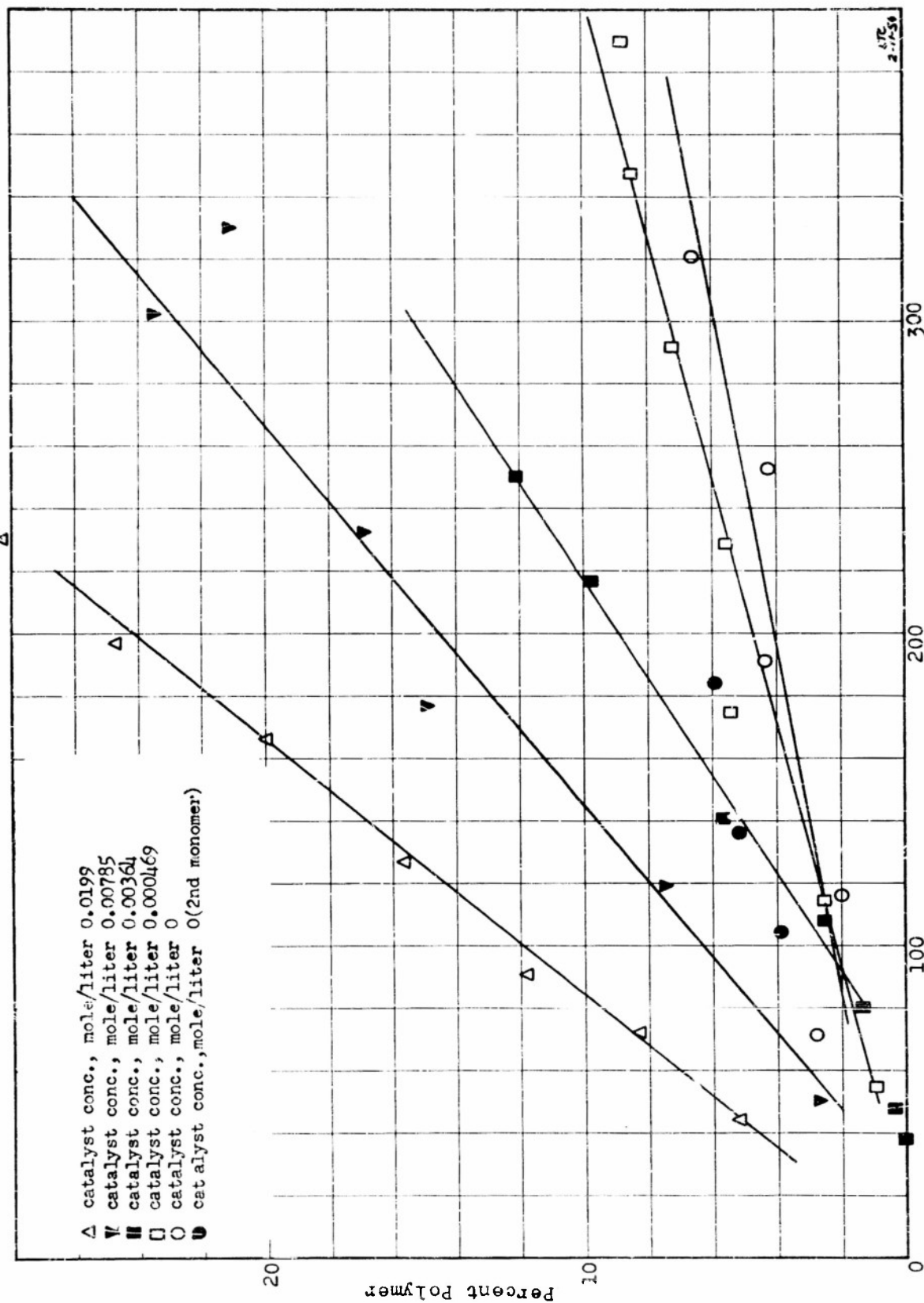


Figure 1

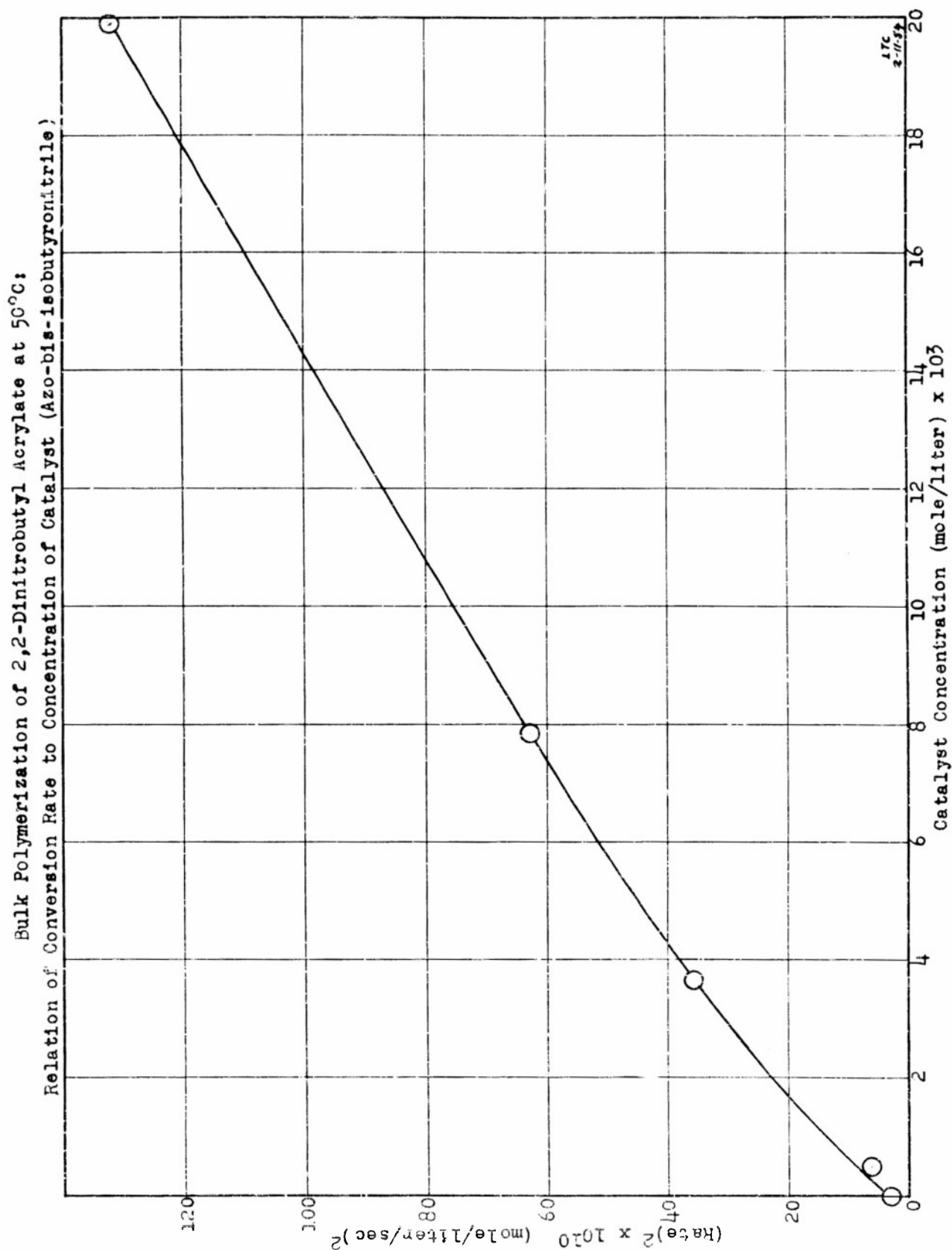


Figure 2

(5) The constancy of degree of polymerization, P_n , as shown on the plot of its reciprocal vs rate of propagation (Figure 3) is simply attributable to the fact that chain transfer to monomer overshadows other termination reactions. Tobolsky and Baysal show the relation* to be

$$\frac{1}{P_n} = \frac{k_{tr,m}}{k_p} + \frac{(2 k_{td} + k_{tc})}{k_p^2 [M]^2} R_p \approx \frac{k_{tr,m}}{k_p} + AR_p$$

in which the rate constants represent

$k_{tr,m}$, chain transfer to monomer

k_p , propagation

k_{td} , termination by disproportionation

k_{tc} , termination by combination.

The equations are somewhat different for some other mechanisms which were considered, but these also lead to constancy of P_n when $k_{tr,m}$ becomes large. The same influences are observable in the bulk polymerization of trinitroethyl methacrylate. In this case, $k_{tr,m}$ was so large in comparison with k_p that the value of P_n was only a few units. Because of the constancy of P_n , an evaluation of A is not possible.

(6) Although there is no question of the constancy of P_n , it should be noted that its absolute value is provisional, being dependent upon an early, rough relationship between molecular weight and intrinsic viscosity of acetone solutions. It may be necessary to shift the position of the horizontal line of Figure 3 when a better relationship is developed.

b. Experimental

(1) Inasmuch as the dinitrobutyl acrylate monomer prepared many months previously had polymerized slightly on standing, it was re-purified by dissolving it portion-wise in boiling hexane, precipitating polymer, and then stripping the solution on a steam bath under reduced pressure. After two such treatments, the product monomer gave a slight cloud when dropped into methanol. This amount of polymer was negligible, and the possibility of further purification was questionable. Accordingly, this product was accepted for use. Five hundred grams was prepared in this manner ($n_D^{26.3} = 1.4585$; original $n_D^{26.3} = 1.4608$). A small amount of one other monomer specimen was used for a check run at zero catalyst concentration. This monomer was purified in the same way except that the first solution in boiling hexane was treated with activated alumina in an effort to remove peroxides (100 g/2000 ml). Nine hundred and forty-five grams was prepared ($n_D^{25} = 1.4601$).

* cf Equation (11), Aerojet Report No. 590

Bulk Polymerization of 2,2-Dinitrobutyl Acrylate at 50°C with Azo-bis-isobutyronitrile Catalyst: Relation of Degree of Polymerization to Conversion Rate

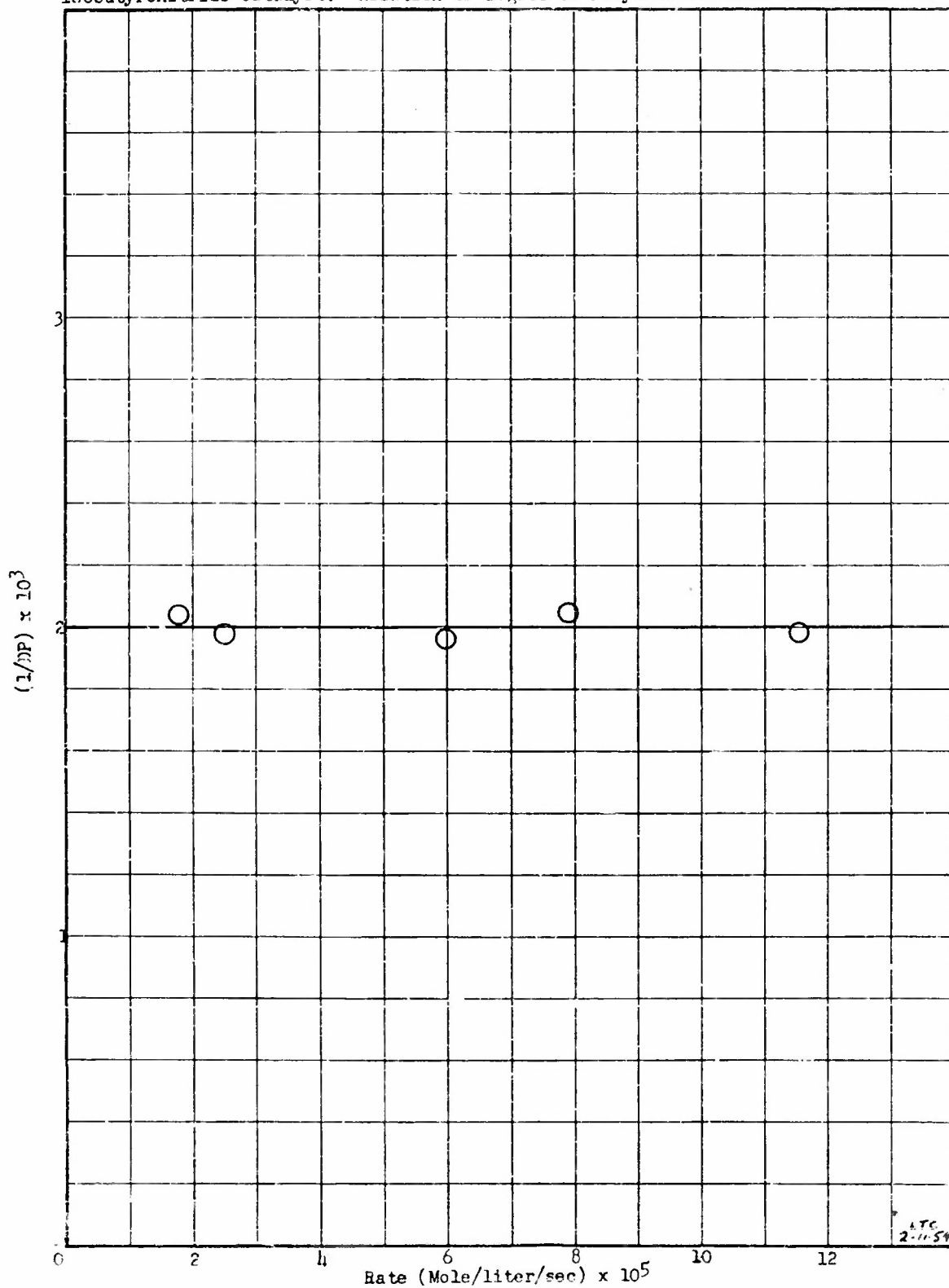


Figure 3

(2) Shortly before use, the azo bis-isobutyronitrile catalyst was recrystallized from ethanol; it was dried in a desiccator and kept stored in the refrigerator.

(3) Bulk polymerizations were conducted by sealing portions of catalyzed acrylate under vacuum in a series of glass tubes, permitting the reaction to proceed for timed intervals at 50°C, and measuring the extent of reaction by precipitating, drying, and weighing the polymer formed. These operations are similar to those described earlier.*

(4) Four runs at different catalyst concentrations, designated D, E, F and G, and two with no catalyst (H and I, using different monomer specimens) were performed in this manner. For these runs, yields are plotted vs time in Figure 1, and the best straight lines are drawn in; the slopes of these lines are values of R_p . Figure 2 shows a plot of R_p^2 vs catalyst concentration.

(5) The molecular weights of three or four polymers from each run were determined individually by dissolving them in acetone and measuring the relative viscosities of the solutions. Using the Baker equation, relative viscosities were converted to intrinsic viscosities, and these in turn were converted to molecular weights by a provisional relationship derived earlier.** These show that there is no trend with reaction time in the value of molecular weight. Then the average molecular weight for each run was converted to degree of polymerization, P_n . Values of the reciprocal of P_n for all runs are plotted against R_p in Figure 3.

(6) The complete body of results is summarized in Table I.

2. Emulsion Polymerization of 2,2-Dinitrobutyl Acrylate

a. A few experiments were performed in the emulsion polymerization of 2,2-dinitrobutyl acrylate in small vials. In order to economize on material, the first tests were performed using an incompletely purified monomer. Following a formulation based on extensive past experience with this problem,*** and using the same specimen of monomer in all preparations, it was found possible to produce consistently smooth, permanent emulsions. The formulation comprised:

Monomer and water
Atlas Tween 40 surface-active agent
Polyvinyl alcohol stabilizer
Lecithin
Ammonium persulfate catalyst

There is some question of the necessity for including the lecithin.

* Aerojet Reports No. 700, p. 4, and No. 686, p. 7.

** Aerojet Report No. 637, p. 13.

*** Aerojet Reports No. 562, 637, 660, and 772.

TABLE I

BULK POLYMERIZATION OF 2,2-DINITROBUTYL ACRYLATE AT 50°C
USING AZO-BIS-ISOBUTYRONITRILE CATALYST

Molecular weights of polymers determined from
viscosities at 25°C in acetone solution

<u>Run</u>	<u>Catalyst Concentra-</u> <u>tion, mol/liter</u>	<u>Polymerization Rate</u> <u>mol/liter/sec</u>	<u>Average</u> <u>Relative</u> <u>Viscosity</u>	<u>Intrinsic</u> <u>Viscosity</u>	<u>Degree of</u> <u>Polymerization</u>
H	0	1.74×10^{-5}	1.66	0.71	490
I	0	Uncertain	--	--	--
E	4.69×10^{-4}	2.46×10^{-5}	1.67	0.72	505
F	36.4	5.97	1.69	0.74	510
D	78.5	7.92	1.65	0.70	490
G	199	11.5	1.68	0.73	505

Run I used second specimen of monomer ($n_D^{25} = 1.4601$).

Other runs used first specimen ($n_D^{26.3} = 1.4585$)

b. A single experiment in which the catalyst was activated with a trace of ferrous ion gave an excellent emulsion in a greatly reduced reaction time. This is considered a promising lead. On the other hand, it is noteworthy that several trials of organic hydroperoxide catalysts, with and without activators, all gave unsatisfactory emulsions. Substitution of a purified monomer greatly reduced the extent of reaction. Addition of a small amount of cyclohexane to the formulation improved the smoothness of the reaction product.

c. It soon became evident that this method of testing emulsions was unsatisfactory for several reasons. The small conversion with purified monomer needed to be increased for the results to be of any practical interest. To accomplish this, the total exclusion of air from the reaction was very important. A quantitative measure of rates of reaction was needed, preferably by taking a series of samples at intervals from one reaction mixture. At the same time, it was desirable to work with larger charges. Accordingly, a reaction tube provided with stopcocks was constructed, permitting filling or sampling during the reaction without contamination by air. Trial runs in the apparatus demonstrated the possibility of achieving 60 to 70% reaction with purified monomer in a reasonable time. Here, as well as in the earlier tests in vials, polymer precipitated out as the reaction approached completion; this separation remains an important, unsolved problem.

B. ADDITION AND CONDENSATION POLYMERS

1. Polyurethanes

a. Kinetic Studies

(1) Introduction

Before attempting to prepare polymers from the new diisocyanate, 2-nitrazo-1,4-butane diisocyanate, it was of interest to compare the reactivity of its functional groups with those of the other diisocyanates which have been used extensively in polymerizations.

(2) Discussion

The rate of polyurethane formation has been studied extensively using J-diol, 2-nitro-2-methyl-1,3-propanediol, with various nitrodiisocyanates.* The rate of reaction of J-diol with the new 2-nitrazo-1,4-butane diisocyanate was determined with and without ferric

* Aerojet Reports No. 590, p. 22; 622, p. 18; 638, p. 24; 663, p. 12; 686, p. 8; 712, p. 6; 740, p. 7.

acetylacetonate catalyst. Using a catalyst concentration of 1×10^{-4} mole FeAA/liter the rate was too fast for accurate measurement. A catalyst concentration of 1×10^{-5} mole FeAA/liter gave a measurable rate and the experimental results are listed in Table II with other systems previously studied for comparison.

(3) Experimental

A solution of 23.28 g 2-nitroazabicyclo[2.2.1]heptane diisocyanate (assay 98%) and 16.89 g 2-nitro-2-methyl-1,3-propanediol in absolute dioxan was diluted to 250 ml, then divided into two 100-ml and one 50-ml portions which were placed in separate flasks. The catalyst solution was made by dissolving 0.0883 g of ferric acetylacetonate in absolute dioxan and diluting to 25 ml. To one 100-ml portion of monomer solution was added 1 ml catalyst solution. To the other 100-ml portion was added 1 ml of catalyst solution that had been diluted ten times. The 50-ml portion was diluted with 0.5 ml dioxan to keep all concentrations equal. The three portions were placed in a 50°C constant-temperature bath and 10-ml portions were periodically removed for isocyanate determination by the standard method.* The experimental results are shown in Table II.

Table II

Rate of Polymerization of Polyurethane XV-J

Initial Concentration: 1 eq/liter (-OH) and (-NCO) in dioxan

Temperature: 50°C

Elapsed Time hr	Degree of Polymerization				
	No Catalyst XV-J	1×10^{-5} XV-J	moles/liter XIII-J**	FeAA Catalyst XII-J**	I-J**
0	1.00	1.00	1.00	1.00	1.00
0.5	--	2.28	1.20	1.02	2.92
1.0	--	3.43	1.57	1.03	5.25
1.5	1.04	4.31	--	--	--
2.0	--	5.18	1.68	1.04	10.5
2.5	1.08	6.00	--	--	--
3.0	--	6.80	2.03	--	12.9
K_{50}° liter/eq hr = 0.03		2.0	0.35	0.02	4.3

* Aerojet Report No. 638, p. 25.

** Aerojet Report No. 740, p. 8.

(4) Conclusions

The XV-diisocyanate reacts rapidly with J-diol in the presence of iron catalyst, being surpassed only by 3,3-dinitro-1,5-pentane diisocyanate. In comparison, the XIII diisocyanate, 3-nitro-3-aza-1,5-pentane diisocyanate, containing one additional methylene group, has one-sixth the rate; and the XII diisocyanate, 3,6-dinitraza-1,8-octane diisocyanate, has one-hundredth the rate of XV, other variables being constant. The increased reactivity of the new diisocyanate over the reactivities of previous nitraza diisocyanates may be due to the proximity of the nitraza group to one isocyanate group. This result will influence further synthetic work.

b. New Polyurethanes

(1) Introduction

(a) The availability of the new XV-diisocyanate, 2-nitraza-1,4-butane diisocyanate, makes possible the preparation of new polyurethanes from the available diols. The structures and estimated specific impulse values are shown in Table III.

(b) Two previously described polyurethanes, XII-H and XIII-M, have been successfully nitrated.

(2) Preparation of Polyurethane XV-A (JRA-265) from 2-Nitraza-1,4-butane Diisocyanate and 2,2-Dinitro-1,3-propanediol

A solution of 28.83 g of 2-nitraza-1,4-butane diisocyanate (assay 98%) in absolute dioxan was added dropwise to a solution of 25.11 g of dinitropropanediol and 0.026 g ferric acetylacetonate in absolute dioxan, maintaining the temperature in the range 30 to 40°C with intermittent ice bath cooling. The ultimate monomer concentration was 50 wt % with a calculated excess of 0.5% (-NCO). The reaction mixture was maintained at 50°C for 54 hr, then diluted with acetone, and the polymer was precipitated by pouring the solution into rapidly stirred ice water. After washing and drying, a yield of 50 g polymer was obtained.

