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# RESEARCH IN NITROPOLYMERS AND THEIR APPLICATION TO SOLID SMOKELESS PROPELLANTS

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**Contract N7 onr-462 Task Order I**

**Contract NOas 54-399-C**

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

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# RESEARCH IN NITROPOLYMERS AND THEIR APPLICATION TO SOLID SMOKELESS PROPELLANTS

Contract N7onr-462, Task Order I

and

Contract NOas 54-399-c

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## CONTRACT FULFILLMENT STATEMENT

This quarterly report is submitted in partial fulfillment of Contract N7onr-462, Task Order I.

## SUMMARY

I. This quarterly report covers research conducted in partial fulfillment of Contract N7onr-462, Task Order I, during the period from 16 May through 15 August 1954.* The objective of this contract is to prepare and characterize nitropolymers and select those which may be useful in various military applications. This quarterly report also continues the reports on mechanical and ballistic properties under Contract NOas-54-399-c.** The ultimate goals of this contract are to evaluate the polymers synthesized on the ONR contract in terms of rheological and ballistic properties, and to formulate a nitropolymer grain of high performance.

II. The most important results are summarized below:

A. The emulsion polymerization of 2,2-dinitropropyl acrylate was successfully conducted using the same technique developed for 2,2-dinitrobutyl acrylate. A conversion of 90% at 60°C was achieved in 5 hr.

B. Monomer purity was found to be a very critical factor in obtaining high-molecular-weight 2,2-dinitropropyl acrylate. The influence of method of preparation and purification was checked by standard bulk polymerization. Indications are that specifications for monomeric 2,2-dinitropropyl acrylate may be written, inasmuch as there was some correlation found between monomer quality and refractive index.

C. The copolymer ratio between 2,2-dinitropropyl acrylate and glacial acrylic acid was found to be 1:1. On this basis a copolymer consisting of 20.5 mole % acrylic acid and 79.5 mole % 2,2-dinitropropyl acrylate was prepared, which will be used for vulcanization studies.

D. Kinetic studies were performed using the XIII-J polyurethane system (3-nitraza-1,5-pentane diisocyanate and 2-nitro-2-methyl-1,3-propanediol) in order to determine the catalytic efficiency of triethylamine in polyurethane formation. It has been found that a concentration of $1 \times 10^{-3}$ mole per liter triethylamine is equivalent to $1 \times 10^{-5}$ mole per liter of ferric acetyl acetonate. Other kinetic studies were conducted in order to obtain information on the reactivity of the recently prepared 2,5-dinitraza-1,6-hexane diisocyanate (XVI series). It was found that this diisocyanate reacts rapidly with diols in the presence of ferric acetyl acetonate (about 35 times as fast as in 3,6-dinitraza-1,8-octane diisocyanate and twice as

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*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, 772, 807, and 833.

**Previous work on this subject is covered in Aerojet Reports No. 720, 740, 772, 807, and 817.

fast as in 3-nitraza-1,5-pentane diisocyanate at the same catalyst concentration). However, it has also been observed that apparently some of the catalyst is consumed at the initial stages of the polymerization. Thus, the reactivity per unit catalyst concentration is even greater than the measured reactivity.

E. Using the recently reported 2,5-dinitraza-1,6-hexane diisocyanate, two new polyurethanes have been prepared and characterized:

| Polymer | Diol |
|---|---|
| XVI-A | 2,2-dinitro-1,3-propanediol |
| XVI-J | 2-nitro-2-methyl-1,3-propanediol |

F. In the preparation of new polyurethanes an effort is being made to diversify the monomers so that a wide variety of products will be available. It is also of interest to collect information on the physical properties of homologous nitropolyurethanes. Such data are of value in formulation experiments. For these reasons three new polyurethanes were prepared utilizing the commercially available 2-nitro-2-ethyl-1,3-propanediol (C). These polyurethanes are:

| Polymer | Diisocyanate |
|---|---|
| I-C | 3,3-dinitro-1,5-pentane |
| XII-C | 3,6-dinitraza-1,8-octane |
| XIII-C | 3-nitraza-1,5-pentane |

G. Polyurethanes obtained from the highly energetic 3,3,5,7,7-pentanitro-5-aza-1,9-nonane diisocyanate (XIV series), previously reported, were of rather low molecular weight. It was found that the failure to achieve high molecular weights was caused by certain impurities in the diisocyanate. Using highly purified starting materials it was possible to obtain a fibrous Polyurethane XIV-J of higher molecular weight. In order to avoid decomposition of the polymer the reaction was conducted at 30°C.

H. The majority of the polyurethanes thus far prepared are amorphous polymers. However, the study of polycrystalline nitropolyurethanes is desirable in order to investigate their applicability to a plastisol process. Unfortunately, all polycrystalline nitropolyurethanes prepared in the past were of low molecular weight and of low degrees of crystallinity, so that they were not applicable to plastisol processing. Using butyrolactone and high temperature for the polymerization, the moderately crystalline Polyurethane XIII-N was obtained, having a higher molecular weight than that reported previously.