Anal. Calc'd for $C_8H_{12}N_6O_{10}$: %C, 27.28; %H, 3.44; %N, 23.86

Found %C, 27.46; %H, 3.46; %N, 23.92

Heat of combustion, calc'd: 2748 cal/g
found: 2717 cal/g

Softening range: 85-95°C

Impact stability: >100 cm/2kg

Relative viscosity: 1.47, 1% acetone; 1.73, 1% Butyrolactone and
1.75, 1% DMF

KI-Starch stability at 65.5°C, 2 hr.

(3) Attempted Preparation of Polyurethane XV-AN by Nitration of Polyurethane XV-A, Obtained from 2-Nitrazo-1,4-butane Diisocyanate and 2,2-Dinitro-1,3-propanediol

(a) Two attempts to nitrate Polyurethane XV-A with 100% nitric acid at 0°C, followed by removal of excess acid in vacuo, failed to yield a product insoluble in methylene chloride. Nitration with 100% nitric acid for 5 min at 0°C, then pouring the acid solution into ice water, gave a product that was not in agreement with the calculated values for heat of combustion and elementary analysis. The product had the following characteristics: η_{sp}/c acetone = 1.05.

Anal. Calc'd for $C_8H_{10}N_8O_{14}$: %C, 21.73; %H, 2.28; %N, 25.34

Found: %C, 21.02; %H, 2.53; %N, 24.76

Heat of Combustion, Calc'd: 2100 cal/g
Found: 2335 cal/g

KI-Starch Stability at 65.5°C: 4 min

Softening range: 90-100°C

Impact Stability: >100 cm/2 kg.

(b) Polyurethanes prepared from methylene diisocyanate also suffer extensive degradation during nitration.* Inasmuch as Polyurethane XV-AN is similar in structure,** having two nitraza groups separated by one methylene group, it is believed that such a system is unstable and degradation during nitration results in a mixture of low-molecular-weight products (see also attempts to nitrate Polyurethane XV-J, below).

(4) Preparation of Polyurethane XV-H (JRF-266) from 2-Nitrazo-1,4-butane Diisocyanate and 5,5,5-Trinitro-1,2-pentanediol

A dioxan solution of 28.14 g diisocyanate (assay 98%) was added dropwise to a solution of 35.16 g of diol and 0.052 g ferric acetylacetonate, while the temperature was maintained in the range from 30 to 40°C. The ultimate monomer concentration was 50 wt % with a calculated excess of 0.77% (-NCO). The solution viscosity leveled off after 24 hr at 50°C, and addition of 0.25% diol did not raise the viscosity. After 51 hr at 50°C the batch was diluted and precipitated into water; the dry wt was 60 g.

* Aerojet Report No. 563, pp. 25-57.

** See Table V.

Anal. Calc'd for $C_{10}H_{15}N_7O_{12}$: %C, 28.24; %H, 3.55; %N, 23.06

Found: %C, 28.25; %H, 3.55; %N, 23.04

Heat of combustion calc'd: 2954 cal/g
found: 2931 cal/g

Softening range: 80 to 90°C

Impact stability: 55 cm/2kg

Relative viscosity: 1.22, 1% acetone; 1.32, 1% Butyrolactone; and
1.45, 1% DMF

KI-Starch stability at 65.5°C: trace at 38 min, failure at 2 hr

(5) Preparation of Polyurethane XV-J (JRF-264) from
2-Nitrazo-1,4-butane diisocyanate and 2-Nitro-2-methyl-1,3-propanediol

A solution of 36.98 g 2-nitrazo-1,4-butane diisocyanate (assay 98%) in absolute dioxan was added dropwise to a solution of 26.19 g 2-nitro-2-methyl-1,3-propanediol and 0.0137 g ferric acetylacetonate in absolute dioxan, maintaining the temperature in the range 30 to 40°C with intermittent ice-bath cooling. The ultimate monomer concentration was 50 wt % with a calculated excess of 0.5% (-NCO). The reaction mixture was maintained at 50°C for 100 hr, then diluted with acetone, and the polymer was precipitated by pouring the solution into rapidly stirred ice water. After washing and drying, a yield of 60 g polymer was obtained. Heat of combustion calc'd: 3497 cal/g
found: 3512 cal/g

Anal. Calc'd for $C_9H_{15}N_5O_8$: %C, 33.65; %H, 4.71; %N, 21.80

Found: %C, 33.72; %H, 4.66; %N, 21.55

Softening range: 90 to 100°C. KI-Starch stability at 65.5°C > 5 hr

Impact stability: 100 cm/2kg Relative viscosity: 1.21 1% acetone
1.78 1% DMF
1.61 1% Butyrolactone

(6) Attempted Preparation of Polyurethane XV-JN by
Nitration of Polyurethane XV-J, Obtained from 2-Nitrazo-1,4-butane Diisocyanate
and 2-Nitro-2-methyl-1,3-propanediol

(a) Attempts to nitrate Polyurethane XV-J with 100% nitric acid at 0°C, followed by removal of excess acid in vacuo, failed to yield a product insoluble in methylene chloride. As in the case of XV-AN above, nitration with 100% nitric acid for 5 min at 0°C followed by precipitation in ice water gave a product that was not in agreement with the calculated values for heat of combustion and elementary analysis. The dried product had the following characteristics:

$\eta_{sp}^{1\%}$ acetone = 1.02

Anal. Calc'd for $C_9H_{13}N_7O_{12}$: %C, 26.28; %H, 3.19; %N, 23.84

Found: %C, 29.19; %H, 3.14; %N, 22.54

Heat of Combustion Calc'd: 2636 cal/g
Found: 2998 cal/g

Softening Range: 80 to 90°C

Impact Stability: >100 cm/2 kg

(b) Here again two nitro groups are separated by a single methylene group, resulting in instability (see attempts to nitrate Polyurethane XV-A, above).

(7) Preparation of Polyurethane XII-HN by Nitration of Polyurethane XII-H; Obtained from 3,6-Dinitro-1,8-octane Diisocyanate and 5,5,5-Trinitro-1,2-pentanediol

(a) The preparation of Polyurethane XII-H was described in Aerojet Report No. 740, p. 22. Because of the low relative viscosity of the first preparation, several others were made in an attempt to obtain higher-molecular-weight starting material for nitration.* One of these, JRF-257, $\eta_{sp}^{1\%}$ DMF = 1.67 was nitrated.

(b) Experimental (JRF-262)

To 25 g of Polyurethane XII-H, JRF-267, $\eta_{sp}^{1\%}$ DMF = 1.67 was added 400 ml of 100% nitric acid at 0°C. After the polymer was completely dissolved, the excess acid was removed by distillation at reduced pressure. The resulting viscous mass was washed twice with anhydrous dioxan, then dissolved in anhydrous acetone. The polymer was precipitated by pouring the acetone solution into methylene chloride. The dried product was characterized as follows:

* Described in Aerojet Quarterly Report No. 772, p. 23.

Anal. Calc'd for $C_{13}H_{19}N_{11}O_{18}$: %C, 25.29; %H, 3.10; %N, 24.96

Found: %C, 25.27; %H, 3.27; %N, 25.07

Heat of combustion, calc'd: 2749 cal/g

found: 2712 cal/g

KI-Starch stability at 65.5°C: failure in 3 min

η_{sp}/c 1% acetone = 1.23

η_{sp}/c 1% butyrolactone = 1.21

η_{sp}/c 1% dimethylformamide = 1.43

Softening range: 70 to 80°C

Impact stability: 82 cm/2kg

(8) Preparation of Polyurethane XIII-MN by Nitration of Polyurethane XIII-M Obtained from 3-Nitroazela-1,5-pentane Diisocyanate and N,N'-bis(2-hydroxyethyl) Oxamide

(a) An attempt to nitrate this polymer using the standard technique with 100% nitric acid at 0°C failed to give complete nitration. Using 100% nitric acid at 50 to 60°F for 1 hr gave complete nitration.

(b) Experimental (JRF-233)

To 15 g Polyurethane XIII-M, JRF-222, 1% formic acid = 1.10, was added 150 ml of 100% nitric acid at 0°C. After complete solution of the polymer the excess acid was removed at reduced pressure. The viscous mass was dissolved in absolute DMF, and the polymer was precipitated by pouring the solution into methylene chloride. After being dried, the product had the following characteristics: η_{sp}/c 1% DMF = 1.06

Anal. Calc'd for $C_{12}H_{16}N_{10}O_{16}$: %C, 25.90; %H, 2.90; %N, 25.18

Found: %C, 30.83; %H, 4.25; %N, 25.58

Heat of Combustion calc'd: 2630 cal/g

found: 3127 cal/g

KI-Starch stability: failure in 9 min

Softening range: 75 to 85°C

Impact stability: 100 cm

(c) Experimental (JRF-261)

To 15 g Polyurethane XIII-M, JRF-222, η_{sp}/c 1% formic acid = 1.10, was added 250 ml nitric acid. Temperature was maintained^r at 50 to 60°C for 1 hr, then the acid solution was poured into 2 liters ice water. The product was filtered, washed, and dried. It was characterized as follows:

Anal. Calc'd for $C_{12}H_{16}N_{10}O_{16}$: %C, 25.90; %H, 2.90; %N, 25.18

Found: %C, 26.33; %H, 3.03; %N, 25.51

Heat of Combustion calc'd: 2630 cal/g

found: 2631 cal/g

η_{sp}/c 1% DMF = 1.05

KI-Starch stability at 65.5°C: failure in 8 min

Softening range: 65 to 75°C

Impact stability: 47 cm/2kg

c. Further Work on Previously Described Polyurethanes

(1) Preparation of Polyurethane XIII-AN by Nitration of Polyurethane XIII-A Obtained from 3-Nitroazido-1,5-pentane Diisocyanate and 2,2-Dinitro-1,3-propanediol Plus 1% tris-Hydroxymethyl Nitromethane

(a) The introduction of branching and cross-linking in the polyurethane chain results in polyurethanes with improved physical and mechanical properties.* In the case of Polyurethane I-A, information has been obtained on the degree of chain degradation and change in solubility characteristics that occurred when a cross-linked, insoluble Polyurethane I-A was post-nitrated.** This work has now been extended to Polyurethane XIII-A branched with 1% nib glycerol. The XIII-A used as starting material was insoluble in all solvents, hence, no relative viscosity measurements could be made. Since some degradation occurs during nitration, it was expected that the nitrated product would be soluble.

* Aerojet Report No. 772, p. 30.

** Aerojet Report No. 772, p. 23.

(b) Experimental (JRF-260)

To 20 g Polyurethane XIII-A (OB-29) containing 1% nib glycerol as branching agent was added 400 ml 100% nitric acid at 0°C. After standing 1 hr at room temperature, the excess nitric acid was removed in vacuo and the residue was dissolved in 250 ml anhydrous acetone. The acetone solution was filtered free of a few gel particles, and the polymer was precipitated by pouring the filtered solution into methylene chloride. The dried product had the following properties:

η_{sp}/c 1% acetone = 1.53; η_{sp}/c 1% DMF = 1.74

Heat of Combustion, Calc'd: 2388 cal/g

Found: 2375 cal/g

KI-Starch stability at 65.5°C: failure in 4 min

(c) Compared with linear Polyurethane XIII-AN previously described* (η_{sp}/c = 1.27, 1% acetone), a higher-molecular-weight product was obtained.

(2) Preparation of Polyurethane XIII-JN by Nitration of Polyurethane XIII-J, Obtained from 3-Nitroazabicyclo[3.1.0]hexane-2,5-dithiocarbamate and 2-Nitro-2-methyl 1,3-propanediol

(a) Extensive studies of nitration conditions in the I-A system have been made.** If Runs 160a and 163a are compared, it is observed that the relative viscosity of the postnitrated polymer was higher when phosphorus pentoxide was used during the nitration. However, this higher viscosity may have been due to the loss of low-molecular-weight polymer during the ether washing of the product.

(b) It was of interest to determine the effect of phosphorus pentoxide during the nitration of XIII-J. Previous attempts to increase the relative viscosity of XIII-JN have not been successful.*** The use of phosphorus pentoxide did not improve the molecular weight.

* Aerojet Report No. 740, p. 23.

** Aerojet Report No. 712, p. 24.

*** Aerojet Report No. 772, p. 20.

(c) Experimental (JRF-259)

To 250 ml 100% nitric acid was added 10 g phosphorus pentoxide and 20 g Polyurethane XIII-J JRF-218-B, η_{sp}/c DMF = 2.32. Excess acid was then removed in vacuo and the product was washed twice with absolute dioxan. The polymer was then dissolved in absolute γ -butyrolactone, precipitated into dioxan, redissolved in butyrolactone, and precipitated by pouring into methylene chloride; η_{sp}/c in butyrolactone was 1.63. Omitting the phosphorus pentoxide resulted in a product of η_{sp}/c in butyrolactone equal to 1.66.

(3) Preparation of Polyurethane I-A from 2,2-Dinitro-1,3-propanediol and 3,3-Dinitro-1,5-pentane Diisocyanate plus 0.5% tris-Hydroxymethylnitromethane

(a) It was of interest to test the performance of the new Beken mixer* on a known system using a higher monomer concentration than had heretofore been possible because of inadequate mixing methods.

(b) Experimental (RDH-4)

A solution of 247.77 g 3,3-dinitro-1,5-pentane diisocyanate (assay 98.01%) in absolute dioxan was added dropwise to a solution of 164.207 g 2,2-dinitro-1,3-propanediol (assay 99.6%), 0.4984 g tris-hydroxymethylnitromethane, and 0.0702 g ferric acetylacetonate in absolute dioxan. During the first 0.5 hr of the diisocyanate addition no rise in temperature was observed. Accordingly, the heat-exchange system was turned on and slowly warmed to 40°C. The temperature of the reaction mixture was then kept below 45°C by adjustment of the rate of diisocyanate addition. The ultimate monomer concentration was 75 wt % with a calculated excess of 0.5% (-NCO). At the completion of the diisocyanate addition the reaction mixture was kept at 50°C, with mixing for 0.5 hr out of each 9.0-hr period. The polymerization was followed by measurements of relative viscosity. The equivalence of monomers was subsequently adjusted by the addition of 1.1% diisocyanate, making a total of 1.6% excess diisocyanate. The reaction was terminated after 72 hr at 50°C. The very viscous polymer was then dispersed in acetone and dioxan. The polymer was quite insoluble, and final dispersion was performed in the Morehouse mill set at the finest grind. The polymer was then precipitated in water using the Morehouse mill. The precipitated polymer was next washed and ground in successively finer grinds until the finest grind on the mill was reached. A representative sample was then dried in vacuo. The polymer was insoluble in acetone, dimethyl formamide and dioxan.

(c) Monomer concentrations up to 75 wt % can be run in the Beken mixer. A more efficient method of following the rate of polymerization in the mixer is needed. Neither the pilot batch nor the relative-viscosity methods are completely satisfactory. It was hoped to be able

* Aerojet Report No. 772, Appendix A.

to follow the run by use of an ammeter which measures the load on the motor during mixing. It was found that the readings were of such a nature that no correlation could be found between them and the known relative viscosities. With a larger run the readings might be more constant and future polymerizations in the Beken mixer could be followed by this method.

(4) Fractionation of Polyurethane I-AN

(a) In the preparation of postnitrated polyurethanes, a good deal of effort has been expended in developing conditions for maximum nitration with a minimum of chain degradation. Quantitative nitration has been achieved, but some unknown degree of chain degradation occurred. In addition, the thermal stability of the postnitrated product left much to be desired.* In a recent attempt to determine osmotically the molecular weight of a sample of Polyurethane I-AN, it was observed that about 30% of the sample diffused through the membrane.** This indicated that a good deal of degradation must have occurred during the nitration. It is believed that these small fragments having nitrate end groups may be the cause of thermal instability in postnitrated polymers. During the past period, a partial fractionation was conducted on a sample of Polyurethane I-AN.

(b) (JFF- 7)

Polyurethane I-A, 70 g JKE-174 $\eta_{sp}^{1\%}$ acetone = 1.81, was dissolved in 700 ml of 100% nitric acid at 0°C. Excess acid was then removed in vacuo at 0 to 20°C, and the residue was dissolved in anhydrous dioxan. The nitrated polymer was precipitated by pouring the dioxan solution into methylene chloride. The dry polymer weighed 81 g and 1% in acetone had a relative viscosity of 1.66. Eighty grams of Polyurethane I-AN was dissolved in 8 liters absolute dioxan, and dry hexane (880 ml) was added until a slight turbidity was produced. The addition of hexane was continued dropwise with stirring until a total of 1 liter had been added. The precipitated polymer was allowed to settle, the mother liquor was decanted, and the polymer was redissolved in 4 liters absolute dioxan. The addition of 425 ml hexane produced turbidity, then 75 ml more hexane was added dropwise. The mother liquor was decanted and the polymer was dissolved in dioxan and precipitated into methylene chloride, giving fraction 267-2, 10 g. To the mother liquor from 267-2 was added 500 ml hexane, giving 267-3, 8 g. All mother liquors were combined, concentrated in vacuo at 30 to 40°C, then poured into methylene chloride giving 267-4, 52 g (see Table IV).

* Aerojet Reports No. 712, p. 12; 740, p. 10.

** Aerojet Report L831-61.

TABLE IV

POLYURETHANE I-AN FRACTIONS

Fraction	Weight g	1% acetone η_{sp}	Warburg Stability at 65.5°C, ml/100g/hr, (vol. reduced to STP)	KI-Starch Stability at 65.5°C
267-2	10	1.63	0.60	12-min failure
267-3	8	1.63	0.60	13-min failure
267-4	52	1.31	1.1	13-min failure

(c) Conclusions

Degradation occurred during the fractionation. Although the higher-molecular-weight fractions evolve less gas than the low-molecular-weight material, there is no improvement over unfractionated I-AN, which has a Warburg stability of 0.30 to 0.64 ml/100g/hr at 65.5°C.*

d. A Study of the Effect of Monomer Equivalence on
Molecular Weight: Depolymerization

(1) Interchange reactions in condensation polymers are known to occur.** Examples are alcoholysis of polyesters, ammonolysis of polyamides, and polyester interchange. It has been suspected that a dynamic equilibrium exists in the polyurethane reaction catalyzed by a metal chelate. With the use of the very effective ferric acetylacetonate catalyst it was observed that adjustment of monomer equivalence was almost as simple as an acid-base titration. When the reaction mixture was deficient in isocyanate function, addition of diisocyanate resulted in an increase in solution viscosity. When an excess of isocyanate function existed, the addition of diol resulted in an increase in solution viscosity. In some instances, addition of an excess of monomer caused a decrease in solution viscosity. Figure 4 depicts a preparation of Polyurethane I-J from 3,3-dinitro-1,5-pentane diisocyanate and 2-nitro-2-methyl-1,3-propanediol in which this effect was observed.

(2) If polyurethane interchange occurs in the presence of the iron catalyst the above experimental observations can be explained. The highest molecular weight and hence highest solution viscosity are observed at exact equivalence of monomers and further addition of either monomer, through interchange with polymer, results in a different equilibrium molecular-weight distribution. One would expect the solution viscosity and degree of polymerization to decrease as monomer is assimilated in excess of equivalence.

* Aerojet Report No. 740, p. 11.

** Burk and Grummitt, High Molecular Weight Organic Compounds, (Interscience Publishers, Inc., N. Y., 1949).

(3) Runs have been made with two known (I-A and I-J) polyurethane systems at different monomer concentrations to find the correlation between solution and relative viscosities and the amount of monomer added after true monomer equivalence has been reached.

(4) Experimental (RDH-12)

To 71.129 g (0.8513 eq, assay 99.4%), of 2,2-dinitro-1,3-propanediol and 0.077 g ferric acetylacetonate (1×10^{-4} eq) in absolute dioxan was added 105.191 g (0.8513 eq, assay 98.8%) of 3,3-dinitro-1,5-pentane diisocyanate in absolute dioxan. The temperature of the reaction mixture was maintained below 50°C by application of a water-ice bath. The ultimate monomer concentration was 50 wt %. After completion of the diisocyanate addition the reaction vessel was placed in a 50°C bath. The polymerization was followed by measurements of the solution viscosity. At intervals samples were withdrawn for measurements of relative viscosity. Each time a sample was taken an addition of diisocyanate was made. The results of this experiment are shown in Table V and Figure 5.

(5) Experimental (RDH-14)

To 30.776 g (0.45554 equivalent) 2-nitro-2-methyl-1,3-propanediol and 0.1608 g (5×10^{-4} equivalent) ferric acetylacetonate in absolute dioxan was added 56.289 g (0.45554 eq., assay 98.8%) 3,3-dinitro-1,5-pentane diisocyanate. Temperature during the diisocyanate addition was held below 50°C by means of a water-ice bath. The ultimate monomer concentration was 35 wt %. The reaction mixture was then placed in a 50°C bath, and the polymerization was followed in the manner described in Paragraph 4, above. Results of the experiment are shown in Table VI and Figure 6.

(6) These results show that both solution and relative viscosities decrease when monomer equivalence is exceeded. Furthermore, this indicates that interchange with the polyurethane occurs, resulting in a lower weight average molecular weight.

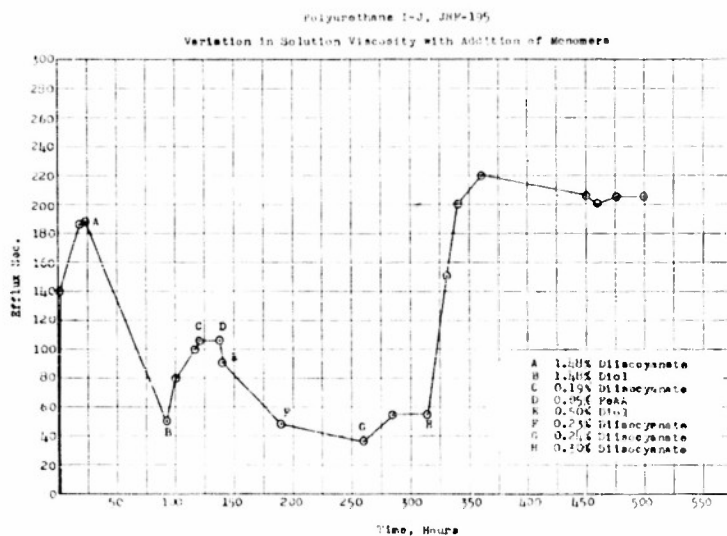


Figure 4

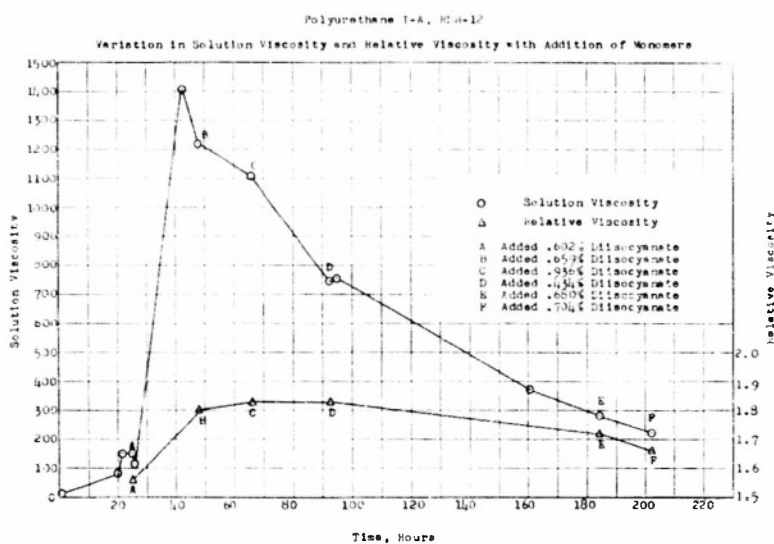


Figure 5

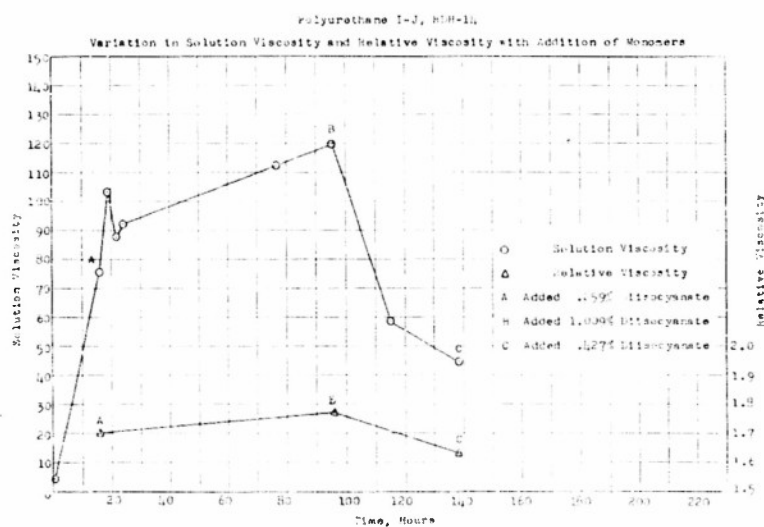


Figure 6

TABLE V

POLYURETHANE I-A, RDH-12

Variation in Solution and Relative Viscosities with Monomer Equivalence

<u>Sample No.</u>	<u>Time hr</u>	<u>Diisocyanate eq.</u>	<u>Diol eq.</u>	<u>Diisocyanate % Excess</u>	<u>Solution Viscosity sec</u>	<u>Relative Viscosity 1% acetone</u>
12-A	25.0	0.8513	0.8513	0.0	153	1.56
12-B	48.0	0.8564	0.8513	0.602	1220	1.80
12-C	66.5	0.8620	0.8513	1.261	1106	1.83
12-D	92.5	0.8700	0.8513	2.197	744	1.83
12-E	184.5	0.8737	0.8513	2.631	281	1.72
12-F	208.5	0.8795	0.8513	3.311	225	1.66

TABLE VI

POLYURETHANE I-J, RDH-14

Variation in Solution and Relative Viscosities with Monomer Equivalence

<u>Sample No.</u>	<u>Time hr</u>	<u>Diisocyanate eq.</u>	<u>Diol eq.</u>	<u>Diisocyanate % Excess</u>	<u>Solution Viscosity sec</u>	<u>Relative Viscosity 1% acetone</u>
14-A	16.0	0.45554	0.45554	0	75	1.70
14-B	96.0	0.45855	0.45554	0.659	120	1.77
14-C	138.5	0.46313	0.45554	1.656	45	1.63

III. TECHNICAL PROGRESS: FORMULATION STUDIES (Contract N7onr-462)

A. INTRODUCTION

1. During the past year a great deal of information has been collected on the effect of branching and crosslinking on polyurethanes. Many other factors, such as the rate and the order of addition of the components, the use of an excess of one of the reactants and subsequent monomer adjustment, have been investigated. These tedious and time-consuming experiments, together with theoretical considerations,* form the basis for the development of a casting process which may be used in the preparation of a nitropolymer propellant grain. During the past quarter the emphasis in the formulation work has been shifted from the step-by-step accumulation of information to the use of all the previous experience in actual casting experiments. The present report deals with the development of a casting technique which would lead to gelled, bubble-free polymer grains, using only simple, two-component systems (nitropolymer and solvent-plasticizer). Two approaches studied have been the one-stage casting process and the two-stage casting process. A measure of success was achieved using each process, and their relative merits have been evaluated. It was also found possible to obtain gelled castings exhibiting good physical properties using polynitro compounds as solvent-plasticizers.

2. The possibility of extruding nitropolymers was also studied during this period, and it was found that in the presence of inorganic salts, plasticized nitropolyurethanes could easily be extruded to give smooth-surfaced, uniform rods possessing remarkably high tensile strengths. This discovery led to the preparation and evaluation of extruded formulations containing ammonium nitrate and ammonium perchlorate with nitropolyurethane binders. The preliminary results of these studies have been encouraging, and the formulations show promise of wide utility.

B. CASTING STUDIES

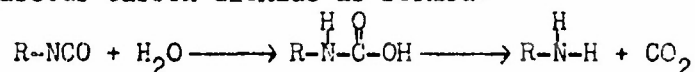
1. Discussion

a. Some of the many problems encountered in attempting to cast nitropolyurethane grains have been the following: (1) dissipation of the heat of polymerization; (2) bubble formation; (3) maintaining anhydrous conditions; (4) working at low solvent concentrations; (5) thermal stabilities; (6) reproducibility; (7) curing schedule; and (8) mold release. Each of these problems has been touched on in this past period; and it is possible to state that in the two-component systems, at least, these problems have been largely solved. It is believed that the solutions found will be applicable to more complex formulation systems, or if not, they will represent sound starting points for further study. Each of these problems is discussed below.

* Aerojet Report No. 772, p. 34.

b. It is well known that the formation of simple urethanes occurs with vigor, and in the catalyzed polycondensation of a diol with a diisocyanate this same vigor is very much apparent. The energy release involved in urethane formation is about 52 kcal per mole, about three times the value for olefinic polymerization. The dissipation of this large amount of heat proves, in practice, to be no problem. Using a low catalyst concentration and a low-temperature cure (made possible by the use of the metal-chelate catalysts) represents the solution in the one-stage casting process. If a low-molecular-weight prepolymer is made, using portionwise addition of one monomer to the other, and at a monomer ratio not equal to unity, it is possible to remove rapidly most of the heat energy before the casting is made. To the prepolymer is then added the remainder of monomer and cross-linking agent, thereby bringing the monomer ratio to equivalence. The still viscous solution is then transferred to molds, and the cure is carried out. This latter technique is the essence of the two-stage process.

c. The problem of bubble formation in grain castings is not a new one. However, in polyurethane systems the problem is much more acute. One of the many active hydrogen compounds that react with isocyanates is water. The initial carbamic acid reaction product is unstable toward heat, and on decomposition gaseous carbon dioxide is formed:



Without using the extremes in anhydrous conditions, it is virtually impossible to avoid some carbon dioxide formation. One-tenth gram of water forms 124 ml (STP) of carbon dioxide on reacting with an excess of an isocyanate. Thus, the problem is best met by using a vacuum degassing technique while the polymer solution is still thin enough to allow the bubbles to escape. It is obvious that the gel time in these systems must be much greater than the time for all the water to be consumed. Gel time is best adjusted by varying catalyst concentration. In the two-stage process the prepolymer solution in the presence of catalyst is completely degassed of air and carbon dioxide in several hours. In the one-stage process, the monomer solution is degassed prior to the addition of catalyst.

d. From the considerations stated above, it is obvious that great care must be used to minimize contact with moisture. Besides being a potential gas-forming agent, water consumes diisocyanate, and thus alters the monomer ratio. It is seen that small quantities of water could easily destroy equivalence to the extent of preventing gelation. In practice, a slight calculated excess of diisocyanate (1 to 2%) is always used to compensate for such losses.

e. Although optimum plasticizer levels have yet to be determined for these nitropolyurethane systems, it is probable that the level will be low. Thus, when the plasticizer is used as the polymerization solvent, there is a certain limit of solvent-plasticizer concentration below which the necessary handling operations are impossible. It is in this regard that the one-stage casting process has great advantage. All the handling and transfer operations in the one-stage process take place prior to any polymerization, and hence it can be expected that much lower plasticizer levels can be attained. Using the two-stage casting, operations become difficult at about 25 wt % solvent-plasticizer. The use of liquid monomers would of course facilitate working at still lower plasticizer levels.

f. Thermal stability is an ever-present problem with nitro-polymers. However, based on previous polymer stability studies, we have available a number of nitropolyurethane systems of fair impulse exhibiting stabilities (KI-starch and gassing rate at 65.5°C) as good or better than stabilized double-base propellant. End-group stability studies have indicated the desirability of maintaining isocyanate end groups when using the A-diol, 2,2-dinitro-1,3-propanediol.

g. The necessity of reproducibility in preparing a nitro-polymer grain is fundamental. In the past, great difficulty has been encountered in reproducing relative viscosities of linear and branch-chained polyurethanes. The ultimate molecular weight is extremely sensitive to monomer ratio, and thus weighing errors and/or handling losses of small magnitude can easily be amplified to show large differences in chain length between two apparently identical polymer preparations. Now, as the trifunctional monomer concentration is increased to the critical level for gel formation (about 1% in these systems) this amplification is even greater. For these reasons the preliminary casting experiments conducted in this period have utilized a higher level of cross-linking agent to avoid the precariousness of working in this critical zone. In all cases studied, a gel obtained once was able to be duplicated. Reproducibility of the more subtle properties of these grains has yet to be determined by stress-relaxation analysis. Calculations based on Flory's gel-point criteria indicate that at a given cross-linking level the maximum variation in monomer ratio which still produces a gel is equal to slightly less than twice the concentration of cross-linking agent. Thus, a polyurethane system containing 2% cross-linking agent would theoretically produce a gel in the range of 2% excess diol to 2% excess diisocyanate. The necessity for extremely high precision in weighing monomers becomes less and less important for the obtaining of a gel as the cross-linking level increases. The effect on mechanical properties of variation of monomer ratio within the gel limits is yet to be determined.

h. The curing of most of the systems studied was conducted at 50°C. Gel times were from 5 to 20 hours depending on the system and catalyst concentration used. Several runs cured at 65.5°C showed signs of decomposition. Runs cured at room temperature, while showing much longer gel times, produced castings of similar properties to the 50°C cures. It was observed that when too high a catalyst concentration was used, the cure was exceedingly fast, and the large thermal gradients arising in the casting gave rise to what appeared as mixing lines. These lines, usually at the center of the casting, often were the nuclei for void formations as the grain was cooled during the release operation.

i. It was found that silicone high-vacuum grease used against glass was an excellent mold release for these systems.

2. The One-Stage Casting Process

a. The superiority of the one-stage process, as previously indicated, lies in the possibility of working at low solvent-plasticizer levels, as well as the obvious simplicity of the system. The main liabilities are the longer degassing and curing times. Table VII shows typical systems studied in the one-stage process.

b. Experimental

Monomers were weighed into a 125-ml Erlenmeyer flask in quantities always giving 2% excess diisocyanate. The cross-linking agent used was tris-(hydroxymethyl) nitromethane. The solvent-plasticizer was added, and after a homogeneous solution was obtained, the flask was placed in a 50°C bath and vacuum degassed until all gassing ceased (5 to 10 hr). The monomer solution was then cooled to 0°C, a solution of ferric acetylacetonate was added, and the liquid was then transferred to the molds (silicone-greased test-tubes). The test-tube castings were placed in a 50°C bath, given a final degassing, and then allowed to cure. Mold-release was effected by cooling the castings to below 0°C, and then breaking the glass away from the grain.

3. The Two-Stage Casting Process

a. In brief, the two-stage process involves the preparation of a low-molecular-weight prepolymer, using the plasticizer as the polymerization solvent, and the subsequent addition of a small amount of monomer and cross-linking agent to bring the monomer ratio to unity. This system then leads to a gelled structure during the second-stage curing. During the first-stage prepolymer preparation, most of the heat of polymerization is easily disposed of. The degassing operation is rapidly accomplished during the first stage, being done in the presence of catalyst which promotes the reaction of water with isocyanate, as well as the desired urethane formation. The degree of polymerization of the prepolymer can be adjusted over wide limits simply by varying the initial monomer ratio in the first stage. In practice, the prepolymer DP must be very low for the solution to be workable; at the time any solid, immiscible components are added to these systems, it will be possible to prevent solid-phase settling simply by adjusting prepolymer DP. Table VIII shows the relationship between initial monomer ratio, degree of polymerization, molecular weight, and extent of total reaction. The value of extent of total reaction is also equivalent to the fraction of total heat content of the system released in the first stage.

TABLE VII
ONE-STAGE CASTINGS

Run No.	Poly-urethane	Solvent-Plast.	Solv. Conc. (wt%)	Nib Glycerol Conc. (equiv %)	Cat. Conc. (moles FeAA/equiv NCO)	Cure	Results
202	XIII-A	Dioxan	50	8	1×10^{-4}	17 hr at 50°C	Rubbery gel, slight odor of dioxan
203	"	DNH ¹	50	8	1×10^{-4}	70 hr at 50°C	Soft, rubbery gel
204	"	TNP ²	50	8	1×10^{-4}	16 hr at 50°C	Hard gel, polymer separated as solid phase
205	I-A	TNP	33	6	1×10^{-4}	24 hr at 50°C	Hard, rubbery gel
206	XIII-A	Dioxan	33	4	1×10^{-4}	16 hr at 50°C	Rubbery gel, faint odor of dioxan
220	"	"	20	2	1×10^{-5}	5 days at 50°C	No gel. Conclude monomer impurities consumed catalyst.
221	"	"	40	2	2×10^{-5}	4 days at 50°C	Rubbery gel
222	"	"	40	10	2×10^{-5}	3 days at 50°C	Hard, rubbery gel
223	"	MDNV ³	25	4	3×10^{-5}	16 hr at 50°C	Very hard gel
224	"	Dioxan	40	10	2×10^{-5}	4 days at 50°C	Hard, rubbery gel
225	I-A	NM ⁴	23	4	2×10^{-5}	3 days at 50°C	Rubbery gel
226	XIII-A	Dioxan	40	10	2×10^{-5}	4 days at 50°C	Hard, rubbery gel

¹ DNH is 5,5-Dinitro-2-hexanone

² TNP is 5,5,5-Trinitro-2-pentanone

³ MDNV is Methyl 4,4-dinitrovalerate

⁴ NM is Nitromethane

TABLE VIII

DEGREE OF POLYMERIZATION OF PREPOLYMER AS A FUNCTION OF MONOMER RATIO

Monomer Ratio First Stage (moles OH/moles NCO)	Degree of Polymerization	Molecular Weight		Extent of Total Reaction
		I-A	XIII-A	
0.50	3.00	600	550	0.67
0.60	4.00	820	730	0.75
0.70	5.67	1160	1040	0.82
0.80	9.00	1840	1650	0.89
0.90	19.00	3900	3500	0.95

b. To facilitate the handling and transfer of the viscous prepolymer solutions, a special piece of apparatus was conceived and fabricated. The apparatus, in essence, is a resin flask fitted at the bottom with a wide-bore stopcock and a special vacuum take-off, permitting the casting of extremely viscous solutions with no contact to air or moisture. The lower workable limit of plasticizer level has been markedly decreased by the use of this apparatus.

c. Table IX shows pertinent data on some of the systems studied in the two-stage process.

TABLE IX

TWO-STAGE CASTINGS

Run No.	Solvent	Solv. Glycerol		Cat. Conc. (moles FeAA/equiv NCO)	Prepolymer DP	Cure	Results
		Conc. (wt%)	Nib Conc. (equiv %)				
208	Dioxan	33	4	10^{-4}	9.0	20 hr at 50°C	Rubbery gel Faint odor of dioxan
211	Dioxan	25	4	10^{-4}	4.0	20 hr at 50°C	Hard rubbery gel
216	Dioxan	25	4	7.5×10^{-5}	4.0	20 hr at 50°C	Hard rubbery gel

d. Experimental

All runs were made with Polyurethane XIII-A, obtained from 3-nitro-1,5-pentane diisocyanate and 2,2-dinitro-1,3-propanediol. To the diol and catalyst in the casting vessel were added dropwise a solution of the diisocyanate. In every case the prepolymer had isocyanate end groups. The prepolymer solution was then placed in a 50°C bath, and vacuum degassed for several hours. After gassing had ceased, the vessel was removed from the bath, and the solution was cooled to room temperature. At this time the remainder of diol and the required triol (nib glycerol) were added, and the mixture was stirred until the solids were dissolved. The final monomer ratio gave 2% excess diisocyanate. A quick degassing was made at this point, to eliminate mixing bubbles. The polymer solution was then transferred under vacuum through the bottom stopcock into silicone-greased test-tubes. The test-tubes were then placed in a 50°C bath, and given a final degassing. Complete cure was effected within 20 hours at 50°C.

4. Isolation of I-H Prepolymer

a. To study further the two-stage casting process, it was of interest to attempt to isolate and characterize a low-molecular-weight prepolymer. The Polyurethane I-H system (3,3-dinitro-1,5-pentane diisocyanate and 5,5,5-trinitro-1,2-pentanediol) was chosen for study because of the relatively stable structure of the diol. An attempt to isolate a I-A prepolymer (3,3-dinitro-1,5-pentane diisocyanate and 2,2-dinitro-1,3-propanediol) with hydroxy end-groups resulted in a violent fume-off.

b. Experimental

To 673 milliequivalents 5,5,5-trinitro-1,2-pentanediol, 35 milliequivalents nib glycerol, 0.067 milliequivalent ferric acetylacetonate, and 75 ml absolute dioxan in a 500-ml resin flask was added dropwise a solution of 636 milliequivalents 3,3-dinitro-1,5-pentane diisocyanate in 75 ml absolute dioxan. After remaining 19 hr at 50°C, the slightly viscous prepolymer solution was diluted with acetone, filtered, and precipitated into water. After vacuum drying the following data were obtained:

Yield: 99%

Softening Range: 60 to 70°C

Molecular Weight Found: 3770 (Isopiestic)

Calc'd: 4500 (From initial monomer ratio)

Relative Viscosity: 1.07 (1% acetone)

Solubility: Soluble in acetone, dioxan

Anal. Calc'd for $(C_{12}H_{17}N_7O_{14})_n$: %C, 30.07; %H, 3.90; %N, 22.32

Found: %C, 29.92; %H, 3.67; %N, 21.55

c. As can be seen from the experimental details, the initial monomer ratio of isocyanate groups to hydroxy groups is equal to 0.90; and of the total hydroxy equivalents, 5% are contributed by the cross-linking agent, nib glycerol. This set of conditions has led to the isolation of a soluble, branched, low-molecular-weight prepolymer, which, as shown below, still possesses reactive hydroxyl groups capable of forming a gel with the theoretical amount of diisocyanate.

d. Four small-scale runs were made in which the I-H prepolymer was combined with various amounts of monomeric diisocyanate. Three of the four runs produced a gel, and judging from differences in strength of the gelled samples, the optimum ratio of prepolymer to diisocyanate corresponds to a prepolymer molecular weight of about 3000, which is in good agreement with the isopiestic molecular weight.

e. The value of this soluble, branched prepolymer to the formulation program is manifold. The prepolymer, which can be easily synthesized and conveniently stockpiled as an intermediate, is amenable to most methods of processing. The prepolymer can be used in the casting process, as discussed above. It would also be possible to utilize the isolated prepolymer in extrusion and compression-molding processes. Future work will investigate these and other processes where the isolated prepolymer may be of use.

C. EXTRUSION STUDIES

1. Previous attempts to extrude plasticized nitropolyurethanes have produced only malformed extrusion shapes. It has been assumed that the elastic and other intermolecular forces binding these polyurethanes are too great to allow the flow processes necessary for normal extrusion. In an attempt to reduce and dilute these polymeric binding forces, an inorganic salt was added to a plasticized nitropolyurethane. It was then found that extrusion was easy, giving rise to smooth-surfaced, uniform rods possessing remarkably high tensile strengths.

2. The first extrusions were made using sodium chloride as the inorganic salt. The binder was Polyurethane XIII-A (1% cross-linked) plasticized with 5,5-dinitro-2-hexanone. The handling process is as follows: After polymer and plasticizer are loosely mixed in an open container, the mixture is further worked on a roller mill for about 30 minutes at 150°F. To this rubbery base-material the salt is slowly added; and then a number of folded passes through the heated mill brings the mixture to a high degree of homogeneity. This mass is then rolled into a cylinder of 1-inch diameter, placed in the extrusion press, and extruded at a temperature of about 150°F and a pressure of 10,000 to 20,000 psi. The extrusion-die diameter is 3/16 inch. The linear density of the extruded product is about 30 grams per meter.

3. The successful extrusions using sodium chloride immediately suggested the use of ammonium nitrate and ammonium perchlorate. These compositions were accordingly made up, and, using appropriate safety measures, were milled and extruded in the same manner as the sodium chloride runs. Equally good extrusions were obtained. They burned rapidly, completely, and with a smokeless flame. The extruded products were characterized by impact stabilities and burning rates. Data are given in Table X. The burning rates obtained under Contract N0a(s) 53-618-c are extremely high for the nitropolymer containing ammonium perchlorate and ammonium dichromate. Ballistic modifiers should be investigated for reducing the pressure exponent, and a process should be developed which avoids the high extrusion pressures required for these compositions.