I. The successful use of a casting process for the production of crosslinked, rubbery, plasticized polyurethanes in the absence of inorganic oxidizers has been reported. However, when inorganic salts were added to the mixture, in no instance was a gelled casting obtained. It was also observed that ferric acetyl acetonate catalyst was being decomposed, and thus the polymerization and gel formation were interrupted. In a series of experiments it was demonstrated that the catalyst is decomposed only when both an isocyanate function and the catalyst are present, while other functional groups are without apparent influence. It is believed that the metal chelate reacts with the salt dissolved in the solvent plasticizer mixture after complexing with the isocyanate group, thereby producing ferric ion. This was proved by color reactions with thiocyanate ion. The variation in decomposition rate with salt and solvent is interpreted in terms of differences in the solubility of various salts in the solvents or plasticizers.

J. The failure of ferric acetyl acetonate as a catalyst of polyurethane castings in the presence of inorganic oxidizers made a re-investigation of catalyst imperative. It was necessary to find catalysts which are stable in the presence of inorganic salts. Among all the catalysts investigated vanadyl acetyl acetonate gave the best results in the presence of inorganic oxidizers. This material was not only effective in producing a satisfactory rate, but was also sufficiently stable under the casting conditions.

K. Scaling up of polymerization experiments from small laboratory scale to larger scale requires the solution of many problems, such as reproducibility and uniformity of the product, dissipation of heat of reaction, reaction time, and the method of work-up. Polymerization runs in the Beken mixer were performed in order to produce linear polyurethanes under manufacturing conditions. It has been found that the runs were satisfactorily reproducible and that the product conformed to expectations. However, the reaction time required to produce high-molecular-weight linear polymers was far greater than when slightly branched polyurethanes were produced. Process control methods were studied and, although only a crude measure, the efflux time was still found to be the best control for polymerization.

L. Osmometric molecular-weight determinations on emulsion polymerized poly-2,2-dinitropropyl acrylate gave values from 100,000 to 120,000. Only a small amount of low-molecular-weight material diffused through the membrane.

M. The excellent properties of nitromorpholine as a plasticizer for nitropolyurethanes required the determination of its energetic properties. Heat-of-combustion runs on this compound indicated that a ring correction of 6 kcal/mole is required for the six-membered ether ring. From the data obtained the specific impulse for nitromorpholine is estimated to be 146 lbf sec/lbm.

N. Starting with hexamethylene tetramine and aqueous hydrocyanic acid as raw materials, 3-nitraza-1,5-pentanedioic acid was obtained as the intermediate for the preparation of 2-nitraza-1,3-propane diisocyanate.

O. 2-Bromo-2-nitro-1,3-propanediol, a nitrodiol to be used for second-stage crosslinking experiments, was obtained in pure form, mp 133 to 134°C. This value is to be compared with the reported value of 120 to 122°C.

P. 5,5,5-Trinitro-1,2-pentanediol was reported some time ago as a viscous oil. The diol had been used extensively for polymerization reactions in the liquid form. Recently a sample crystallized suddenly to give a product having a melting point of 54 to 55°C. Upon seeding samples of previous batches obtained as oils, all the samples solidified immediately.

Q. Swelling measurements on nitropolymer binders have been used to determine interaction constants with various nitroplasticizers. In all cases the constant k has the value of unity. Potentially good nitroplasticizers are trinitrobutane, methyl nitraza valerate, nitromorpholine, and methyl dinitrovalerate. Specific-impulse considerations suggest the use of trinitrobutane or mixtures of it with other nitroplasticizers.

R. Burning-rate studies have been undertaken with stoichiometric mixtures of Nitropolyurethane XIII-A and ammonium perchlorate, which were modified by various ballistic additives. The burning rate of the unmodified roll-milled mixture at 1000 psi is 2.1 in. $sec^{-1}$.

# PART I

## PREPARATION AND CHEMICAL PROPERTIES OF NITROPOLYMERS
(Contract N7onr-462, Task Order I)

## I. TECHNICAL PROGRESS: NITROPOLYMERS

### A. VINYL POLYMERIZATION

### 1. Emulsion Polymerization of 2,2-Dinitropropyl Acrylate

a. Discussion

(1) Studies of the emulsion polymerization of nitroacrylates emphasized work with 2,2-dinitropropyl acrylate (DNPA). This monomer is of greater interest than the 2,2-dinitrobutyl acrylate studied in the preceding quarter because of its higher specific impulse. The technique in working with this monomer follows the pattern of much past experience obtained in the study of 2,2-dinitrobutyl acrylate.*

(2) The emulsion polymerization of 2,2-dinitropropyl acrylate in bottles was developed to the point of giving consistent yields of 90% in 5 hr reaction time at 60°C. The recipe used had been fixed on the basis of much earlier work with dinitrobutyl acrylate.** Product emulsions were smooth and relatively permanent; molecular weights of the polymer were estimated at 50,000 to 100,000. This process is considered ready for scale-up to operation in pilot plant mixers.

(3) When the requirement of fast conversion is balanced against adequate molecular weight, the optimum temperature for the polymerization appears to lie near 60°C. Some runs were performed at 45°C, giving inconveniently slow conversions. On the other hand, a series of polymerizations conducted in a reaction flask at refluxing water temperature gave polymers of such low quality that they were largely dissolved away by the solvents used in working them up.

(4) Monomer purity is critical for the success of the process. Small amounts of an unknown contaminant which usually can be removed by distillation act as a retarder. A good criterion of purity is the molecular weight of a control sample of bulk polymer prepared from the monomer under standard conditions, using 0.2% azo catalyst at 50°C. Following this criterion, "good" monomers, behaving as described above in emulsion polymerization, gave satisfactory bulk polymers, judging from the relative viscosity,

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*Aerojet Reports No. 833, p. 4, No. 807, p. 11, No. 772, p. 4, and No. 637, p. 24.

**Aerojet Report No. 833, p. 4.

$\eta_r$ = 1.8 (1% in acetone). On the other hand, a monomer giving a polymer having a relative viscosity of $\eta_r$ = 1.2 (1% in acetone), behaved very poorly in the emulsion polymerization. Conversions were less than 20% in 5 hr, and the product obtained was poor. It is conceivable that higher purity than is attained in the present "good" monomers may improve the emulsion reaction even further.

(5) Accordingly, to establish the best means of obtaining pure monomer, a number of specimens prepared in various ways were compared by polymerizing small control samples in bulk and measuring the relative viscosities of the resulting polymers. These specimens fall into two groups:

(a) Products from the process of esterification in the presence of sulfuric acid, redistilled twice in a dry, reduced-pressure distillation.

(b) Products from the method of esterification in the presence of polyphosphoric acid, worked up by steam distillation one or more times.

(6) Results show that good specimens are obtainable from either type of esterification when the product is distilled twice, either dry or with steam. Certain specimens from group (b) were distilled only once, and these were all poor except for one which was the last of three cuts, a small fraction of the total distillate. It is concluded that good monomer may be prepared but at the expense of an excessive material loss, either through redistillation or by discarding a large fore-cut. The collected results also show a fair degree of correlation between monomer quality and refractive index; high refractive indices generally indicate good quality.

(7) Furthermore, even a good monomer specimen contained 3 to 4 mole % impurity, according to its melting-temperature curve. The size of this figure encourages the hope that an efficient purification could materially improve the emulsion polymerization process over its present condition.

b. Experimental

(1) Emulsion polymerizations of DNPA were conducted in bottles at 45°C and 60°C by the procedure described in Aerojet Report No. 833. The recipe contained

20 ml monomer
0.25 g polyvinyl alcohol in 20 ml water
1.70 g Atlas Tween 40
0.25 g $(NH_4)_2S_2O_8$ in 2 ml water
3 mg $FeSO_4 \cdot 7H_2O$ in 1 ml water.

Four different monomer specimens were used (Table I). Three of these, specimens I, cut 2, II, and III (identified further in Table II) were "good" monomers;

## TABLE I

## EMULSION POLYMERIZATION OF 2,2-DINITROPROPYL ACRYLATE

| Run | Specimen | Temp. °C | Time hr | % Reacted From Test* | % Reacted From Workup | Appearance of Final Emulsion | Rel. Visc.** |
|---|---|---|---|---|---|---|---|
| | | | Runs in Bottles | | | | |
| 4/30/C | I, cut 2 | 45 | 6 | 60 | 51 | | >1.82 |
| 4/30/D | I, cut 2 | 45 | 6 | 62 | | Smooth, solids cake after several weeks | |
| 5/12/A | I, cut 2 | 60 | 1 | 38 | | Smooth, solids cake after several weeks | |
| 5/12/C | III | 60 | 1 | 45 | 51 | | 1.45 |
| 5/12/D | III | 60 | 1 | 46 | | Smooth, solids cake after several weeks | |
| 6/10/A | II | 60 | 1 | 36 | | | |
| | | | 3 | 74 | | | |
| | | | 5 | 88 | 95 | Smooth | 1.33 |
| 6/10/B | II | 60 | 1 | 41 | | Smooth, slight sep'n of water in several days | |
| | | | 3 | 77 | | | |
| | | | 5 | 92 | | | |
| 6/10/C | III | 60 | 1 | 43 | | | |
| | | | 3 | 76 | | | |
| | | | 5 | 92 | 91 | Smooth | 1.33 |
| 6/10/D | IV | 60 | 1 | 4 | | Smooth, fluid, marked sep'n of water in several days | |
| | | | 3 | 17 | | | |
| | | | 5 | 18 | | | |
| 6/10/E | IV | 60 | 1 | 5 | | Smooth, fluid | |
| | | | 3 | 9 | | | |
| | | | 5 | 18 | | | |
| 6/11/A | II + 5 mg methylene | 60 | 1 | 36 | | | |
| | | | 3 | 83 | | | |
| | | | 5 | 94 | 93 | Smooth | 1.25 |
| | | | Runs in Reaction Flask | | | | |
| 5/14/B | III | Reflux. water | 1/2 | -- | Small | Uneven | |
| 5/14/A | III | Reflux. water | 1 | -- | 5 | Uneven | 1.12 |
| 5/14/C | III | Reflux. water | 2 | -- | 12 | Uneven | 1.11 |