IV. TECHNICAL PROGRESS: PHYSICAL STUDIES (Contract N7onr-462)

A. HEATS OF COMBUSTION

1. Introduction

Correct values for the heat of combustion are required for exact specific-impulse calculations. They also serve as excellent means for confirming the structures of organic nitro compounds. During the last quarter heat-of-combustion runs have been conducted on several nitropolymers and nitroplasticizers.

TABLE X

NITROPOLYURETHANE - OXIDIZER EXTRUSIONS

Run	Formulation Polyurethane Plasticizer	Oxidizer ³	Calc'd I _{sp} (lb f · sec/lbm)	Extrusion Temp. (°F)	Pressure (psi)	Impact Stab. cm/2kg	Burning Rate (in/sec at 600°F, 1000 psi)	Pressure Exponent
241	XIII-A (28%) ¹ DNH (12%) ²	NH ₄ NO ₃ (60%)	222	150	15,000	100	0.16	0.76
243	XIII-A (24%) ¹ DNH (10%)	NH ₄ ClO ₄ (65%) ⁴	247	160	20,000	35-40	2.6	1.2
		+ 1% (NH ₄) ₂ Cr ₂ O ₇						
244	XIII-A (30%) ¹ DNH (10%)	NH ₄ ClO ₄ (60%)	242	125	15,000	35-40	1.5	0.9
245	XIII-A (25%) ¹ DNH (10%)	NH ₄ ClO ₄ (65%) ⁴	247	125	15,000	---	1.6	0.7
248	XIII-A (30%) DNH (10%)	NH ₄ ClO ₄ (60%)	242	130	20,000	35-40	1.7	0.9
250	XIII-A (27%) MDNV(13%) ⁵	NH ₄ ClO ₄ (60%)	245	150	20,000	---	1.8	0.8
252	XIII-A (28%) TNB (12%) ⁶	NH ₄ ClO ₄ (60%)	248	120	20,000	20	1.7	0.8
253	XIII-A (28%) TNB (12%)	NH ₄ ClO ₄ (60%)	248	120	20,000	---	1.6	0.8
		+ 0.1% FeAA ⁷						

¹ The polyurethane had been prepared with 1 equiv. % nib glycerol, and was acetone-insoluble.

² DNH is 5,5-dinitro-2-hexanone.

³ All solids were ground at 2200 rpm, except the dichromate catalyst, which was ground at 9600 rpm.

⁴ Stoichiometric weight of oxidizer.

⁵ MDNV is methyl 4,4-dinitrovalerate.

⁶ TNB is 1,3,3-trinitrobutane.

⁷ FeAA is ferric acetylacetonate.

2. Nitropolymers

a. Heat-of-combustion determinations were run on several nitropolymers; the results are compiled in Table XI. Polyurea XIII-AN is the postnitrated polyurea of 3,3-dinitro-1,5-pentane diisocyanate and 3,3-dinitro-1,5-pentane diamine. Experience has shown that usually only one-half the imido hydrogens of the polyurea group can be replaced by nitro groups in a postnitration process; the value of 3071 cal g⁻¹ for III-AN was computed on this basis. Indications are that preparation JKE-198 is slightly more than one-half nitrated. Another explanation for the lower value may be given by a degradation of the urea linkage to a nitramino group.

b. The nitropolyurethanes denoted (XL) in Table XI are modifications in which one equivalent percent of the di-functional diol was replaced by nib glycerol as a cross-linking agent. The predicted values listed in Table XI were computed on the basis of complete reaction of the tri-functional molecule. The resulting agreement with experimental values is considered satisfactory. The preparation of XIII-AN(XL) gave corrosive burning, as have all preparations of XIII-AN.

3. Nitroplasticizer

1,3,3-Trinitrobutane has been found to be compatible with nitropolyurethanes and is being used as plasticizer in nitropolymer formulations. In order to calculate exactly the specific impulse of the compositions, the heat of combustion of 1,3,3-trinitrobutane is required. The experimental heat of combustion of 1,3,3-trinitrobutane was found to be higher than the predicted value. This compound contains a nitro group bound to a primary carbon atom, to which a correction term of 13 kcal mole⁻¹ was applied, in computing the predicted value. It may be noted in Report No. 712* that the correction term for a nitro group bound to a tertiary carbon atom was determined to be -1 kcal mole⁻¹, whereas the value given by Kharasch** is +13 kcal mole⁻¹, with no distinction made as to the nature of the carbon atom to which the nitro group is bound. It may be that the correction of +13 kcal mole⁻¹ is accurate only for a nitro group bound to a secondary carbon atom, and that the correction is higher for a primary carbon atom. This possibility will be kept in mind if other compounds with a nitro group on a primary carbon atom are found to give a high experimental value. The agreement between experimental and predicted values for the other preparations listed in Table XI is considered satisfactory.

* Aerojet Report No. 712, 10 July 1953, pp. 24-26.

** M. S. Kharasch, J. Res. Nat. Bur. Stand., 2, 359 (1929).

TABLE XI
HEAT-OF-COMBUSTION DETERMINATIONS

<u>Polymer</u>	<u>Preparation</u>	<u>Heat of Combustion, cal g⁻¹</u>	
		<u>Obtained</u>	<u>Predicted</u>
Polyurea III-AN	JKE-198	2954	3071
Polyurethane XIV-J	JRF-249	3159	3116
" I-AN(XL)	JRF-241-A	2336	2330
" XIII-AN(XL)	JRF-260	2375	2388
" XIII-MN	JRF-261	2631	2630
" XII-H	JRF-257-B	3228	3292
" XII-HN	JRF-262	2712	2749
" XV-A	JRF-265	2717	2748
" XV-H	JRF-266	2931	2954
" XV-J	JRF-264	3512	3497
1,3,3-trinitrobutane	---	2983	2931

Legend

Diisocyanates:

I	3,3-dinitro-1,5-pentanediiisocyanate
XIV	3,3,5,7,7-pentanitro-5-aza-1,9-nonanediisocyanate
XIII	3-nitrazo-1,5-pentanediiisocyanate
XII	3,6-dinitrazo-1,8-octanediisocyanate
XV	2-nitrazo-1,4-butanediisocyanate

Diols

A	2,2-dinitro-1,3-propanediol
J	2-nitro-2-methyl-1,3-propanediol
M	N,N - <u>bis</u> (2-hydroxyethyl) oxamide
H	5,5,5-trinitro-1,2-pentanediol

B. OSMOMETRIC MOLECULAR WEIGHT STUDIES

1. Introduction

The osmometric molecular weight determinations of polyurethanes have been reported previously.* Up to this time the molecular weights of post-nitrated polyurethanes have not been determined. This report deals with the observation of diffusion problems in the determination of the osmometric molecular weight.

2. Polyurethane I-AN

An attempt was made to determine the molecular weight of the postnitrated product of preparation JKE-174. The postnitrated preparation, designated I-AN, JRF-240-D, had a relative viscosity of 1.41. This postnitrated preparation diffused through the membrane to an extent of 30% or more, so it was not considered reasonable to attempt any estimate of molecular weight by the osmometric method. An attempt to determine the molecular weight by the isopiestic method is described in Section C of this report.

3. Poly-2,2-dinitrobutyl Acrylate

A rapid estimation of the molecular weight of preparation DNBA 53 of poly-2,2-dinitrobutyl acrylate, giving a result of about 258,000, was reported previously.** During the past quarter, a large number of runs were made on the same preparation in an effort to obtain a more reliable value for the average molecular weight. The reproducibility of the runs was poor. The straight line calculated by the method of least squares for the π/c versus c plot had an intercept of $0.0106 \text{ ml cm}^{-2}$, with a mean square error for the 32 points of ± 0.00031 . All the error was assumed to be in the determination of π/c . This is equivalent to a molecular weight of $238,000 \pm 8000$. The reason for the poor precision of the runs is not known. It is not attributed to diffusion through the osmotic membrane, because no evidence of diffusion could be obtained.

C. ISOPIESTIC MOLECULAR WEIGHT STUDIES

1. Introduction

The isopiestic method of molecular-weight determination, described in earlier reports,*** has proved to be very valuable for analyzing polymers which are too low in molecular weight for determination by the osmometric method. A means of checking the isopiestic technique by an independent method of molecular-weight determination has been desired. During the past quarter, two such checks have been obtained, with satisfactory agreement in both cases. The isopiestic method has also proved to be very effective in providing positive evidence of decomposition of polymer in solution, in cases where decomposition is suspected.

* Aerojet Reports No. 772, p. 41; 740, p. 34; 712, p. 26; 686, p. 26.

** Aerojet-General Report No. 740, 15 September 1953, p. 39.

*** Aerojet Reports No. 638, 7 October 1952, pp. 53-62; No. 663, 23 December 1952, pp. 32-35.

2. Determination of Thiokol Resins

a. In order to confirm the isopiestic method for low-molecular weight polymers, three samples were run by an alternative method in an independent laboratory. The samples were liquid polysulfide polymers, furnished by the Thiokol Chemical Corporation, with molecular weights determined by the cryoscopic method. The isopiestic determinations run in the Aerojet laboratory were made in benzene as a solvent at 46°C. The comparison of results is shown in Table XII. It is concluded that the agreement between values is sufficient to verify the isopiestic technique.

TABLE XII

MOLECULAR WEIGHTS, THIOKOL RESINS

<u>Polymer</u>	<u>Aerojet-General (Isopiestic)</u>	<u>Thiokol (Cryoscopic)</u>
ZL-152	2560	2590
ZL-151	843	725
ZL-159	595	581

3. Polyurethane I-J, JRF-195-Q-2

a. A further verification of the isopiestic technique was made by running one of the fractions of the fractionated batch of Polyurethane I-J, on which a determination by the osmometric method was made in this laboratory. The osmometric determination gave a result of 43,800, which is now considered about the upper practicable limit for molecular-weight determination by the isopiestic method. The result of seven runs by the isopiestic method is shown in Figure 7. The straight line calculated by the method of least squares for the six points conforming most closely to a linear plot gives an intercept of 2.34×10^{-5} , with a mean square error for the six points of $\pm 0.23 \times 10^{-5}$. All the error was assumed to be in the determination of apparent molecular weight. This is equivalent to a molecular weight of $42,700 \pm 4,500$. If all seven points are included in the calculation, the result is $57,000 \pm 19,000$ to $-14,000$.

b. The chief disadvantage in the attempt to obtain the molecular weights of polymers in the range of preparation JRF-195-Q-2 is demonstrated by the deviating run at 0.0671 g ml^{-1} concentration. Because the intercept is small, the effect of a random error on the final molecular weight value is large; accordingly, it is necessary to make a large number of runs, in order to ensure that random deviations will not result in a gross error in the final value. By making a sufficiently large number of runs, it is possible to obtain reliable results in the molecular weight range up to 40,000, but the determination becomes laborious.

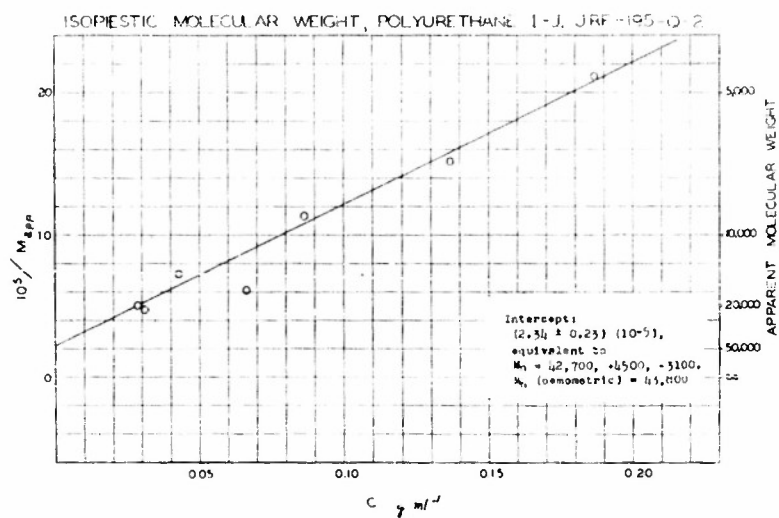


Figure 7

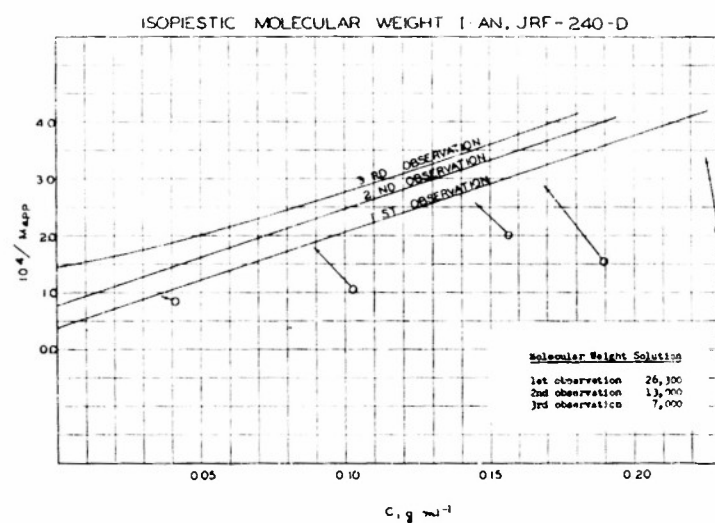


Figure 8

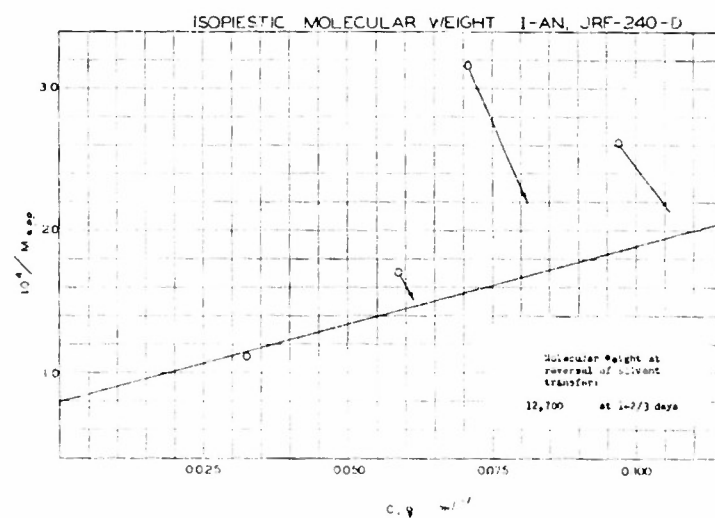


Figure 9

c. The main significance in determinations of the molecular weight of fraction JRF-195-Q-2 is the fact that for the first time a polymer has been run successfully by two methods -- the isopiestic method, which is best suited for low-molecular-weight compounds, and the osmometric method, which is best suited for high-molecular-weight compounds. The values are in good agreement, so that proved methods are now available in this laboratory for determining polymers of all molecular-weight ranges up to 100,000, if the polymers are stable and soluble in applicable solvents.

4. Polyurethane I-AN

a. Because the preparation of I-AN, JRF-240-D, showed excessive leakage by diffusion through the osmotic membrane, an attempt was made to determine the molecular weight by the isopiestic method. A previous attempt to measure this polymer by the isopiestic method was unsuccessful, because the postnitrated preparation forms a gel in acetone solution.* An investigation of other possible solvents for the isopiestic method showed that methyl ethyl ketone did not form a gel with I-AN, that it would dissolve the polymer to a high concentration, and that its vapor pressure at 46°C was higher than that of acetone at 25°C. The attempt to obtain the molecular weight of preparation JRF-240-D was unsuccessful, however, because the polymer proved to be unstable in solution. The results of the attempt are shown in Figure 8, in which the points represent the concentrations at which the isopiestic tubes were initially set up, and the vectors drawn from the points indicate the approximate direction and relative speed of solvent transfer, expressed in terms of apparent molecular weight. In this series of runs, the initial concentrations were set up so that the solvent transfer in the approach to isopiestic equilibrium was from reference solution to polymer solution, which is the same direction of transfer which would result from decomposition of the polymer. Under this circumstance it was not possible to distinguish the transfer due to decomposition from the transfer due to normal approach to isopiestic equilibrium, so that there is no choice between observations 1 and 2 in Figure 8. Both observations gave a satisfactory linear plot. (The points have been omitted from the curves in Figure 8 for the sake of clarity.) Decomposition was not clearly indicated until observation 3, at which time the decomposition had progressed far enough (at different rates for the respective points, depending partially on the concentration) that a non-linear plot was obtained.

* Aerojet Report No. 663, 23 December 1952, pp. 35-37.

b. A better demonstration of the decomposition was obtained on the second series of runs on preparation JRF-240-D, shown in Figure 9. In this series the initial concentrations, indicated by the points in Figure 9, were set up so that the solvent transfer was from polymer solution to reference solution in the approach to isopiestic equilibrium. (An exception is the run at 0.0321 g ml⁻¹; the transfer in this run was from reference solution to polymer solution, and the rate was too slow to indicate by a vector in Figure 9.) As the solutions approached equilibrium, the effect of decomposition became predominant, so that at 1-2/3 days a reversal of solvent transfer took place, the solvent transferring in all cases from reference solution to polymer solution, in the reverse direction of the vectors in Figure 9. The best straight line through the points at the occurrence of the reversal is shown in the figure, giving a molecular-weight value of about 13,000. The only conclusion that can be drawn is that the molecular weight of JRF-240-D before decomposition in solution is greater than 13,000; how much greater can not be determined.

D. RELATIVE-VISCOSITY STABILITY TEST FOR POLYMERS

1. It is presumed that the decomposition in solution also accounts for the difficulties encountered in attempting to measure the molecular weight of JRF-240-D in acetone solution by the osmometric method, described in Section IV B of this report. More than 30% by weight of the polymer diffused through the membrane. It is believed that the bulk of this diffusible material consists of low-molecular-weight fragments resulting from the decomposition. A further investigation of the decomposition was conducted by storing a 1% acetone solution at 25°C for two weeks, making relative-viscosity measurements periodically. The results are shown in Table XIII. Two solutions were set up, one containing dry acetone normally used in relative-viscosity measurements, the other containing acetone to which 0.2% water was added, in order to determine whether water condensed from the atmosphere in the osmometers accelerates the decomposition. The data in Table XIII indicate no appreciable difference between the wet and dry acetone solutions. It is also apparent that the decomposition in solution is rapid, and that molecular-weight values obtained at any given time will not have much significance.

TABLE XIII

RELATIVE VISCOSITY, I-AN, JRF-240-D, IN ACETONE, 25°C

<u>Time, days</u>	<u>Wet Acetone</u>	<u>Dry Acetone</u>
Zero	1.38	1.38
1	1.32	1.33
2	1.30	1.30
7	1.21	1.23
15	1.16	1.18

2. The batch of preparation JRF-240-D was subjected to a fractional precipitation, as described in Section II, in an effort to determine whether the high- or low-molecular-weight fractions were most subject to decomposition. Preliminary tests by the isopiestic method have been made on the two lower-molecular-weight fractions of the three fractions obtained. Both fractions have proved to be unstable in solution, because they have demonstrated the solvent-transfer reversal described in Figure 9. A relative-viscosity stability test on the highest-molecular-weight fraction is in progress.

V. TECHNICAL PROGRESS: RHEOLOGICAL STUDIES (CONTRACT NOas 53-618-c)

A. INTRODUCTION

1. The objectives of the mechanical-properties program have been to determine the bulk properties of experimental nitropolymers and to characterize them by parameters which will aid in selecting suitable materials for use in formulating and fabricating rocket propellants. The bulk properties of a polymer arise from the structure of the polymer chain and the forces between polymer chains.

2. The bulk structure of the polymer is a function of the chemical composition of the monomer, the symmetry of the polymer, the number and nature of the side groups along the chain, and the distribution of the lengths of the polymer chains. This basic structure determines whether the polymer chains can be arranged in a crystalline array or can only assume the random orientation characteristic of an amorphous material. The X-ray diffraction photograph and the softening point of the material are aids in classifying nitropolymers as amorphous, moderately crystalline, or extremely crystalline. Whether or not a nitropolymer exhibits crystallinity depends not only on the basic structure but also on the thermomechanical history of the material.

3. Three techniques appear to be useful for examining the nature and magnitude of the inter-chain forces and thereby characterizing the nitropolymers with respect to suitability for propellant fabrication and formulation. Measurement of thermal expansivity has been used to define a second-order or "glass" transition temperature below which the polymer is brittle. The cohesive-energy density of a polymer can be determined from measurements of the amount of swelling of the polymer by a "poor" solvent. This quantity in turn can serve as a guide in the choice of good solvents or good plasticizers for the polymer and can be useful in formulating propellants for fabrication by a plastisol casting process or by an extrusion process. Lastly, measurement of the relaxation of stress as a function of time and temperature is used to determine a graphical equation of state (master curve) which associates a value of Young's modulus with a given temperature and given rate of strain. This master curve, which is a plot of the logarithm of the modulus vs the logarithm of reduced time, gives a concise summary of many mechanical properties, e.g., those involved in temperature-cycling and embrittlement at low temperatures.

4. Investigations during the current report period have been concerned with the measurement and interpretation of stress-relaxation and flexure measurements on various nitropolymers as well as on a representative polycrystalline plasticized propellant, N-4 double base.