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*Aliquot samples removed and the polymer precipitated.

**1 g polymer dissolved to 100 ml with acetone, run at 25°C.

the fourth, specimen IV, was a "poor" monomer. In addition, one reaction was performed with 5 mg methylene blue added to Monomer II, to ascertain whether this inhibitor, which is carried over to the monomer in traces by vacuum steam distillation, has any noticeable effect on the emulsion polymerization. The results appear in Table I.

(2) For comparison, a series of plots of the percent monomer reacted with time, all performed at 60°C with sampling at the same time intervals, is depicted in Figure 1. Plots are given for two good monomers, for one poor monomer, and for the good monomer with added methylene blue.

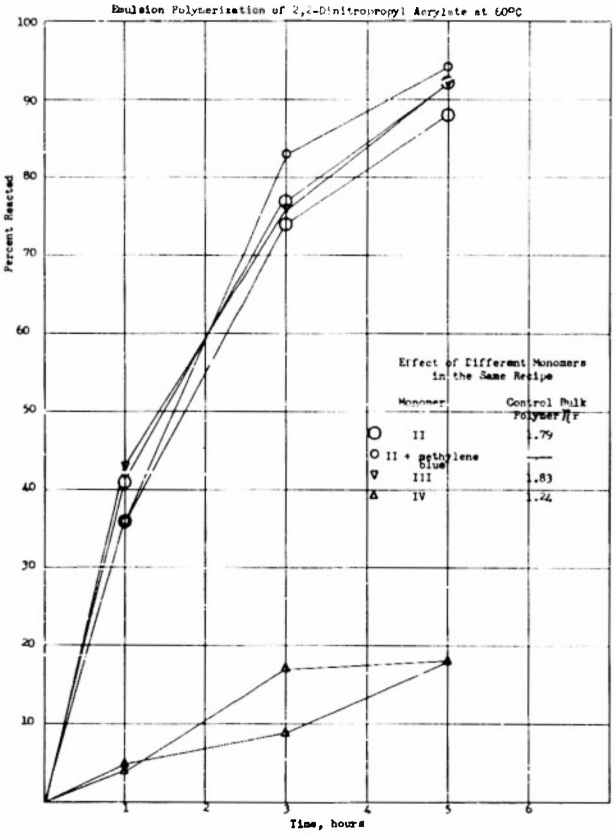

Figure 1

(3) Using the same recipe, three polymerizations were performed in a 100-ml reaction flask heated to refluxing water temperature. Nitrogen was bubbled continuously through the reaction mixture, which was also stirred electrically. The emulsions were worked up by the standard procedure; a large loss of low-molecular-weight polymer into the solvents was observed. Results of these reactions are also given in Table I.

(4) A comparative study was made of monomer specimens prepared in different ways. The criterion of quality adopted was the relative viscosity of polymer prepared from the monomer under standard conditions of a bulk polymerization. In this preparation, 10 g monomer was catalyzed with 0.2% azo bis-isobutyronitrile, then allowed to react at 50°C for at least 80 min. The reaction product was poured into 200 ml of methanol containing a few milligrams of hydroquinone. The precipitated polymer was washed, redissolved in a few milliliters of acetone, reprecipitated from 20 volumes of hexane, and dried. One gram of dried polymer was dissolved with acetone to 100 ml, and the relative viscosity of the solution was measured.

(5) Table II lists the monomers studied in this way, with the types of reaction and workup used in preparing them. Refractive indices are also shown, although their value is to some extent vitiated by the incomplete drying of the steam-distilled specimens. All monomers following Number III also contain methylene blue, added to the charge before distillation and carried over in part into the product. A melting-temperature curve obtained by the Smit method was also obtained on Specimen II. Using an estimated heat of fusion, analysis gave 3.4 mole % impurity.

## 2. Emulsion Polymerization of 2,2-Dinitrobutyl Acrylate

### a. Discussion

(1) A few additional preparations of polydinitrobutyl acrylate (DNBA) were also made, supplementing those described in Aerojet Report No. 833. These showed that the substitution of $K_2S_2O_8$ for $(NH_4)_2S_2O_8$ in otherwise identical recipes gave inferior conversion. They also provide additional evidence that the polymerization reactions vary in conversion rate, molecular weight of product, or quality of emulsion, from one specimen of monomer to another.