B. STRESS-RELAXATION STUDIES

1. Investigation of N-4 Double-Base Propellant

a. A plasticized nitrocellulose-base propellant was selected for study in order to characterize the behavior of a plasticized, linear, polycrystalline material. Previously linear amorphous nitropolymers had been studied and compared with a typical amorphous plastic, polymethyl methacrylate. However, polycrystalline nitropolymers such as XII-A have not yet been compared with well known polycrystalline polymers. Since N-4 is a propellant of established manufacturability, it provides a convenient reference point with which to compare other propellants. It is also interesting to compare N-4 with polymethyl methacrylate in order to see how this propellant differs from a typical base material - the linear amorphous polymer.

b. The material studied was supplied by the Naval Ordnance Test Station and has the following composition:

Material Designation: N-4 Double Base

Lot Number 53

Equilibrium Moisture 0.2%

Composition* (wt %):

Nitrocellulose (12.6% N)	51.0
Nitroglycerin	34.3
Diethyl phthalate	10.6
2-Nitrodiphenylamine	2.0
Lead stearate	0.5
Carbon black	0.1
Potassium sulfate	1.5

* SPIA Propellant Powder Manual, SPIA/M2, Unit No. 260.

c. Strands 6 in. long, 0.5 in. wide, and 0.1 in. thick were prepared by compression molding the extruded material. An investigation of the relaxation properties of the material was carried out over the range of temperature from -10 to 110°F. At each temperature the strand was strained 1%.

d. The stress-relaxation data for N-4 propellant obtained at six different temperatures are summarized in Figures 10 and 11. Over the range of five cycles of log time the modulus has slowly relaxed from a value of 3×10^9 dynes cm^{-2} to a value of 3×10^7 dynes cm^{-2} . It is estimated that another four cycles of log time are needed to allow for relaxation from 3×10^{10} dynes cm^{-2} . There is no indication from the shape of the incomplete master curve that it will display a region of rubbery behavior at longer times or higher temperature. A rough estimate of the inflection point of this incomplete master curve places it at 0.74 on the reduced time scale. This means that $\log K = 0.74 + \log \kappa$. The curve in Figure 11 which shows the temperature dependence of the shift factors, possesses an inflection point at about 45°F. This is defined as the distinctive temperature, and the corresponding distinctive relaxation time K_d is approximately 3000 sec. Thus at 45°F, the relaxation times of N-4 propellant will be distributed roughly from 0.3 sec to 3×10^7 sec on the absolute time scale.

e. Since it is known that nitrocellulose in double-base propellants is polycrystalline, it is interesting to compare the above results with those obtained on the polycrystalline Nitropolymer XII-A, for which K_d equals 3200 sec.* This coincidence suggests that the nitroglycerin in the double-base propellant does not act like a true plasticizer, or alternatively that unplasticized nitrocellulose has a K_d very much higher than 3200 sec. Evidence to show that plasticizers lower the value of K_d in nitropolymers for example, will be presented in a later section. It is also of interest that the activation energy for viscous flow calculated from the slope of the dashed line in Figure 11 is very high, 67 kcal. Again this compares favorably with the value of 70 kcal estimated from the data for Nitropolymer XII-A.*

f. In order to indicate the significance of the master curve for N-4 propellant, the master curve for polymethyl methacrylate is also presented in Figure 10. The Young's modulus for this material undergoes a rapid transition from the glassy modulus of 3×10^{10} dynes cm^{-2} to the rubbery modulus of 2.7×10^7 dynes cm^{-2} within the range of four cycles of log reduced time. The distinctive relaxation time for this material has been found to be 2 min at a distinctive temperature of 233°F.** Thus the complete spectrum of relaxation times of N-4 propellant (measured by the spread of the dispersion region between the glassy and rubbery moduli) comprises roughly twice as many cycles of log time as the spectrum of polymethyl methacrylate. This means that, at the distinctive temperature, N-4 has a higher mean relaxation time but a much broader dispersion of relaxation times than polymethyl methacrylate. Thus, while the latter substance will shatter like a glass when subjected to a high

* Aerojet Report No. 740, p. 46.

** ONR Technical Report R11-4, "Viscoelastic Properties of Polymethyl Methacrylate," J. McLoughlin and A. V. Tobolsky, April 1952.

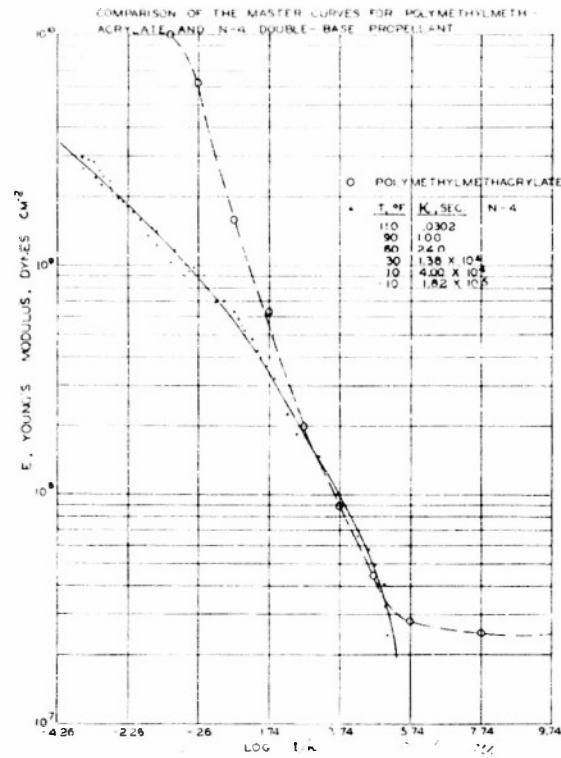


Figure 10

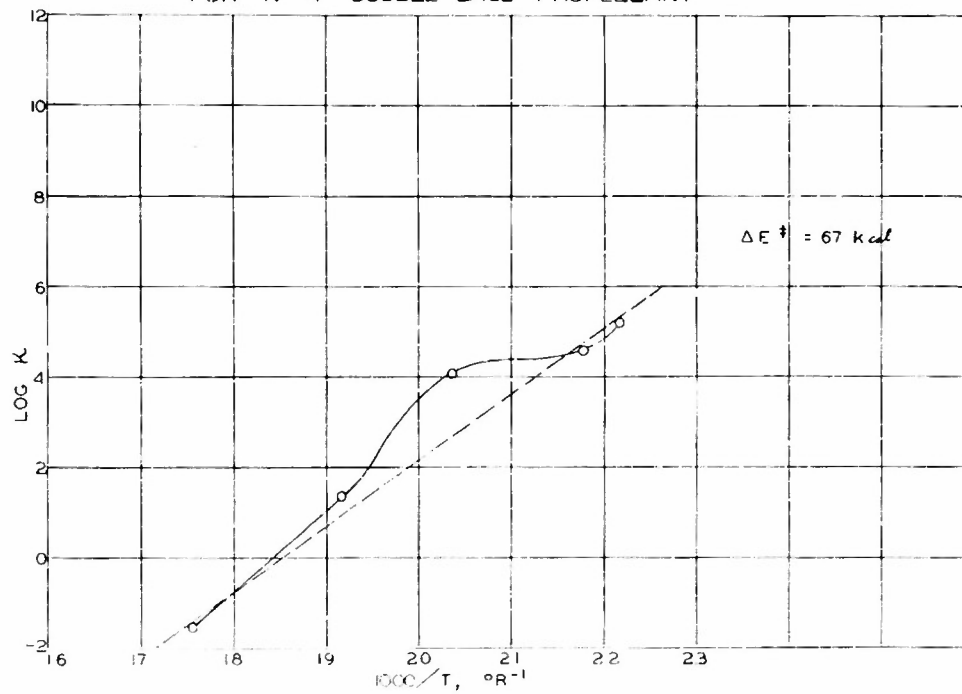
TEMPERATURE DEPENDENCE OF THE SHIFT FACTORS
FOR N-4 DOUBLE-BASE PROPELLANT

Figure 11

rate of stress at a temperature not far below its distinctive temperature, N-4, on the other hand, will dissipate the stress very slowly under the same conditions. Another way of phrasing this comparison is in terms of the dependency of the so called brittle temperature on rates of loading. In polymethyl methacrylate there is very little dependence; in N-4, it should be possible to shift the brittle temperature by as much as 40°F (this is the temperature range in Figure 10 which corresponds to a change of modulus from 10^9 to 10^8 - the leathery region) by varying the time scale of the method used to determine it.

2. Study of Plasticized, Crosslinked Nitropolymer XIII-A

a. The results of a study of the relaxation behavior of a typical crosslinked and plasticized nitropolymer are summarized by the portion of the master curve depicted in Figure 12. The polymer chosen, XIII-A, a polyurethane of 2,2-dinitro-1,3-propanediol and 3-nitroazela-1,5-pentane diisocyanate, contains 10% of a branching agent, nitroisobutylglycerol, and 40% of a plasticizer, dioxan. Over the range of five cycles of log reduced time, the modulus declines from a value of 3×10^8 dynes cm^{-2} to roughly 6×10^6 dynes cm^{-2} . Uncertainty in the experimental technique (discussed in Section C) precludes attaching any significance to the data falling below this value. It is estimated that 10 to 12 cycles of log time would be necessary to allow for complete relaxation from the glassy modulus. Thus, as in the case of N-4 double-base propellant, the relaxation spectrum of a plasticized, crosslinked nitropolymer is extremely broad. This, in itself, is a desirable property in a propellant, as it enables the propellant to withstand a wide frequency of stress loadings and also means that embrittlement is gradual.

b. A rough estimate of the inflection point of a cross-linked material places it midway between the log of the glassy modulus (3×10^{10} dynes cm^{-2}) and the log of the rubbery modulus (1.4×10^6 dynes cm^{-2} , see Section C). This midpoint of 2×10^8 dynes cm^{-2} occurs at $\log t/K$ equal to -1.85. Therefore $\log K = \log K = -1.85$. Further reference to Figure 13, which shows the temperature dependence of the shift factors, does not permit an estimate of the distinctive temperature, the data being insufficient. However, experience in handling the polymer permits estimation of the distinctive temperature as approximately 40°F. From Figure 13 then, $\log a_d = 0.4$, $\log K_d = -1.45$, and the distinctive relaxation time equals 0.03 sec at 40°F. Most linear, amorphous polymers are characterized by a K_d equal to 2 min. One of the advantages of a crosslinked plasticized nitropolymer is now clear. Above its relatively low transition temperature, it will sustain rates of loading as high as 30 cps. It is expected that a further study of plasticizer types as well as controlled addition of the branching agent will lead to a material able to sustain rates of loading as high as several kilocycles.

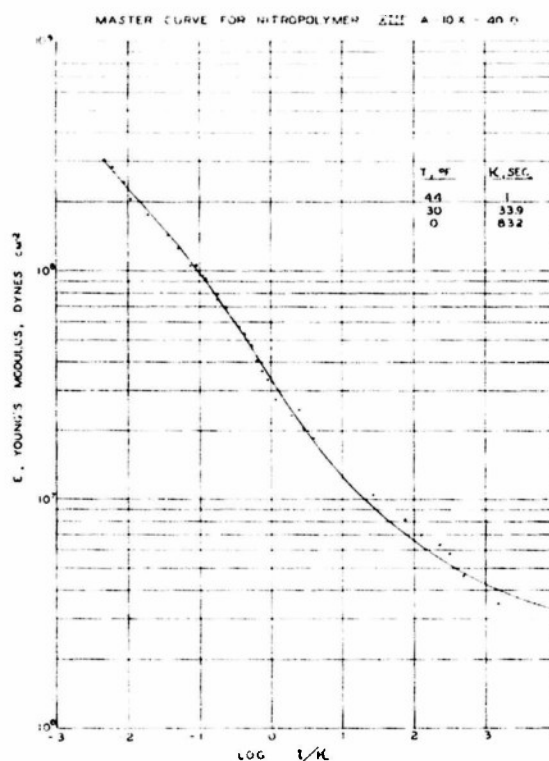


Figure 12

TEMPERATURE DEPENDENCE OF THE SHIFT FACTORS
OF XIII A - 10X - 40D.

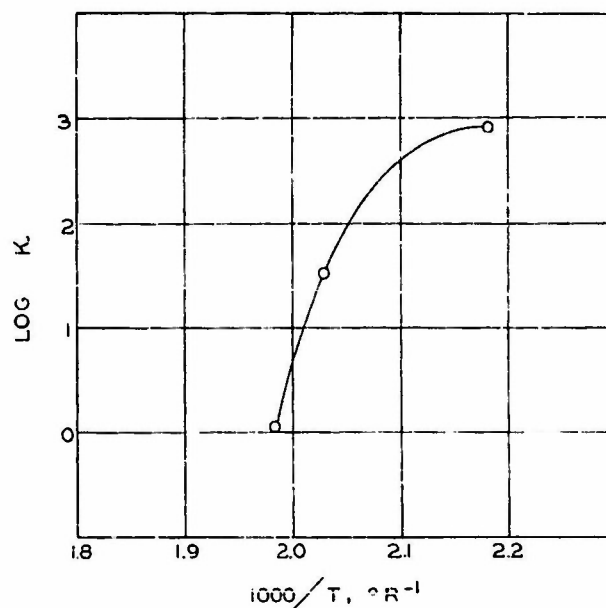


Figure 13

C. MODULIMETRY

1. One of the limitations of the stress relaxometer is that the measured load at any time is proportional to the difference between two relatively large numbers. As time increases the difference becomes smaller and the percentage error increases. In order to aid in determining the long-time or rubbery modulus of crosslinked materials, a modulimeter manufactured by the American Instrument Company is being used. This piece of equipment consists of two fixed knife edges, upon which a beam sample is rested, and one movable knife edge by means of which a fixed load is applied to the sample. The motion of the movable knife edge is transmitted to a dial gage which gives the deflection of the beam in thousandths of an inch. In the following paragraphs are discussed the method of calculating modulus from these measurements and the results of applying the instrument to the study of various plasticized and crosslinked preparations of Nitropolymer XIII-A.

2. Under the assumption that the entire transverse section of the beam, at any point along the beam, remains plane and normal to the longitudinal fibers of the beam after bending, it is readily shown that

$$EI_z \frac{d^2 y}{dx^2} = -M \quad (1)$$

where

E is the Young's modulus of the material

z is the axis of intersection of the neutral surface and any transverse section; the neutral surface is that surface above which the fibers undergo compression, below which they undergo tension

I_z is the moment of inertia of the transverse section with respect to the z axis

x is the distance from the transverse section to one of the fixed ends of the beam

y is the deflection of the beam at point x , and M is the bending moment at point x

If the load W be applied at the middle of the span the maximum deflection at the middle is given by:

$$y_m = \frac{W l^3}{48 E I_z} \quad (2)$$

where l is the span of the beam. For a beam of rectangular cross-section, it can be shown that

$$I_z = bd^3/12 \quad (3)$$

where b is the width and d the depth. For a beam of circular cross-section,

$$I_z = \pi d^4/64 \quad (4)$$

where d is the diameter. The final explicit formulae for calculating Young's modulus from the deflection of the beam are given by:

$$E \text{ (rect.)} = \frac{W\ell^3}{4bd^3y} \quad (5)$$

and

$$E \text{ (circ.)} = \frac{4W\ell^3}{3\pi d^4y} \quad (6)$$

3. Formulae (5) and (6) were used to calculate the rubbery moduli of a number of nitropolymers from data obtained on the modulimeter at 75°F. Since all the materials have transition temperatures below room temperature, the instantaneous modulus declines to the value of the rubbery modulus within a few seconds at 75°F;

The results are as follows:

	<u>Nitropolymer</u>	<u>E (dynes cm⁻²)</u>
a)	XIII A-10X-40D	9.2×10^6
b)	XIII A-2X-40D	8.3×10^6
c)	XIII A-10X-30D	1.5×10^7
d)	XIII A-4X-25D	1.5×10^7

Inasmuch as X refers to the branching agent, nitroisobutylglycerol, and D to the plasticizer, dioxan, it is significant that a fivefold change in the amount of branching agent (a-b) does not effect a significant change in the modulus. This indicates that two percent of nitroisobutylglycerol is already sufficient to convert the linear polymer to a crosslinked structure, in agreement with the results of viscosity measurements.* It is also significant that a concentration of dioxan plasticizer in excess of 30 wt % serves to lower the value of the modulus from that of a true rubber toward that of a jellylike material.

* Aerojet Reports No. 740, p. 54 and 772, p. 30.

4. In view of the fact that the plasticized crosslinked nitropolymers became available only recently, swelling measurements were postponed until the results and interpretations of stress-relaxation data could be completed.

D. POST-YIELD PROPERTIES OF LINEAR NITROPOLYMERS

1. A prerequisite for the design of propellant grains from nitropolymers is a knowledge of the post-yield and ultimate properties of these materials. As a start in this direction, a number of samples of the linear, amorphous Nitropolymer I-J (mol wt $\sim 200,000$) were sent to the Thickol Division of Redstone Arsenal for testing on the Instron machine. Samples were strained at rates ranging from 0.01 min^{-1} to 10 min^{-1} . Within this range, no pronounced dependence upon strain rate is shown by any of the results in Table XIV. The values cited are average values and are compared with equivalent values for extruded N-4 and cast AN-525 in Table XIV.

TABLE XIV

POST-YIELD PROPERTIES IN TENSION OF VARIOUS PROPELLANTS AT 75°F

Property	I-J-195	extr. N-4	AN-525
Young's Modulus, dynes cm^{-2}	2.4×10^{10}	6×10^8	5×10^9
Ultimate Strain, %	9	18	1
Maximum Stress, psi	9000	500	500
Work to Rupture/Unit Vol., in.-lb/in. ³	700	80	240

2. The most significant results that stem from the comparison of Table XIV are the relatively high ultimate strain and extremely high maximum stress values of the linear Nitropolymer I-J. In general, nitropolymers can be classified as extremely "tough" materials, as the value of 700 in.-lb/in.^3 for work to rupture indicates. It is planned to extend the above comparison to include measurements on the newly developed crosslinked nitropolymers.

VI. TECHNICAL PROGRESS: BALLISTIC STUDIES (CONTRACT NOas 53-618-c)

A. INTRODUCTION

The objectives of the ballistic studies have been to determine the burning rates and pressure exponents (at 60°F) of experimental nitropolymers and of mixtures of these nitropolymers with substances which increase their specific impulses and/or burning rates.

Burning Rate - Pressure Data at 60°F for Nitropolymers AII-AN and IA-1.5X

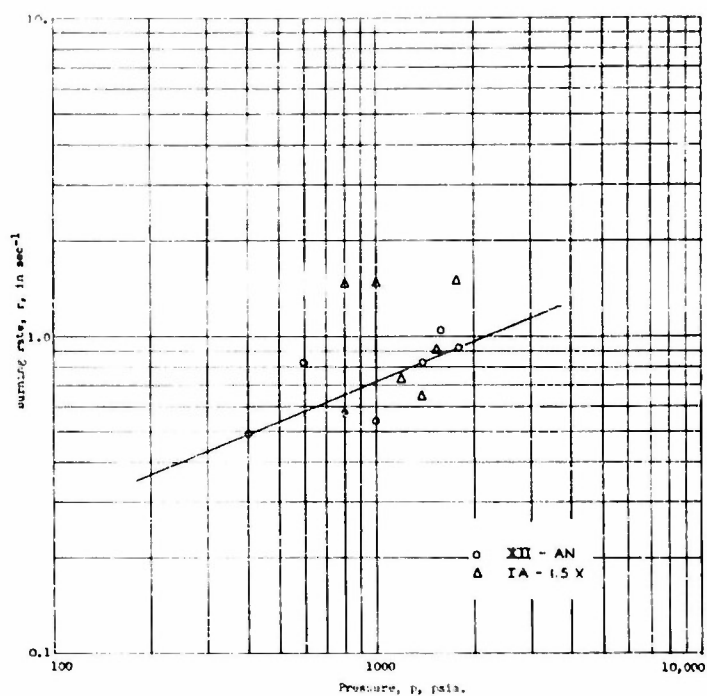


Figure 14

Burning Rate - Pressure Data at 60°F for Nitropolymers IA-II and IIIIA-24

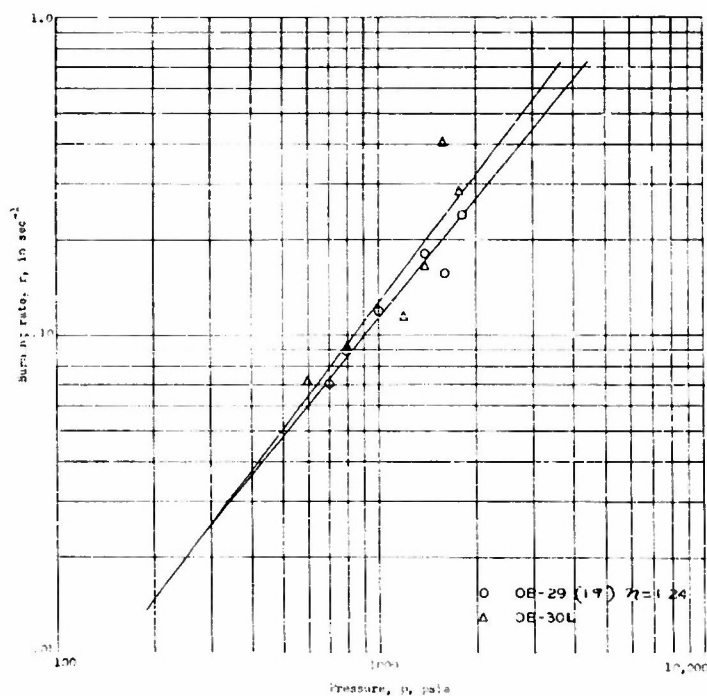


Figure 15

D. BALLISTIC PROPERTIES

1. Burning rate vs pressure data were determined for a post-nitrated linear Nitropolymer XII-AN, for several crosslinked nitropolymers, and for mixtures of the crosslinked nitropolymer with ammonium nitrate and Bentone 18 and ammonium dichromate with and without lead dioxide. The results are shown in Figures 14, 15, and 16. Although the data presented in Figure 14 scatter markedly about a "mean" line, it is remarkable that the burning rates for both XII-AN and IA-1.5X (1.5X signifies 1.5% nib glycerol) over the range of pressure from 400 to 1800 psia exceed 0.5 in. sec^{-1} . In an attempt to reduce this marked general scatter in the values obtained for the burning rates of nitropolymers, other techniques of restricting will be tried. The burning rates of crosslinked I-A and XIII-A at 1000 psia are approximately $0.12 \text{ in. sec}^{-1}$, according to Figure 15. Figure 16 presents a study of the effect of lead dioxide on the pressure exponent of the burning rate of a 50/50 mixture of ammonium nitrate and IA-2X catalyzed by three parts Bentone 18 and one part ammonium dichromate. It has been previously reported* that the burning rate of a 50/50 mixture of Nitropolymer I-A and ammonium nitrate is $0.14 \text{ in. sec}^{-1}$ at 1000 psia and the pressure exponent is 0.73. The inorganic substances, Bentone 18 and ammonium dichromate, were added in order to accelerate the rate, and lead dioxide was added to decrease the slope. The marked scatter of the points precludes the possibility of a significant comparison.

* Aerojet Report No. 712 (10 July 1953), p. 38.

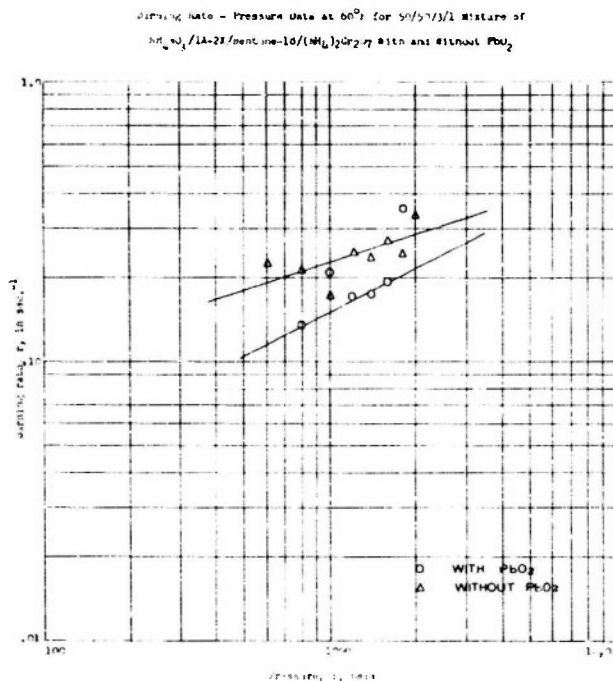


Figure 16

VII. TECHNICAL PROGRESS: ORGANIC SYNTHESIS (Contract N7onr-462)

A. INTRODUCTION

The synthesis of nitromonomers is fundamental to the development of nitropolymers. Various structures such as gem dinitro compounds, compounds containing the trinitromethyl group, and the nitramines have been found to be suitable structures for the preparation of the monomers for polymer formation. This report deals with the preparation of new nitramino diisocyanates and their respective intermediates, as well as nitramino diols.

B. NITRO ALCOHOLS

1. Preparation of 3-Nitrazo-1,5-pentanediol

a. Discussion

(1) The synthesis of 3-nitrazo-1,5-pentanediol was described previously.* Only the crude material had been obtained at that time by the hydrolysis of 3-nitrazo-1,5-pentanediol dinitrate and by the oxidation of 3-aza-3-nitroso-1,5-pentanediol. This diol, a low-melting solid, was characterized by preparing crystalline derivatives. However, before the material could be used for polymerization some investigations had to be made of various methods for isolating pure material suitable for use in polymerization studies.

(2) An aqueous solution of the diol, as obtained from the hydrolysis of the nitrate ester followed by neutralization with alkali, was slightly yellow, and this color could not be removed by treatment with charcoal. Neutralization of the nitric acid, formed during the hydrolysis, by passage over an anion-exchange resin (Amberlite IR-4B), likewise gave a yellow solution. The crude alcohol was isolated by continuous extraction of the water solution with ether, followed by evaporation of the ether. This yellow product, melting at about 10°C, could be distilled in a macro bulb tube at 3μ and an air-bath temperature of 150 to 160°C. This purified material was colorless, mp 23 to 24°C, but this boiling point is perhaps too high for safe distillation on a large scale. Low-temperature crystallization has not yielded the diol with a melting point or lack of color comparable to that of the distilled material.

(3) The two methods used here for the preparation of the 3-nitrazo-1,5-pentanediol are in some ways not suitable for use on a large scale. The dinitrate (DINA) is a high explosive and hence is an undesirable intermediate. The oxidation procedure requires the use of trifluoroacetic acid, an expensive reagent. More work will be done on the preparation of this desirable compound.

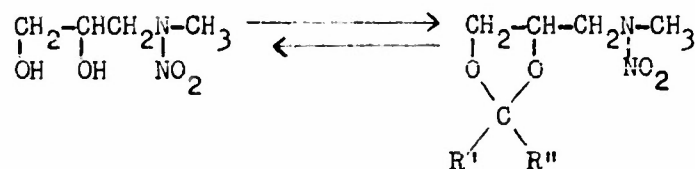
2. Preparation of 4-Nitrazo-1,2-pentanediol

a. Discussion

(1) The previously unreported 4-nitrazo-1,2-pentanediol has been prepared by the hydrogen peroxide-trifluoroacetic acid oxidation of the corresponding nitroso compound, also a new compound. Both the nitroso and nitro amines were obtained as undistillable oils and were identified and characterized by their solid dibenzoates. The synthesis is illustrated by the equation below:

* Aerojet Report No. 772, p. 71.

(2) Several procedures have been investigated for preparing a 1,3-dioxolane of the diol, since such a derivative should offer a convenient path for purification by distillation or crystallization of the derivative followed by hydrolysis back to the diol.



All attempts to condense the glycol with acetone ($\text{R}'=\text{R}''=\text{CH}_3$) were unsuccessful. Treatment of an acetone solution of the diol with anhydrous copper sulfate and a catalytic amount of boron trifluoride etherate at room temperature yielded only the water-soluble diol, identified by its dibenzoate. The use of excess boron trifluoride etherate for 5 min apparently caused decomposition of the nitramino diol, since the only isolable products were about 4 per cent of the starting material and a few drops of a water-insoluble, but acid-soluble oil, bp $80^\circ\text{C}/3\mu$. This oil may have been the desired isopropylidene compound, but there was not enough isolated for further investigation. A 1.5-hr treatment with boron trifluoride etherate yielded no water-insoluble or distillable product.

(3) The preparation of a benzaldehyde derivative ($\text{R}'=\text{C}_6\text{H}_5$, $\text{R}''=\text{H}$) was likewise unsuccessful. From a dioxan solution of the diol and benzaldehyde with anhydrous copper sulfate and a catalytic amount of boron trifluoride etherate, or an excess of the boron complex, only benzaldehyde could be identified (50 and 25% respectively), isolated as its bisulfite addition compound. Refluxing a mixture of diol, benzaldehyde, and p-toluenesulfonic acid in benzene gave 78% of the expected amount of water by azeotropic distillation. However, 59% of the benzaldehyde and 10 to 20% of the diol were recovered from the reaction mixture. It would seem that under acidic conditions either the nitramino diol eliminates water or the desired dioxolane is not stable.

(4) In view of the results outlined above, no further attempts will be made to obtain the dioxolane under acid catalysis. The easy formation of 4-nitrazo-1,2-pentanediol dibenzoate with benzoyl chloride and aqueous sodium hydroxide indicates that perhaps the purification can be accomplished by preparation of distillable or easily hydrolyzable esters. Work will be conducted in this direction.

b. Experimental

(1) 4-Nitroso-4-aza-1,2-pentanediol

A solution of 6.9 g (0.1 mole) of sodium nitrite in 20 ml of water was added over a 15 min period to a mixture of 10.5 g (0.1 mole) of 4-aza-1,2-pentanediol, 8.5 ml (0.1 mole) of conc. HCl, and 10 ml of water. After 0.5 hr of stirring at room temperature the water was removed in vacuo, and the product was separated from the inorganic salts by washing with absolute ethanol. Removal of the alcohol left 12.6 g (94%) of a red oil (n_D^{25} 1.4856). The dibenzoate of this oil was prepared by the Schotten-Baumann procedure and melted at 72.5 to 73.5°C after recrystallization from ethanol, chloroform, and three times from methanol.

Anal. Calc'd for $C_{18}H_{18}N_2O_5$: %C, 63.15; %H, 5.30; %N, 8.19

Found: %C, 63.33; %H, 5.07; %N, 8.18

(2) 4-Nitrazo-1,2-pentanediol

To a mixture of 16.5 g (0.44 mole) of 90% hydrogen peroxide and 100 ml of trifluoroacetic acid was added dropwise 53.5 g (0.4 mole) of 4-nitroso-4-aza-1,2-pentanediol with stirring and cooling to maintain the temperature below 40°C. After the 1 hr required for the addition and 2 more hours of stirring at 30°C, another 6 g of peroxide was added, and the mixture was allowed to stand at room temperature for two days. Dilution with 300 ml of ice water followed by extraction with 100 ml of methylene chloride in four portions and evaporation of the extracts then yielded 6.2 g (4.5%) of a yellow oil, n_D^{25} 1.4220, probably mostly the bis-trifluoroacetate. The aqueous portion of the reaction mixture was neutralized with base, and the water was removed in vacuo. The residue was extracted with dioxan, and the dioxan was removed by extraction with hexane and evaporation in vacuo. The 55.6 g (93%) of brown oily residue, n_D^{25} 1.4444, yielded a dibenzoate, mp 105 to 105.5°C, by the Schotten-Baumann procedure which was identical with that obtainable from the bis-trifluoroacetate, as shown by the fact that no melting point depression occurred when the two were mixed.

Anal. Calc'd for $C_{18}H_{18}N_2O_5$: %C, 60.33; %H, 5.06; %N, 7.82

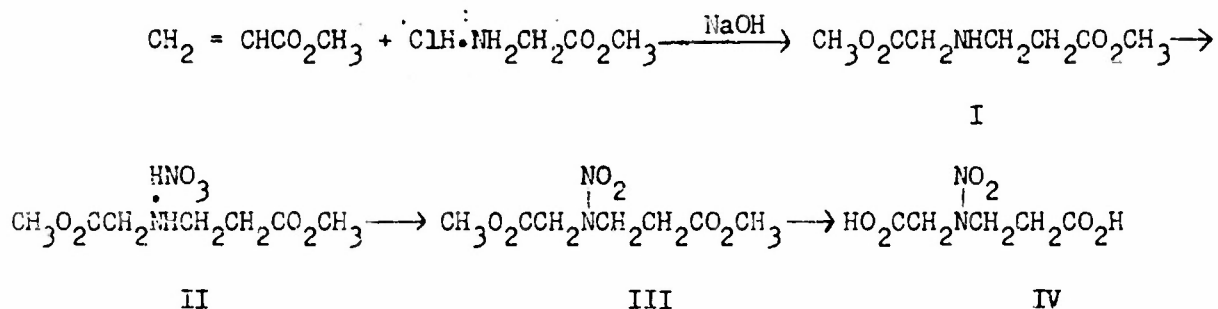
Found: %C, 60.61; %H, 5.03; %N, 8.18

C. NITRO DICARBOXYLIC ACIDS

1. Preparation of 3-Nitroaza-1,6-hexanedioic Acid

a. Discussion

The previous quarterly report described the preparation of 3-nitroaza-1,6-hexanedioic acid (IV).^{*} An alternative method has been developed for the preparation of the intermediate dimethyl ester, dimethyl 3-nitroaza-1,6-hexanedioate (III). By replacing acrylonitrile with methyl acrylate in the first step in the original synthesis, it was possible to eliminate a subsequent step, the conversion of methyl 3-aza-5-cyanopentanoate to dimethyl 3-nitroaza-1,6-hexanedioate. Otherwise, the reactions involved in the two syntheses are parallel. The final hydrolysis is identical in both syntheses.



b. Experimental

(1) Preparation of Dimethyl 3-Aza-1,6-hexanedioate

A solution of 82.6 g (2 moles) 97% sodium hydroxide in 250 ml water was added dropwise with vigorous stirring to a mixture of 251 g (2 moles) methyl glycine hydrochloride, 150 ml water, and 177 ml (2 moles) methyl acrylate while the temperature was held below 30°C. The reaction mixture was stirred for one hour at 30° and then stored at room temperature overnight. The mixture was extracted three times using a total volume of 650 ml methylene chloride. The combined extracts were washed with saturated sodium chloride solution, dried, and stripped of solvent. The fluid residue weighed 213.5 g, corresponding to a 61% yield of dimethyl 3-aza-1,6-hexanedioate.

* Aerojet Report No. 772, p. 73.

(2) Preparation of the Nitric Acid Salt of Dimethyl 3-Aza-1,6-hexanedioate

To a well-stirred solution of 213.5 g (1.22 moles) dimethyl 3-aza-1,6-hexanedioate in 900 ml methanol was added 85 ml (1.34 moles) 70% nitric acid in a fine stream while the temperature was maintained below 20°C by external cooling. The product was appreciably soluble in methanol, necessitating the chilling of the mixture to -25°C before filtering. The salt was washed with ether and dried. The crude nitric acid salt of dimethyl 3-aza-1,6-hexanedioate weighed 190 g, corresponding to a 65.4% yield. A sample of the product was purified for analysis by recrystallization once from methanol, twice from ethanol, and a fourth time from methanol. The colorless crystals melted at 75 to 76°C.

Anal. Calc'd for $C_7H_{14}O_7N_2$: %C, 35.29; %H, 5.92; %N, 11.76; %OCH₃, 26.06

Found: %C, 35.36; %H, 5.87; %N, 11.82; %OCH₃, 25.81

(3) Preparation of Dimethyl 3-Nitrazo-1,6-hexanedioate

Successive additions of 0.6 ml (0.0072 mole) 37% hydrochloric acid and 1.6 ml (0.038 mole) anhydrous nitric acid were made to 33.6 ml (0.356 mole) acetic anhydride below 20°C. The nitric acid salt of dimethyl 3-aza-1,6-hexanedioate (47.6 g; 0.2 mole) was added portionwise to the resulting solution while the temperature was held at 20 to 25°C by intermittent use of a cooling bath. Stirring was continued for 2 hr at 20 to 25°C. The solution was chilled to 0°C and diluted with 80 ml ice water, causing the separation of the oily product. The mixture was extracted twice with 100 ml methylene chloride, and the extracts were washed twice with dilute sodium carbonate solution and once with saturated sodium chloride solution. The methylene chloride solution was dried, and the solvent was removed by distillation *in vacuo*. The residue of dimethyl 3-nitrazo-1,6-hexanedioate weighed 35.5 g, corresponding to an 80.2% yield.

(4) Preparation of 3-Nitrazo-1,6-hexanedioic Acid

3-Nitrazo-1,6-hexanedioic acid was obtained in 77% yield by the hydrolysis of dimethyl 3-nitrazo-1,6-hexanedioate using concentrated hydrochloric acid, following the method described in the previous report.

2. Preparation of 4,7,10-Trinitraza-1,13-tridecanedioic Acid

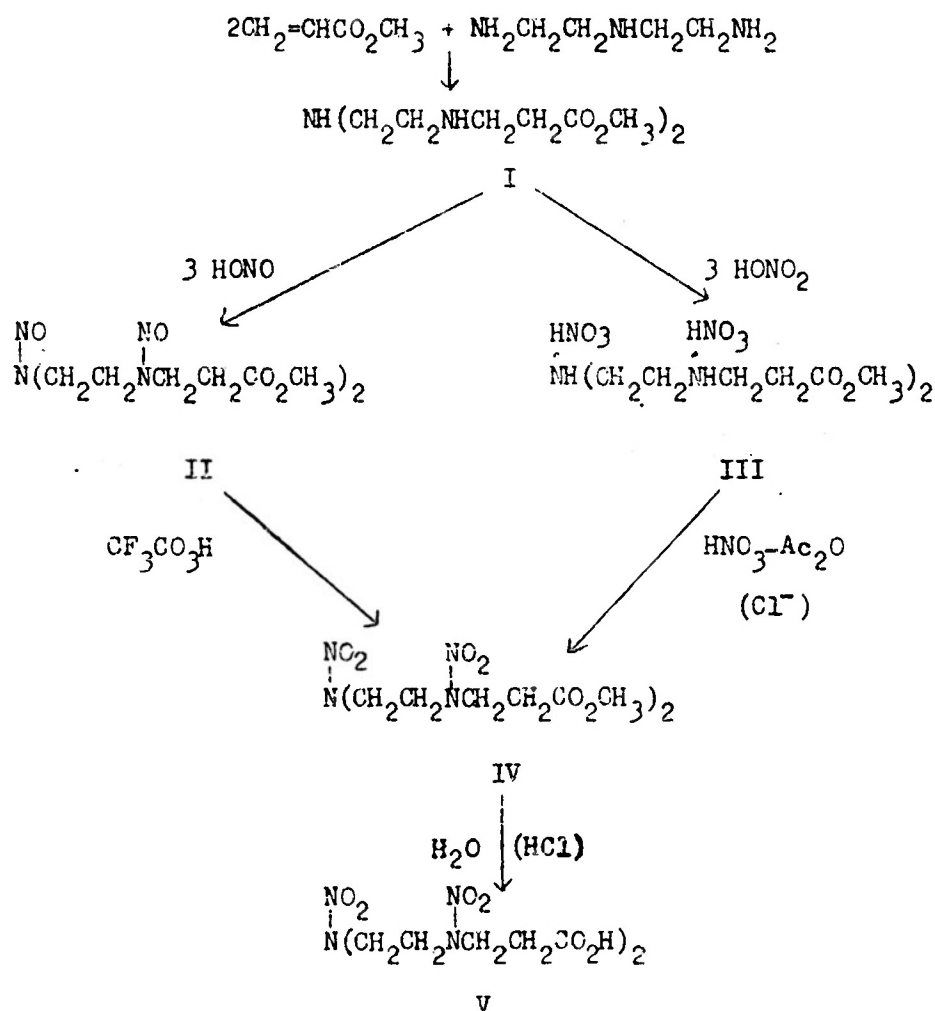
a. Discussion

(1) Previous preparations of 4,7,10-trinitraza-1,13-tridecane dinitrile, an intermediate in the synthesis of 4,7,10-trinitraza-1,13-tridecanedioic acid, have been described.* However, these methods were not desirable for the preparation of large quantities of the dinitrile because of the low yields involved in one case and because of the relative unavailability of starting materials in the other case. Attempts were also made to

* Reports No. 663, p. 76; No. 740, p. 68.

oxidize nitrosamines to nitramines,* a method which would prove valuable in this particular case, as 4,7,10-trinitroso-4,7,10-triaza-1,13-tridecane dinitrile is readily available. Recent work by the Rohm and Haas Co. has shown that trifluoroperacetic acid is a general reagent for the oxidation of nitrosamines to nitramines.** Consequently, this reagent was investigated as a means of oxidizing 4,7,10-trinitroso-4,7,10-triaza-1,13-tridecane dinitrile. The oxidation proceeded smoothly, yielding the colorless 4,7,10-trinitraza-1,13-tridecane dinitrile. Although the product may have been slightly contaminated, as indicated by the melting point, a sharply melting 4,7,10-trinitraza-1,13-tridecanedioic acid was obtained on hydrolysis.

(2) An alternative method was also used for the preparation of 4,7,10-trinitraza-1,13-tridecanedioic acid. The synthesis is shown in the series of reactions that follow.



* Report No. 686, p. 85.

** Emmons and Ferris, J. Am. Chem. Soc. **75**, 4623 (1953).

As indicated above, two routes were used in the conversion of dimethyl 4,7,10-triaza-1,13-tridecanedioate (I) to dimethyl 4,7,10-trinitraza-1,13-tridecanedioate (IV). The first method involved the oxidation of the intermediate, dimethyl 4,7,10-trinitroso-4,7,10-triaza-1,13-tridecanedioate (II), by means of trifluoroperacetic acid, and the second method involved the direct nitration of an intermediate tris nitric acid salt (III). This latter reaction was particularly interesting, as a fair yield of dimethyl 4,7,10-trinitraza-1,13-tridecanedioate (IV) resulted, whereas previous attempts to obtain the corresponding dinitrile, 4,7,10-trinitraza-1,13-tridecane dinitrile, in similar experiments met with little success. This difference in ease of nitration was presumed to be largely due to the greater solubility of the tris nitric acid salt of dimethyl 4,7,10-triaza-1,13-tridecanedioate in the nitrating medium as compared with that of the nitric acid salt of 4,7,10-trinitraza-1,13-tridecane dinitrile rather than any great difference in the basicity of the imino groups in the two compounds.

b. Experimental

(1) Preparation and Hydrolysis of 4,7,10-Trinitraza-1,13-tridecane Dinitrile

An oxidizing solution was prepared by the addition of 16.6 g (0.45 mole) 90% hydrogen peroxide to 74 ml (0.8 mole) trifluoroacetic acid. This solution was warmed to 40°C, and 29.6 g (0.1 mole) 4,7,10-trinitroso-4,7,10-triaza-1,13-tridecane dinitrile was added portionwise during a 10- to 15-min period at 40 to 45°C. The temperature was maintained by intermittent use of an efficient cooling bath. Stirring was continued for 30 to 40 min at 40°C, and intermittent cooling was required. Inadvertent cooling to 35°C caused the product to crystallize from solution. The pasty mass was further chilled to 5°C, poured onto an ice-water mixture, and filtered. The colorless product was washed successively with cold water, methanol, and ether. Air drying yielded 28 g 4,7,10-trinitraza-1,13-tridecane dinitrile, corresponding to 81.4% of the theoretical. The product melted over a range (ca 136 to 141°C) which indicated that the reaction could possibly have been run for a somewhat longer period. The dinitrile was hydrolyzed using concentrated hydrochloric acid (12 ml/gram) during a 6 to 7 hr period to yield 4,7,10-trinitraza-1,13-tridecanedioic acid, melting at 176.5 to 178°C.

(2) Preparation of Dimethyl 4,7,10-Triaza-1,13-tridecanedioate (I)

To a solution of 206 g (2 moles) diethylene triamine in 300 ml methanol was added 344 g (4 moles) methyl acrylate during a 30- to 35-min period while the temperature was held below 50°C. The solution was stirred for 1.5 hr during which time the temperature dropped to 30°C and was then reheated at 45 to 50°C for 30 min. The solution (800 ml, total volume) was divided into two equal portions, and the latter were used in subsequent preparations of the nitric acid salt of dimethyl 4,7,10-triaza-1,13-tridecanedioate and dimethyl 4,7,10-trinitroso-4,7,10-triaza-1,13-tridecanedioate.

(3) Preparation of the tris Nitric Acid Salt of Dimethyl 4,7,10-Triaza-1,13-tridecanedioate (III)

A 400-ml portion of the above reaction solution was diluted with 1000 ml water, and 199 ml (3.15 moles) 70% nitric acid was added in a fine stream with vigorous stirring while the temperature was held below 20°C by external cooling. The resulting mixture was further chilled to 0°C, and the precipitate was collected on a Buchner funnel. The fine, crystalline precipitate made filtration extremely slow. The product was washed with methanol and then dried in a vacuum desiccator over potassium hydroxide pellets with continuous pumping for several hours. The dry product weighed 188.5 g, corresponding to a 40.6% yield of the tris nitric acid salt of dimethyl 4,7,10-triaza-1,13-tridecanedioate (based on diethylene triamine).