(2) A further example of the variability of monomer specimens is provided by the molecular weights of polymer from two different specimens of dinitrobutyl acrylate polymerized in bulk under the same carefully regulated conditions.* Relative viscosities of polymers from the first specimen averaged 1.67, with very slight variations, for about 20 samples prepared using several catalyst concentrations. Relative viscosities of four polymers from the second specimen have now been determined as 1.42, 1.49, 1.49, 1.49. This effect would be expected from the presence, to a greater or less extent, of a retarder, as with dinitropropyl acrylate.

### b. Experimental

(1) Emulsion polymerizations of DNBA were performed in bottles, using the techniques already described. Results appear in Table III.

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*Aerojet Report No. 807.

TABLE II

CHARACTERIZATION OF 2,2-DINITROPROPYL ACRYLATE MONOMERS
Polymerized with 0.2 wt% Azo Catalyst at 50°C

| Specimen | Reaction | Workup | Wt Prod., g | Monomer $n_D^{25}$ | Polymeriz. time, min | Polymer Yield, % | Polymer $\eta_r$* |
|---|---|---|---|---|---|---|---|
| I, Cut 1<br>2<br>3 | Old (using $H_2SO_4$) | 2 Dry dist. | | | | | |
| II | Old (using $H_2SO_4$) | 2 Dry dist. | | 1.4585 | 140 | 22 | 1.79 |
| II, Saturated with $H_2O$ | | | | -- | 140 | 20 | 1.82 |
| III | Old (using $H_2SO_4$) | Dry dist. plus steam dist. | | 1.4585 | 90 | 11 | 1.83 |
| IV | New (using poly-phosphoric acid) | Steam dist. | 624 | 1.4562 | 90<br>1060<br>4176 | 9<br>45<br>43 | 1.24<br>1.18<br>1.26 |
| V | | Steam dist. | 510 | 1.4585 | 90<br>4173 | 9<br>54 | 1.47<br>1.35 |
| VI | | Same; head changed | 826 | 1.4554 | 92 | 11 | 1.26 |
| VII, Fore | | Same; head changed | | | | | |
| Center | | | 342 | 1.4561 | 96 | 9 | 1.33 |
| End | | | 338 | 1.4588 | 90 | 15 | 2.00 |
| VII A | | Same; head changed | 15 | 1.4556 | 91 | 6 | 1.49 |
| Center B | | | 98 | 1.4578 | 85 | 8 | 1.59 |
| Redist. C | | | 58 | 1.4585 | ca. 85 | 8 | 1.72 |
| VIII | | Same; head changed | 640 | 1.4578 | 83 | 7 | 1.33 |
| IX 1 | | Steam redist. of prod. like VI, etc. | 249 | 1.4578 | 80 | 13 | 1.67 |
| 2 | | | 232 | 1.4580 | 81 | 10 | 1.83 |
| X 1 | | Steam redist. of VI | 198 | 1.4578 | 85 | 9 | 1.79 |
| 2 | | | 176 | 1.4585 | 86 | 9 | 1.74 |
| XI 1 | | Steam redist. of IV + V | 257 | 1.4581 | 91 | 10 | 1.64 |
| 2 | | | 244 | 1.4588 | 92 | 13 | 1.71 |

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*1 g polymer diluted to 100 ml with acetone, run at 25°C.

### TABLE III

### EMULSION POLYMERIZATIONS OF 2,2-DINITROBUTYL ACRYLATE

| Run | Monomer Specimen | Temp. °C | Time hr | % Reacted From Test | % Reacted From Workup | Appearance of Final Emulsion | Rel. Visc.* | M.W.** |
|---|---|---|---|---|---|---|---|---|
| 4/22/E | C | 45 | 3-1/2<br>6-1/2 | 49<br>71 | | Smooth, but polymer and water separating | | |
| 4/22/F | C | 45 | 3-1/2<br>6-1/2 | 45<br>76 | | Smooth, but polymer and water separating | | |
| 5/12/E | A | 60 | 1 | 33 | 33 | | 1.27 | 80,000 |
| 5/12/F | A | 60 | 1 | 40 | | Smooth, solids cake after several weeks | | |
| 4/30/A | A | 45 | 6 | 45 | | | | |

($K_2S_2O_8$ substituted for $(NH_4)_2S_2O_8$)

*For 1 g/100 ml acetone solution at 25°C.

**From equation in Aerojet Report No. 833.

(2) The following monomers were used in this work:

DNBA A: Product, hexane-washed, then vacuum distilled, $n_D^{25}$ = 1.4582. Impurity by Smit method = 2.2 mole %.

DNBA C: Similar preparation, $n_D^{25}$ = 1.4589.