(4) Preparation of Dimethyl 4,7,10-Trinitroso-4,7,10-triaza-1,13-tridecanedioate (II)

A 400-ml portion of the reaction solution from the preparation of dimethyl 4,7,10-triaza-1,13-tridecanedioate (see (2) above) was diluted with 150 ml water, and 249 ml (3 moles) 37% hydrochloric acid was added rapidly with vigorous stirring but no external cooling. A solution of 220 g (3.1 moles) 97% sodium nitrite in 400 ml water was added to the hot solution during a 15-min period. The temperature was held at 70 to 80°C during this time by the heat of reaction. Stirring was continued for 45 min while the temperature of the reaction mixture was held at 90°C by means of the steam-bath. The mixture darkened appreciably during this latter heating period. The lower, oily layer could not be crystallized on chilling and was removed by four extractions with methylene chloride (2400 ml, total volume). The combined extracts were washed twice with 750-ml portions of 3% sodium carbonate, once with 750 ml 3% sodium bisulfite, and twice with 500 to 600 ml water. The solution was distilled briefly until all moisture had azeotropically distilled and was then treated with charcoal. The solvent was removed by distillation under reduced pressure, yielding a brown, viscous residue of crude dimethyl 4,7,10-trinitroso-4,7,10-triaza-1,13-tridecanedioate weighing 116 g, which corresponded to a 32.2% yield (based on diethylene triamine). Initial attempts to crystallize the product were unsuccessful, and the material was used without purification in the preparation of dimethyl 4,7,10-trinitraza-1,13-tridecanedioate.

(5) Preparation and Hydrolysis of Dimethyl 4,7,10-Trinitraza-1,13-tridecanedioate (IV)

(a) A solution of 36.2 g (0.1 mole) crude dimethyl 4,7,10-trinitroso-4,7,10-triaza-1,13-tridecanedioate in 55.5 ml (0.6 mole) trifluoroacetic acid was added dropwise with stirring to a solution of 16.6 g (0.45 mole) 90% hydrogen peroxide in 37 ml (0.4 mole) trifluoroacetic acid warmed to 40°C. The addition was completed in 10 to 15 min while the temperature was held at 40°C by intermittent cooling. Cooling was also required for 15 to 30 min following the addition. With continued

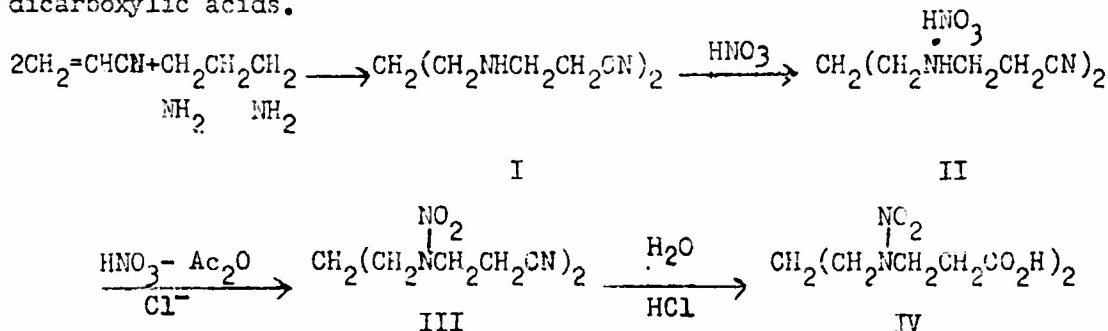
stirring for 1 hr, the temperature of the solution dropped to 35°C. The solution was reheated to 45°C and allowed to stir for 30 min. The solution was chilled to 0°C and diluted with 300 ml ice water, which caused the product to separate as a near-colorless oil. With continued stirring, the latter crystallized and was removed by filtration and washed with cold water. The product was recrystallized from a methanol-acetone mixture to yield 18.5 g material corresponding to 45.1% of the theoretical, although an appreciable amount of product was lost due to spillage during the recrystallization process. The dimethyl 4,7,10-trinitraza-1,13-tridecanedioate melted at 103 to 109°C, indicating some contamination, but hydrolysis in 200 ml 37% hydrochloric acid for 3 hr at 85 to 90°C yielded 12.5 g (72.5%) 4,7,10-trinitraza-1,13-tridecanedioic acid melting at 177 to 178.5°C and 186°C. This double melting point had previously been exhibited by this acid when obtained by the hydrolysis of the corresponding dinitrile.

(b) A nitrating solution was prepared by the successive addition of 0.82 ml (0.0099 mole) 37% hydrochloric acid and 2.5 ml (0.06 mole) anhydrous nitric acid to 47 ml (0.5 mole) acetic anhydride at 20 to 25°C. To this solution was added 46.4 g (0.1 mole) powdered tris nitric acid salt of dimethyl 4,7,10-triaza-1,13-tridecanedioate in portions during a 45-min period. The addition was carried out over this comparatively long period as the salt dissolved slowly at 25 to 35°C. During the addition of approximately the latter one-third of the salt, the precipitation of solid (presumed to be product) from solution obscured the reaction. However, there appeared to be no heat evolved, and no nitrogen dioxide fumes were present during this time. With the addition of 0.82 ml (0.0099 mole) 37% hydrochloric acid, the temperature rose immediately from 31 to 39°C with an accompanying decrease in the viscosity of the reaction mixture. With continued stirring, the temperature gradually rose to 45 to 50°C during a 20 to 25-min period. From this point, the temperature rose rapidly to 55°C with complete solution resulting. The solution was immediately chilled to 45°C, causing the crystallization of appreciable solid. There appeared to be no further reaction as the temperature dropped to 30°C with the precipitation of additional solid during the final 30 min of stirring. The mixture was chilled and diluted with 120 ml ice water followed by filtration and washing of the product with ice water. Recrystallization of the crude product from a methanol-acetone mixture yielded 25.5 g (62.2%) dimethyl 4,7,10-trinitraza-1,13-tridecanedioate melting at 104 to 110°C, indicating some contamination. A small sample of the product was recrystallized repeatedly from methanol without markedly improving the melting point. However, a single recrystallization from boiling water (an extremely dilute solution) gave material melting at 112.5 to 114°C. Hydrolysis of 25 g crude dimethyl ester in 250 ml 37% hydrochloric acid at 85 to 90°C during a 2.5-hr period gave 19.6 g 4,7,10-trinitraza-1,13-tridecanedioic acid (mp 177.5 to 178.5° and 186 to 188.5°) corresponding to an 84.1% yield.

3. Preparation of 4,8-Dinitraza-1,11-undecanedioic Acid

a. Discussion

4,8-Dinitraza-1,11-undecanedioic acid was prepared by the following series of reactions, which directly parallels the synthesis of 4-nitraza-1,7-heptanedioic acid, 4,7-dinitraza-1,10-decanedioic acid, and other dicarboxylic acids.



4,8-Diaza-1,11-undecane dinitrile (I) was not isolated following the Michael reaction of acrylonitrile and 1,3-diaminopropane but was converted in solution to the nitric acid salt (II). The latter gave 4,8-dinitraza-1,11-undecane dinitrile (III) in 46% yield by means of a chloride-catalyzed nitration. The hydrolysis of the dinitrile in concentrated hydrochloric acid yielded 4,8-dinitraza-1,11-undecanedioic acid (IV) in 71% yield. A comparison of the melting points of the above dinitrile and dicarboxylic acid (81 to 82°C and 147.5 to 149°C, respectively) with the melting points of 4,7-dinitraza-1,10-decane dinitrile (130 to 131°C) and 4,7-dinitraza-1,10-decanedioic acid (141.5 to 142.5°C) indicates the marked effect obtained by the introduction of an additional methylene group giving rise to a series of compounds of odd chain length.

b. Experimental

(1) Preparation of the Bis Nitric Acid Salt of 4,8-Diaza-1,11-undecane Dinitrile

To a solution of 99 g (1.34 moles) 1,3-diaminopropane in 50 ml methanol was added 203 ml (3.1 moles) acrylonitrile while the temperature was held at 40°C by external cooling. After stirring overnight at room temperature, the reaction solution was diluted with 700 ml methanol, and 177 ml (2.8 moles) 70% nitric acid was added with vigorous stirring at 15 to 20°C during a 15-min period. The mixture was chilled to 5°C, and the product was collected by filtration and washed successively with methanol and ethyl ether. After thorough drying in a vacuum desiccator over potassium hydroxide pellets, the bis nitric acid salt of 4,8-diaza-1,11-undecane dinitrile weighed 403 g, corresponding to a 98.3% yield. Three recrystallizations from water-methanol mixtures gave product melting at 205 to 206°C.

Anal. Calc'd for $\text{C}_9\text{H}_{18}\text{O}_6\text{N}_6$: %C, 35.29; %H, 5.92; %N, 27.44

Found: %C, 35.28; %H, 5.78; %N, 27.22

(2) Preparation of 4,8-Dinitraza-1,11-undecane Dinitrile

A nitrating solution was prepared by the successive addition of 0.8 ml (0.0066 mole) 37% hydrochloric acid and 1.67 ml (0.04 mole) anhydrous nitric acid to 33.5 ml (0.356 mole) acetic anhydride. The bis nitric acid salt of 4,8-diaza-1,11-undecane dinitrile (30.6 g; 0.1 mole) was added portionwise at 40°C. With the addition of the salt completed, an additional 0.8 ml 37% hydrochloric acid was added, and the reaction mixture was allowed to heat to 50°C, with complete solution of the salt resulting. The solution was cooled to 40 to 45°C, but there was no further tendency for the reaction temperature to rise. With continued stirring, the temperature dropped to 30°C with the precipitation of some solid. The mixture was chilled to 10°C and diluted with 80 ml ice water. The product initially separated as an oil, but the latter crystallized during a brief stirring period. The product was collected by filtration and washed successively with ice water, methanol, and ether. The 18.1 g of product was recrystallized from an acetone-methanol mixture to yield 12.5 g (46.3%) 4,8-dinitraza-1,11-undecane dinitrile, melting at 74.5 to 77.5°C. Three additional recrystallizations from acetone-methanol mixtures yielded a purified material melting at 81 to 82°C.

Anal. Calc'd for $C_9H_{14}O_4N_6$: %C, 40.00; %H, 5.22; %N, 31.10

Found: %C, 40.00; %H, 5.16; %N, 30.98

(3) Preparation of 4,8-Dinitraza-1,11-undecanedioic Acid

A solution of 78 g (0.289 mole) 4,8-dinitraza-1,11-undecane dinitrile in 780 ml 37% hydrochloric acid was heated on the steam-bath at 90°C for 6.5 hr. The product separated in large, colorless crystals on storage of the solution overnight at room temperature. The dicarboxylic acid was removed by filtration, washed well with ice water, and dried. The 4,8-dinitraza-1,11-undecanedioic acid weighed 63.5 g, corresponding to a 71.3 % yield. A sample of the product was further purified by three recrystallizations from hot water to give material melting at 147.5 to 149°C.

Anal. Calc'd for $C_9H_{16}O_8N_4$: %C, 35.07; %H, 5.23; %N, 18.18

Found: %C, 34.84; %H, 5.19; %N, 18.50

D. NITRO DIISOCYANATES

1. Preparation of 2-Nitroaza-1,4-butane Diisocyanate

a. Discussion

An initial preparation and characterization of 2-nitroaza-1,4-butane diisocyanate on a small scale was described in the previous quarterly report.* This reaction has now been carried out on a 1-mole scale to yield the crude diisocyanate in about 94% yield. In order to obtain this desirable diisocyanate in a form suitable for polymerization it was necessary to investigate methods of purification. By low-temperature recrystallizations from absolute ether, the diisocyanate has now been obtained in greater than 98% purity. The material is a liquid at room temperature. The calculated specific impulse of the polyurethane from this diisocyanate and 2,2-dinitropropanediol is 179.2 lbf sec/lbm, and the corresponding postnitrated polyurethane has an estimated I_{sp} of 229.6 lbf sec/lbm.

b. Experimental

A solution of 229 g (1 mole) 3-nitroaza-1,6-hexanedioyl chloride in 1 liter dry, alcohol-free chloroform was added in a fine stream with vigorous stirring to a solution of 198 g (3 moles) sodium azide in 500 ml water. The temperature of the two-phase reaction mixture was maintained at 5°C during the 15 to 20-min period of addition. Stirring was continued for 1.5 hr while the temperature was held below 10°C by means of an ice bath. The mixture was separated, and the aqueous phase was diluted with 300 ml water and extracted with an additional 200 ml chloroform. The combined chloroform solutions were washed successively with 500 ml ice water, 500 ml 5% sodium bicarbonate, and two 500-ml portions water. The chloroform solution was dried over Drierite and then about 250 ml chloroform was distilled in vacuo to insure complete removal of moisture. The azide was then decomposed - the decomposition was self-sustaining after the solution had been warmed to 50°C. After 1 hr, an additional 250 ml chloroform was added and the solution was reheated on the steam bath until this amount of distillate was collected. The remaining solvent was then removed by distillation in vacuo. The residue of crude diisocyanate (yellow-orange color) weighed 177 g, corresponding to about 94% of the theoretical. The product was dissolved in 1600 ml absolute ether and decanted from a small (< 5 g) amount of orange-red oil. The clear solution, protected from moisture by a dry-nitrogen atmosphere, was chilled with vigorous stirring. Following crystallization and further chilling in a dry ice--acetone bath, the solvent was removed by a fritted-glass filter stick. A second recrystallization was made in like manner from 1500 ml absolute ether, and the last traces of solvent were removed by prolonged evacuation, using an oil pump. The crystalline product (160 g) melted on warming to room temperature. Duplicate analyses by titration means showed 97.31 and 97.26% diisocyanate.

* Report 772, p. 76.

The bulk of the material (140 g) was recrystallized twice from 1350 ml and 1500 ml absolute ether as before, followed by complete removal of solvent by pumping overnight. The faint yellow liquid weighed 120 to 121 g, and duplicate analyses showed 98.55 and 98.13% diisocyanate.

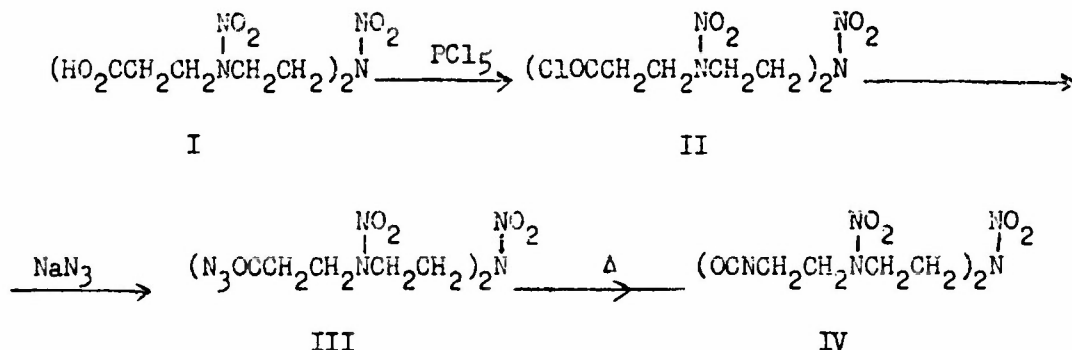
Anal. Calc'd for $C_5H_6O_4N_4$: %C, 32.26; %H, 3.25; %N, 30.10

Found: %C, 32.20; %H, 3.06; %N, 30.08

2. Preparation of 3,6,9-Trinitraza-1,11-undecane Diisocyanate

a. Discussion

The preparation of 3,6,9-trinitraza-1,11-undecane diisocyanate has been successfully completed on a small scale. The material was obtained by conversion of 4,7,10-trinitraza-1,13-tridecanedioyl chloride to 4,7,10-trinitraza-1,13-tridecanedioyl azide followed by rearrangement of the latter material.



Some difficulty was encountered in the attempted purification of 4,7,10-trinitraza-1,13-tridecanedioyl chloride (II), obtained by the action of phosphorous pentachloride on the corresponding acid (I). The acid chloride appeared to be amorphous and did not melt sharply after repeated recrystallizations from ethylene dichloride. The material was characterized by conversion to the dimethyl ester. However, the preparation of the diazide proceeded smoothly using this acid chloride. 3,6,9-Trinitraza-1,11-undecane diisocyanate (IV) was an amorphous solid which dissolved with difficulty in such solvents as the chlorinated hydrocarbons, ethyl acetate, and chlorobenzene, which have been successfully used for the purification of diisocyanates of similar structure. Moreover, once a solution of the diisocyanate was obtained, it was necessary to concentrate to near-dryness in order to recover the diisocyanate. As with the acid chloride, a sharply melting product was not obtained, although the material gave a satisfactory analysis and yielded a dimethyl urethane on treatment with methanol. The calculated specific impulse of the polyurethane from this diisocyanate and 2,2-dinitropropanediol is 157 lbf sec/lbm, and the calculated specific impulse of the corresponding postnitrated polyurethane is 220 lbf sec/lbm.

b. Experimental

(1) Preparation of 4,7,10-Trinitraza-1,13-tridecanedioyl Chloride

A mixture of 3.8 g (0.01 mole) 4,7,10-trinitraza-1,13-tridecanedioic acid and 9 g (0.022 mole) phosphorous pentachloride was charged to a round-bottomed flask with reflux condenser, and the mixture was gradually melted by gently heating with a Bunsen flame. The temperature of the mixture rose to the boiling point of the phosphorous oxychloride liberated which was distilled off as the reaction proceeded. The theoretical amount of phosphorous oxychloride was obtained in this manner. The solidified residue (some slight darkening or charring noted) was titrated with dry carbon tetrachloride, filtered, washed additionally with carbon tetrachloride, and washed with absolute ether. The product was recrystallized from about 15 ml dry ethylene dichloride to yield material melting at 100 to 108°C. This material and the product from a previous experiment were combined and recrystallized three additional times from dry ethylene dichloride. Although the color of the product was improved, there was little change in the melting point, and consequently, the material was not submitted for analysis. Treatment of the product with methanol on the steam-bath for a brief period yielded crude dimethyl 4,7,10-trinitraza-1,13-tridecanedioate, which was recrystallized four times from methanol to yield material melting at 112.5 to 113.5°C.

Anal. Calc'd for $C_{12}H_{22}O_{10}N_6$: %C, 35.12; %H, 5.41; %N, 20.48; %OCH₃, 15.13

Found: %C, 34.92; %H, 5.02; %N, 20.12; %OCH₃, 14.12

(2) Preparation of 3,6,9-Trinitraza-1,11-undecane Diisocyanate

A solution of 45.1 g (0.1 mole) 4,7,10-trinitraza-1,13-tridecanedioyl chloride in 235 ml acetone was diluted with 50 ml glacial acetic acid, and 26 g (0.4 mole) powdered sodium azide was added portionwise with vigorous stirring during a 10-min period, while the temperature was held at 20 to 25°C. The mixture was stirred for 1 hr at 25°C, chilled to 10°C, and diluted with 600 ml ice water. The separation of the product by filtration and subsequent washings with ice water, methanol, and absolute ether were extremely slow. The precipitate was slurried in 650 ml dry ethylene dichloride, and ca 200 ml solvent was distilled in vacuo to insure complete removal of moisture. The 4,7,10-trinitraza-1,13-tridecanedioyl azide was then rearranged by warming the mixture on the steam bath at atmospheric pressure. Additional solvent was added before decomposition was complete, to prevent the solution from becoming too concentrated. The polymeric material (15 g) which had formed during the early stage of the rearrangement was removed by filtration, and the filtrate was concentrated to near-dryness.

This concentrate was diluted with absolute ether, the mixture was filtered, and the solid was dried of solvent. The crude diisocyanate was treated with a large volume of hot methylene chloride, filtered to remove the more highly colored material which failed to dissolve, and then evaporated to near-dryness. On chilling the solution, the diisocyanate crystallized and was separated by filtration and washed with absolute ether. An attempt was made to recrystallize the 12 g of diisocyanate a second time from dry, alcohol-free chloroform, but the greater insolubility of the product in this solvent necessitated the further use of methylene chloride. Evaporation of the solution was again necessary, and the product was obtained in gelatinous form from the mixed solvents. The diisocyanate melted over the range of 90 to 95°C. A third recrystallization was made by dissolving the diisocyanate in methylene chloride and reprecipitating by the addition of absolute ether. The melting point was not improved.

Anal. calc'd for $C_{10}H_{16}O_8N_8$: %C, 31.92; %H, 4.29; %N, 29.78

Found: %C, 31.17; %H, 4.22; %N, 29.70

(3) Dimethyl urethane

A sample of the crude diisocyanate (17 g) was converted to the dimethyl urethane by warming with methanol for a brief period. The dimethyl 5,8,11-trinitra-2,5,8,11,14-pentaza-1,15-pentadecanedioate melted at 186 to 189°C after recrystallization from a methanol-acetone mixture.

Anal. calc'd for $C_{12}H_{24}O_{10}N_8$: %C, 32.73; %H, 5.49; %N, 25.45; %OCH₃, 14.09

Found: %C, 32.53; %H, 5.16; %N, 24.80; %OCH₃, 13.56

3. Preparation of 3,7-Dinitraza-1,9-nonane Diisocyanate

a. Discussion

An initial preparation of 3,7-dinitraza-1,9-nonane diisocyanate has been made and the diisocyanate characterized by analysis and conversion to the dimethyl urethane, dimethyl 5,9-dinitro-2,5,9,12-tetraza-1,13-tridecanedioate. The diisocyanate was prepared in the usual manner from 4,8-dinitraza-1,11-undecanedioyl chloride via the corresponding diazide. Because of the considerably greater solubility of this diazide (as well as the other intermediates in this series) as compared with 4,7-dinitraza-1,10-decanedioyl azide, it was possible to use a heterogeneous reaction medium in the preparation of the diazide and thus avoid the isolation of this material in the solid state. The acid chloride, 4,8-dinitraza-1,11-undecanedioyl chloride, was readily obtained by the action of thionyl chloride on the corresponding acid. The acid chloride melts at 60 to 61°C, and the dimethyl ester at 56 to 57°C as compared with 95 to 96°C and 124.5 to 125.5°C, for the respective melting points of 4,7-dinitraza-1,10-decanedioyl chloride and the corresponding dimethyl ester.

b. Experimental

(1) Preparation of 4,8-Dinitraza-1,11-undecanedioyl Chloride

A mixture of 61.6 g (0.2 mole) 4,8-dinitraza-1,11-undecanedioic acid and 183 ml thionyl chloride was heated at reflux temperature for 1.5 hr. The acid dissolved during this time with cessation of gas evolution and an accompanying rise in the temperature of the reaction solution to the boiling point of the thionyl chloride. The product did not crystallize when the solution was permitted to cool to room temperature, but did crystallize with further cooling. The colorless acid chloride was removed by filtration and washed with absolute ether. A small additional quantity of product was precipitated from the mother liquor by the ether washings. The two fractions weighed 63.5 g and 2.8 g, respectively, corresponding to a combined yield of 87.9%. A sample of the acid chloride was purified for analysis by two recrystallizations from dry, alcohol-free chloroform. The 4,8-dinitraza-1,11-undecanedioyl chloride melted at 60 to 61°C.