3. Copolymers of 2,2-Dinitropropyl Acrylate and Acrylic Acid

a. Discussion

(1) The copolymerization of 2,2-dinitropropyl acrylate (DNPA) and acrylic acid was investigated with the aim of making copolymers of

predetermined composition for studies of vulcanization. The relation of polymer composition to the composition of the monomeric mixture is most conveniently established by evaluating reactivity ratios. Monomer reactivity ratios, $r_1$ and $r_2$, are defined by

$$r_1 = k_{11}/k_{12}$$
$$r_2 = k_{22}/k_{21}$$

in which the k's represent the constants of propagation shown below:

$k_{11}$ for AA radical + AA monomer

$k_{12}$ for AA radical + DNPA monomer

$k_{21}$ for DNPA radical + AA monomer

$k_{22}$ for DNPA radical + DNPA monomer

The reactivity ratios are related to the ratio of concentrations of the two monomers, $M_1/M_2$, as follows:

$$\frac{dM_1}{dM_2} = \frac{M_1}{M_2} \cdot \frac{r_1 M_1 + M_2}{r_2 M_2 + M_1} = \frac{M_1}{M_2} \cdot \frac{r_1 \frac{M_1}{M_2} + 1}{r_2 + \frac{M_1}{M_2}} \qquad (1)$$

in which $dM_1/dM_2$ is the instantaneous molar ratio of monomers reacting to form polymer.

(2) As pointed out by Mayo and Lewis,[*] Equation (1) rearranges to

$$r_2 = \frac{M_1}{M_2}\left[\frac{dM_2}{dM_1}\left(1 + \frac{M_1}{M_2} r_1\right) - 1\right] \qquad (2)$$

Fortunately, the behavior of this particular system is such that monomer composition does not change substantially even for appreciable extents of polymerization; hence this differential equation may be employed (with $\Delta M_2/\Delta M_1$, the average molar ratio, substituted for $dM_2/dM_1$) instead of the much more complex integral equation.

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[*] F. R. Mayo and F. M. Lewis: J. Am. Chem. Soc. 66, 1594-1601 (1944).

(3) From this equation, each set of values may be represented by a straight line relating $r_2$ to $r_1$. Then in theory the sets form a family of lines whose intersection represents the correct values of $r_2$ and $r_1$ for the system.

(4) In the present system, five pairs of values of $M_1/M_2$ and $\Delta M_1/\Delta M_2$ were determined, and a line was drawn for each pair. The three lines which are best established by reason of agreement of duplicate or triplicate analyses of polymer were found to approach closely a common point of intersection at

$$r_1 = 1.03; \; r_2 = 1.07$$

The experimental data were also examined on a plot of mole percent acrylic acid in polymer vs mole percent acrylic acid in the monomer mixture. On this plot also, the line determined by these reactivity ratios is a good mean representation of all the points.

(5) It is recognized that no other monomer pair is known in which both $r_1$ and $r_2$ exceed unity.* Probably the true value of one or both is less than unity in this case, but there is some small error due to the use of only five sets of values. In any case, these values appear to be good enough for predetermining copolymer compositions.

(6) On the basis of these results, a 335-g batch of 2,2-dinitropropyl acrylate polymer containing 20.5 mole % acrylic acid was prepared for vulcanization studies.

b. Experimental

(1) Using steam-distilled DNPA monomer II or III (see Table I) and acrylic acid freshly distilled from inhibitor at reduced pressure, a 20 to 30-g mixture of the two monomers was made up and catalyzed with 0.5 wt % azo catalyst. The catalyzed mixture was divided among two or three test tubes; each was purged with nitrogen, stoppered, and placed in a bath set at 50°C. The test tubes were removed at different times, and polymer was separated immediately after removal.

(2) The polymer was separated by pouring the reaction mixture into 200 ml methanol containing a little hydroquinone, using a few ml of acetone to aid in the transfer. (For polymers of high acid content, which proved to be soluble in pure methanol, it was necessary to precipitate in methanol containing 20 vol % water.) The precipitated solids were separated from the liquid, redissolved in 10 to 20 ml acetone, precipitated from 20

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*T. Alfrey, Jr., T. J. Bohrer. and H. Mark, "Copolymerization," p. 10.

volumes of hexane, and then thoroughly dried and weighed. The dried polymer was analyzed by potentiometric titration of an acetone solution with standard base to a pH of 9.8. This method gives clearly defined values if the titration is performed slowly.

(3) Results for five different monomer mixtures are given in Table IV, with values of $M_1/M_2$ and $\Delta M_1/\Delta M_2$ appearing in the last two columns. By substituting these values in Equation (2) a family of values relating $r_1$ and $r_2$ was obtained. These values are plotted on Figure 2. Three of the lines, representing mixtures 2, 3, and 4, approached closely a common point of intersection at

$$r_1 = 1.03; \; r_2 = 1.07$$

The other two lines, less well established, pass a little farther from this point. The values are also plotted as mole % AA in polymer against mole % AA in monomer in Figure 3.