Anal. calc'd for $C_{11}H_{14}O_8N_4Cl_2$: %Cl, 18.80

Found: %Cl, 18.51

The second crop of acid chloride was converted to the dimethyl ester by warming on the steam-bath briefly with methanol. The ester melted at 56 to 57°C following three recrystallizations from methanol.

Anal. calc'd for $C_{11}H_{20}O_8N_4$: %C, 39.28; %H, 5.99; %N, 16.66; %OCH₃, 18.46

Found: %C, 39.44; %H, 5.92; %N, 16.77; %OCH₃, 18.02

(2) Preparation of 3,7-Dinitraza-1,9-nonane Diisocyanate

A solution of 37.7 g (0.1 mole) 4,8-dinitraza-1,11-undecanedioyl chloride in 225 ml dry, alcohol-free chloroform was added in a fine stream with vigorous stirring to a solution of 19.5 g (0.3 mole) sodium azide in 50 ml water at 5 to 10°C. The temperature was held at 5°C by means of an ice bath while the two-phase mixture was stirred for 1.5 hr. The reaction mixture was further diluted with 200 ml chloroform and 50 ml water, and the aqueous phase was discarded. The chloroform layer was washed with 100 ml 5% sodium carbonate solution and four times with 100 ml of ice water. The chloroform solution was dried over Drierite, diluted with additional dry chloroform, and distilled briefly in vacuo to ensure complete removal of moisture. The 4,8-dinitraza-1,11-undecanedioyl azide was then decomposed on warming the solution on the steam-bath at atmospheric pressure.

When decomposition was complete, the solvent was removed by distillation in vacuo to yield 30.6 g crude 3,7-dinitraza-1,9-nonane diisocyanate as a faint yellow, viscous residue. On storage in a deep-freeze, the product crystallized. The diisocyanate was triturated with absolute ether and dried to yield material melting at ca. 35°C. Further purification has not been investigated.

Anal. calc'd for $C_9H_{14}O_6N_6$: %C, 35.76; %H, 4.67; %N, 27.81

Found: %C, 35.92; %H, 4.58; %N, 28.46

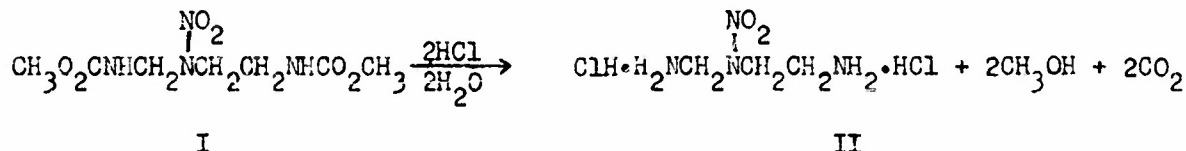
A portion of the product was converted to the dimethyl urethane, dimethyl 5,9-dinitro-2,5,9,12-tetraza-1,13-tridecanedioate, on treatment with methanol. The latter melted at 139.5 to 140°C after recrystallization from methanol.

Anal. calc'd for $C_{11}H_{22}O_8N_6$: %C, 36.06; %H, 6.05; %N, 22.94; %OCH₃, 16.94

Found: %C, 36.20; %H, 5.97; %N, 23.29; %OCH₃, 16.75

E. ATTEMPTED PREPARATION OF 2-NITRAZA-1,4-BUTANE DIAMINE DIHYDROCHLORIDE

An attempt was made to prepare 2-nitraza-1,4-butane diamine dihydrochloride (II) by the hydrolysis of the dimethyl urethane of 2-nitraza-1,4-butane diisocyanate (I) using concentrated hydrochloric acid.



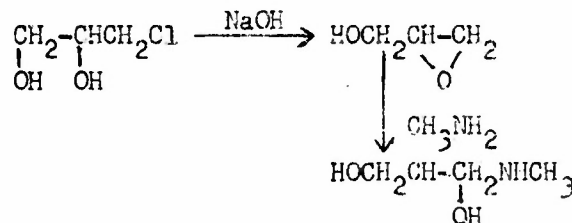
The only material isolated from the hydrolysis solution was ammonium chloride, indicating that degradation had occurred during the extended reaction period.

F. INTERMEDIATES

1. Preparation of 4-Aza-1,2-pentenediol

a. Discussion

The preparation of 4-aza-1,2-pentenediol for conversion to the 4-nitraza compound has been carried out by a modification of the method of Knorr and Knorr.*



* L. Knorr and E. Knorr, Ber., 32, 750 (1899).

The intermediate glycidol is not isolated in the course of the reaction. The amine is reported as boiling at 75°C/12 mm* and at 235 to 250°C/748 mm.** The material obtained here distilled at 123 to 125°C/5 mm, 107 to 109°C/2 mm, and at about 240 to 250°C at atmospheric pressure. The 75°C reported boiling point is apparently in error and probably should refer to 3-methylamino-2-methoxy-3-propanol.***

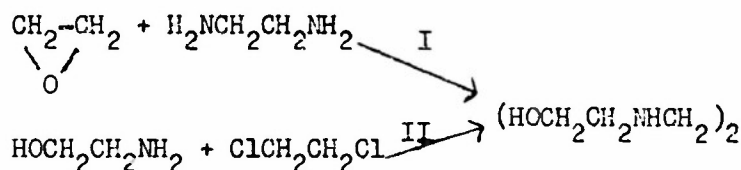
b. Experimental

Glycidol was prepared by adding 40 g (1 mole) of sodium hydroxide in 100 ml of water to a solution of 110 g (1 mole) of 3-chloro-1,2-propanediol in 370 ml of isopropyl alcohol at -5°C. After the mixture had been warmed to room temperature and filtered, it was added to 750 ml of 40% (10 moles) methylamine solution at about 10°C. Distillation of the resulting solution gave 60.0 g (57%) of the amine, bp 107 to 109°C/2 mm. n_D^{25} 1.4738.

2. Preparation of 3,6-Diaza-1,8-octanediol

a. Discussion

The increasing use of nitramino diisocyanates in the preparation of nitropolymers also suggested a thorough study of methods for preparing nitraminodiols. This report deals with the preparation of the intermediate ultimately leading to the preparation of 3,6-dinitraza-1,8-Octanediol. Two procedures have been used to prepare 3,6-diaza-1,8-octanediol, intermediate in the synthesis of 3,6-dinitraza-1,8-octanediol. The first method, Path I, used the condensation of ethylene oxide with ethylene diamine; the second procedure, Path II, involved the reaction of ethylene dichloride with ethanolamine. The first method was found to give a superior product and is preferred.



* E. Fourneau, *Traite de Chemie Organique*, Masson et Cie, Paris, 1935, Vol. XII, p. 514; E. H. Rodd, *Chemistry of Carbon Compounds*, Elsevier Publishing Co., New York, N.Y., 1952, Vol. 1B, p. 1035.

** L. Knorr and E. Knorr, *Ber.* 32, 750 (1899).

*** W. Schoeller and H. Schotte, German Patent 446,324. *Zentr.*, 27II, 863 (1927).

b. Experimental

(1) Reaction of Ethylene Oxide with Ethylene Diamine

Ethylene oxide (22 g, 0.5 mole) was added dropwise to a mixture of 40 ml of methanol and 20 g of 76.5% (0.255 mole) ethylene diamine with stirring and cooling in an ice bath to maintain the temperature at 5 to 10°C. The addition took 0.3 hr and after 0.5 hr more stirring, the mixture was allowed to warm to room temperature and stirred another 3 hr. Methanol was removed on a steam bath, and then distillation was started under 2 mm pressure. After a forerun of water and excess ethylene diamine, 5.0 g of 3,6-diaza-1-hexanol, n_D^{25} 1.4852 (1.4851 reported*), bp 104 to 107°C/2 mm, were obtained. The 22.4 g of residue solidified on cooling and was crystallized from 25 ml of chloroform to give 5.1 g of product, mp 85 to 90°C. A second recrystallization yielded material melting at 100 to 101°C (102 to 103°C reported**). The filtrate from the first crystallization was distilled to give 6.5 g more product, bp 180 to 193°C/3 mm. The total yield was 31% of theoretical.

(2) Reaction of Ethylene Dichloride with Ethanol

Amine***

To 360 g (5.9 moles) of ethanolamine at 130°C was added with stirring 200 g (2 moles) of ethylene chloride at such a rate as to maintain the temperature of the reaction mixture between 130 and 150°C. External heating was needed during most of the addition, which required 5 hr. The solution was then cooled, diluted with 1500 ml of methanol, and stirred with 171 g (4.3 moles) of powdered sodium hydroxide. The precipitated sodium chloride was filtered off, and the methanol was removed on a steam bath. Distillation of the residue gave 139 g of colorless liquid, bp 54 to 56°C/2 mm, n_D^{25} 1.4509 (probably mostly ethanol amine) and then the diol as a yellow solid, bp 179 to 195°C/3 mm, mp 80 to 90°C. Recrystallization of this solid from methanol gave 80.7 g (27%), mp 95 to 98°C.

* L. J. Kitchen and L. B. Pollard, *J. Org. Chem.*, **8**, 342 (1943).** I. G. Farbenind, German Patent 635,904, Oct. 1, 1936. *Zentr.* **36II** 4255 (1936).

*** Kitchen, op. cit.

ERRATA (Report No. 772)

p. 48 Equation (1) should read:

$$\frac{\log E_G - \log E(t/K)}{\log E_G - \log E_F} = F_N \frac{\log t/K}{\sigma}$$

p. 48 the standard deviation of log reduced time, equals 0.85
should read σ , the standard deviation of log reduced time,
equals 0.85

Data Questionnaire on
COMPOUNDS FOR USE AS INGREDIENTS OF PROPELLANTS AND OTHER EXPLOSIVES

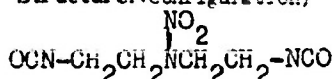
Listed below are the characteristics which are believed to be of importance in the study of a compound which may possibly be used as a constituent of solid propellants or other explosives. It is not expected that all this information will be available for every compound. For example, with a compound showing poor stability, it is probably not advisable to investigate that compound farther. After placing such information as is available for a compound which you have prepared or tested on one of these forms, send it to SOLID PROPELLANT INFORMATION AGENCY, API/JHU, 8621 Georgia Avenue, Silver Spring, Maryland. As additional information on the same or new compounds accrues, forward it on a similar form at a later date. The information submitted on these forms will be rewritten and published by SPIA in loose-leaf manual form. These forms may also be used as work or data sheets for your experimental studies. Extra copies are available upon request from SPIA. Suggestions for improvement of these forms are invited. If insufficient space has been provided for any item, attach separate sheets.

COMPOUND:

Name 3-nitrazo-1,5-pentane diisocyanate

Empirical formula _____

Structure: (configuration) _____

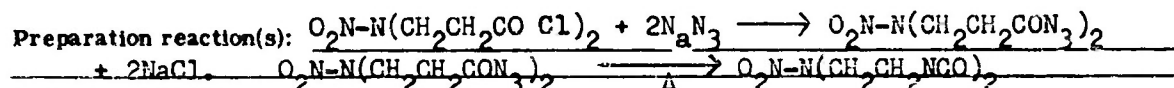


Information submitted by:

Activity Aerojet-General Corporation

Person C.R. Vanneman, R. Parrette

Date 22 January 1954



1. Quantitative analysis: (% by weight)

	Carbon	Hydrogen	Oxygen	Nitrogen		
Calculated from formula	36.00	4.04	—	27.95	—	—
By determination	35.70	4.02	—	28.83	—	—

2. Burning properties: (compared to nitrocellulose, under nitrogen or atmospheric pressure:)

(faster? slower? residue? etc.) _____

3. Stability and Sensitivity: Plot any graphs on separate sheet

Discuss methods used when they vary from references. Give temperature used. (Use separate sheet if necessary.)

Name of test	Recommended method	
a. Impact Sensitivity	OSRD 3185	
b. Thermal Stability	OSRD 3401 p.8	134.5°C, methyl violet paper.
c. Vacuum Stability	OSRD 3401 p.10	
d. Temperature of Explosion	OSRD 3401 p.8	
e. Temperature of Ignition	OSRD 3401 p.8	
f. Thermal Stability, 65.5°C	Picatinny Arsenal No. 1401. 1.3-g. sample, KI-starch paper.	
g. Impact Stability	Bureau of Mines, Bull. No. 346, 2-Kg. wt., 50% shots.	
h. Impact Stability	Same as g, but with 5/0 sand paper on anvil.	

RESULTS OF ABOVE TESTS

Reference compound _____

(designation-TNT, Tetrayl, N.C., etc.)

New Compound test results

a. _____	_____
b. Nitrocellulose, 30 min, no color.	Melted. No color or decomposition, 5 hr.
c. _____	_____
d. _____	_____
e. _____	_____
f. Nitrocellulose, 10 min, no color.	Melted. No color or decomposition, 5 hr.
g. BDX, 28 cm; composition A, > 100 cm.	> 100 cm.
h. BDX, 33 cm; composition A, 55 cm.	> 100 cm.

4. Heat of formation: (ΔH) + -31 Kg. calories at 25°C., 1 atm. pressure
(Indicate sign)

- | | By Experiment | By Calculation | Method |
|--|----------------------------|--|---|
| 5. Energy of explosion (Q)
(at 250°C. H ₂ O liquid) | _____ | cal/gm _____ | _____ |
| 6. Heat of combustion (H _c)
(at 250°C. H ₂ O liquid) | 3873 | cal/gm 3914 | Aerojet Report 417A. |
| 7. Specific impulse (I _{sp}) calc: | _____ | lb-sec/lb _____ | _____ |
| 8. Physical form of compound (viscous liquid, crystalline type, etc.) | White, crystalline solid | | |
| 9. Simple microscope analysis data: White, rhombic crystals.
(crystal studies) | | | |
| 10. Density (Macro method) | 1.473 gm/cm ³ . | (Micro or other method) _____ gm/cm ³ . | (Explain on separate sheet any unique methods you use.) |
| 11. Index of refraction: (n _D ^{25°C.}) | _____ | 12. Color White | 13. Odor None |
| 14. pH at 25°C. _____ (Method reference OSRD 3401 p.4, or OSRD 5968. Indicate method used, i.e. solvent and concentrations used. pH indicator used or Beckman pH meter.) | | | |

15. Hygroscopicity:
- | New Compound | Reference Compound |
|---|--|
| Visible change on exposure to ambient air. <u>Hydrolyses spontaneously.</u> | _____ (designation) |
| % wt increase by* (a) or (b)
(Strike out method (a) or (b) if not used.) | _____ |
| *Method: | (If other than below methods are used, explain on separate sheet.) |
| <p>(a) The sample (approx. 5-10 g. of whole grain small powder or 1 grain of large powder) is placed in a glass weighing bottle. The weighing bottle (cover removed) is placed in a vacuum drying oven for 5 hrs. @ 55°C. Remove weighing bottle from oven, cover with glass stopper, cool in a desiccator and weigh accurately. This is taken as original dry weight of sample. Then place weighing bottle (cover removed) in a humidior (a 10-in. desiccator is a satisfactory vessel) containing 1 liter of 18.6 ± .5% H₂SO₄. (This gives relative humidity 90 ± .25%). Place in an oven maintained at 30 ± 2°C. On the fourth day remove weighing bottle from the humidior, cover with glass stopper, cool in a desiccator and weigh. Then return to humidior for 24 hours, cool and reweigh. Continue daily weighings until constant weight indicates sample has reached equilibrium with 90% R.H. The % weight increase is then reported as hygroscopicity of the sample.</p> <p>(b) An alternate method is in OSRD 3401 p.3.</p> | |
16. Volatility: Report as rate of loss in wt % per unit area (for liquid samples measure the surface area; for solids, the sample should be screened between 100-120 mesh U.S. Standard certified sieve) per 4 hrs., after constant rate of loss is obtained during three consecutive 4-hr. periods at (a) 25°C in a vessel through which a stream of dry air is forced, (b) in an oven at 65.5°C or (c) under other test method or conditions.

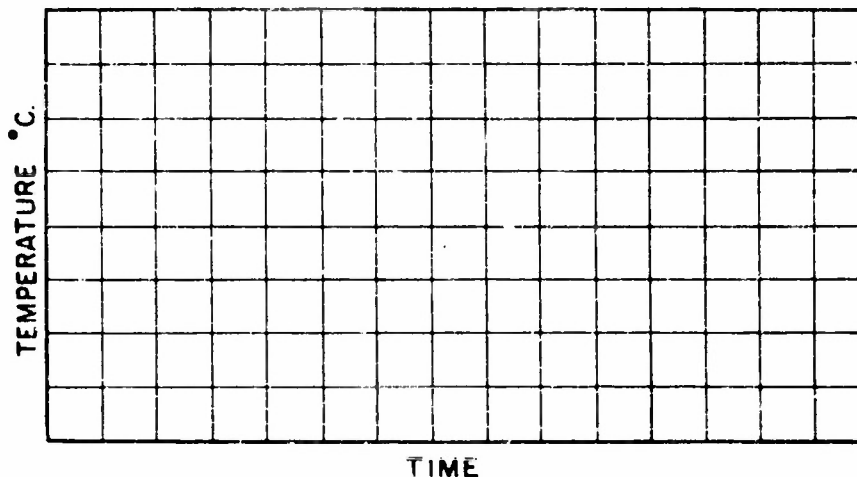
(Description or reference to other test or conditions used. Use separate sheet if necessary.)

Volatility results on:	New Compound	Reference Compound
a.	_____	_____ (designation)
b.	_____	_____
c.	_____	_____

17. Boiling point, or decomposition temperature: _____ °C.
(underline which temperature is reported)
18. Heat of Vaporization: _____ g-cal./gm _____ BTU/lb.
19. Heat of Fusion: _____ g-cal./gm _____ BTU/lb.
20. Melting point: 35.5 °C.

21. Freezing point vs. Time Curve: (Please mark the coordinates with scale values that apply to the compound under study.)

Polymerizes, hydrolyzes with heat.

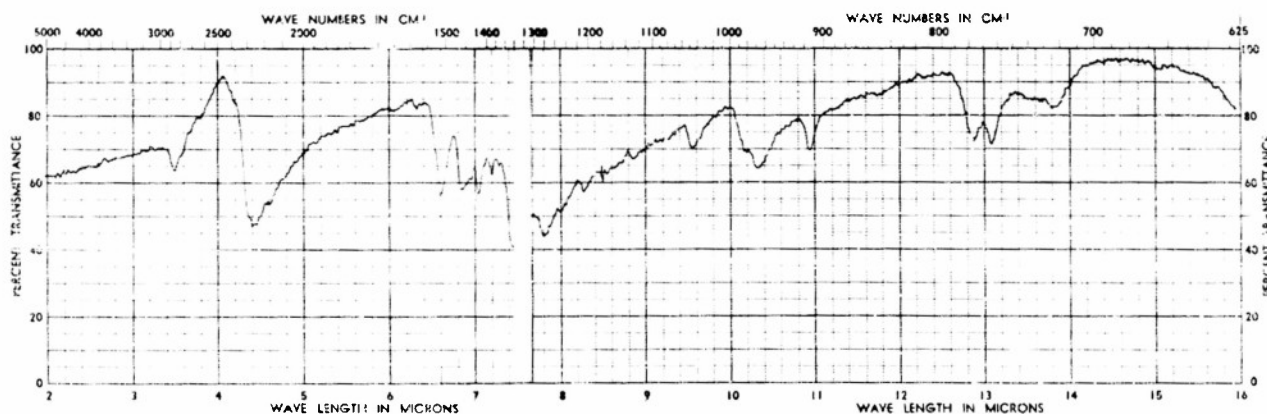


22. Solubility of new compound:

Insoluble, cold. g/100 ml H₂O at 25°C. Hydrolyzes, hot g/100 ml H₂O at _____ °C.
 0.66 g/100 ml n-heptane at 25 °C.
 (name material used as solvent)
 1.60 g/100 ml carbon tetrachloride at 25 °C.
 3.90 g/100 ml ether at 25 °C.

Can be recrystallized from a mixture of methylene dichloride and ether.

23. Infra red spectrum:



3-methyl-5-pentene diisocyanate, 2.00 to 7.55 microns - mull in
Fluorolube, F. S. 7.55 to 16.00 microns - mull in crystal oil.

12 min. scan. 12/16/53. R.P.

Under compatibility we are considering the ability of two compounds to be in intimate contact (Note CGRD 5758 p. 21-22) over a long period of time without adverse effects on either the chemical or physical properties of either material. These tests will probably be of varied extent. They might be some of the following: (a) Standard stability tests. (b) Simple observations of exudation or separation at ambient or accelerated temperature. (c) Prepare thin sheets (.025" thick, 1" square) of the plasticized material. Separate the sheets with strips of cigarette paper or carbon paper and compress the stack in a "C" clamp. After several days note the oily collection on the paper. Please give reference to or describe procedure used. Item 28 is to indicate results when the compound is in contact with some material other than ethyl cellulose, nitrocellulose or rubber. Test performed by dissolving sample and standard in a common solvent drying rapidly on a glass plate and examining the resulting film for clarity and homogeneity.

25. Compatibility with ethyl cellulose:

26. Compatibility with nitrocellulose: Ratio, wt sample/wt NC:

20/80	compatible
50/50	compatible
80/20	compatible

27. Compatibility with rubber: Ratio, wt sample/wt rubber:

20/80	compatible
50/50	compatible
80/20	compatible

28. Compatibility with _____:

29. Polymerizing properties of the new compound:

- (a) By itself Gradually polymerizes except at low temperatures.
- (b) In mixtures (with additives) Copolymerizes with diols to form polyurethanes.
- (c) Inhibiting action on polymerization of:

Thiokol _____
Methacrylate _____
Other compounds _____

30. Availability

- a. Amount now available? Research quantities.
- b. When was available material first prepared? _____
- c. Amount prepared at that time? _____
- d. Is large production feasible? _____
- e. Plant capacity in existence, lbs/day? _____
- f. Outline steps for a quantity production method _____

31. Additional information: (toxicity, hazards, deterioration, oxygen balance, detonation rate, explosive power, ease of hydrolysis by water, etc. List references, reports, data books, etc. that refer to the compound.)

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