## TABLE IV

COPOLYMERIZATION OF 2,2-DINITROPROPYL ACRYLATE WITH ACRYLIC ACID AT 50°C

Using 0.5 wt % Azo Catalyst

| Mixture | Mole % AA in Orig. Mixt. | Reaction Time min | Precipitating Solvent | Wt % Conv. | Polymer Mole % AA | Av $M_1/M_2$ | Av $\Delta M_1/\Delta M_2$ |
|---|---|---|---|---|---|---|---|
| 1 | 22.8 | 45 | Methanol | 15 | 16.4 | 0.301 | 0.228 |
| | | 80 | | 23 | -- | | |
| | | 100 | | 29 | 20.6 | | |
| 2 | 7.3 | 60 | Methanol | 11 | 6.8 | 0.079 | 0.0735 |
| | | 75 | | 19 | 7.2 | | |
| | | 90 | | 22 | 6.5 | | |
| 3 | 34.0 | 84 | Methanol | 26 | 33.2 | 0.518 | 0.497 |
| | | -- | | 24 | 33.1 | | |
| 4 | 40.2 | 80 | 80 vol methanol | 26 | 39.3 | 0.676 | 0.652 |
| | | 80 | 20 vol water | 28 | 39.5 | | |
| 5 | 19.5 | 33 | 80 vol methanol | 8 | 18.3 | 0.243 | 0.243 |
| | | 37 | 20 vol water | 10 | 20.8 | | |

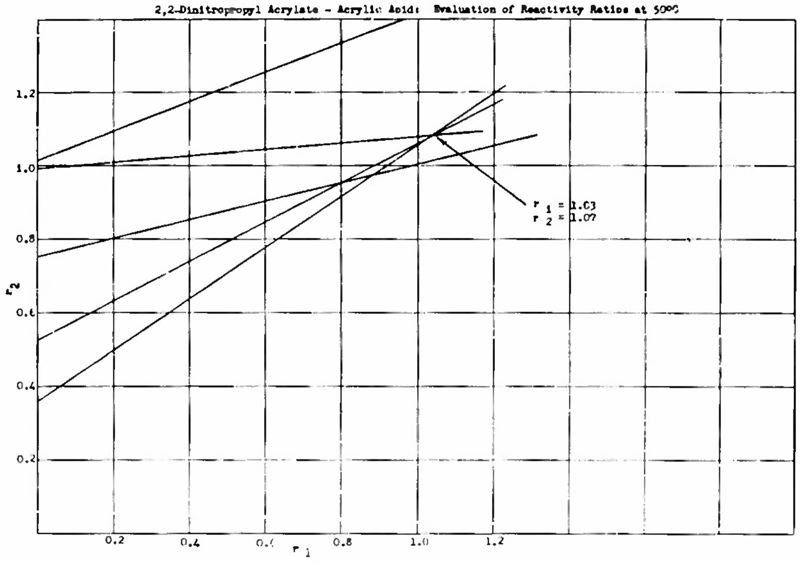

Figure 2

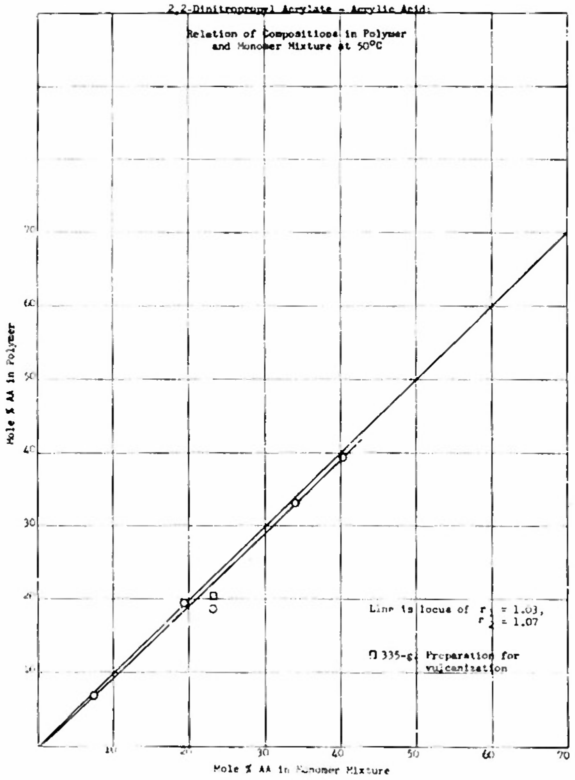

Figure 3

(4) To prepare a larger quantity of this copolymer for subsequent vulcanization, 47.0 g AA and 470.3 g DNPA were catalyzed with 0.5% azo catalyst. (The DNPA monomer was a composite of several "good" specimens described in Table II. In the control test, it gave polymer of 1.82 relative viscosity.) The reaction mixture was divided among five test tubes, and polymerized for 23 hr. The mixtures were then added to methanol containing 20 vol % water to precipitate the polymer, which was worked up in the usual way. The final product weighed 335 g, and analyzed 20.5 mole % AA in duplicate tests.

(5) The mathematical treatment described above is not strictly applicable here because the value of $M_1/M_2$ "drifts" as the reaction proceeds to completion. Nevertheless, a plot on Figure 3 of mole % AA in polymer, 20.5, against average mole % AA in monomer, 23.5, agrees fairly well with the line established by the reactivity ratios.

## 4. Copolymers of 2,2-Dinitropropyl Acrylate and Ethylene Glycol Diacrylate

### a. Discussion

(1) The copolymerization of 2,2-dinitropropyl acrylate with small amounts of divinyl monomers is also of interest because of the structural permanence of the resulting gel. The situation in which gelation occurs near the end of the polymerization is of particular interest. Accordingly, some bulk copolymerizations were performed with ethylene glycol diacrylate at various compositions, using the insolubility of the resulting polymer as the criterion of gelation. The results showed that in a monomer mixture containing about 0.2 wt % diacrylate the reaction has largely proceeded to completion at the onset of gelation.

### b. Experimental

(1) Mixtures of dinitropropyl acrylate with small amounts of ethylene glycol diacrylate were polymerized in bulk at 50°C, with either 0.2% or 0.5% azo catalyst. The reaction was stopped after a timed interval in each case, and the reaction mixture was transferred to 200 ml methanol containing a little hydroquinone. The precipitated solid was worked up in the same way as the acrylic acid copolymer to determine the yield, when possible. In any event, the solubility of the polymer in acetone was noted. Results of this work are summarized in Table V. The dinitropropyl acrylate used was Specimen II (Table II); the ethylene glycol diacrylate was a commercial preparation.

## TABLE V

## 2,2-DINITROPROPYL ACRYLATE AND ETHYLENE GYLCOL DIACRYLATE COPOLYMERS

Prepared in Bulk at 50°C with Azo Catalyst

| Monomer wt % EGDA | Catalyst Conc., wt % | Time min | Wt % Reacted | Nature of Polymer |
|---|---|---|---|---|
| 0.19 | 0.2 | 192 | 18 | soluble |
| | | 213 | 9 | soluble |
| | | 233 | 14 | soluble |
| 0.22 | 0.5 | 186 | 61 | just soluble |
| | | 187 | 38 | soluble |
| | | 26 hr | | insoluble |
| 0.25 | 0.2 | 60 | 8 | soluble |
| 0.39 | 0.2 | 60 | 8 | soluble |
| 0.67 | 0.2 | 156 | 17 | soluble |
| | | 218 | | insoluble |
| | | - | 19 | insoluble |
| 0.99 | 0.2 | 60 | 7 | soluble |
| 1.97 | 0.2 | 86 | 5 | soluble |
| | | 111 | 10 | just soluble |
| | | 146 | | insoluble |
| 3.43 | 0.2 | 60 | 8 | soluble |
| 4.60 | 0.2 | 45 | | soluble |
| | | 73 | 3 | soluble |
| | | 90 | | insoluble |

## B. ADDITION AND CONDENSATION POLYMERS

### 1. Polyurethanes

#### a. Kinetic Studies

#### (1) Introduction

(a) It has been observed that ferric acetyl acetonate is decomposed in the presence of an isocyanate and inorganic salt.[*] Thus, it has become necessary to search for other polymerization catalysts that are more stable in the presence of salts. It is well known that urethane formation is base-catalyzed, tertiary amines being specially effective.[**] Therefore, the use of triethylamine as a catalyst for nitropolyurethane formation has been studied.

(b) A new diisocyanate, 2,5-dinitraza-1,6-hexane diisocyanate, became available in sufficient quantity and purity for kinetic studies and polymerizations during this period.[***] It has been assigned the Roman numeral XVI for convenience.[****]

#### (2) Discussion

(a) Early in the nitropolymer program the use of triethylamine as a catalyst for nitropolyurethane formation was studied.[*****] It was found that triethylamine catalyzed the polymerization but also caused some decomposition of the 3,3-dinitro-1,5-pentane diisocyanate (I). 3-Nitraza-1,5-pentane diisocyanate (XIII) and 2-nitro-2-methyl-1,3-propanediol (J) are stable in the presence of triethylamine; hence, the XIII-J system was used for the present rate study.

(b) A dioxan solution of XIII-J containing 1 eq/liter of each monomer was divided into 5 portions. One was kept as control, one was catalyzed with $1 \times 10^{-5}$ mole/liter ferric acetylacetonate, and the other three with triethylamine at concentrations of $1 \times 10^{-1}$, $1 \times 10^{-2}$, and $1 \times 10^{-3}$ mole/liter. The experimental results are summarized in Table VI and Figures 4 and 5. The rate of reaction using $1 \times 10^{-1}$ mole/liter triethylamine was too rapid for accurate measurement. The observed rate in the

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[*] This report, Section II,B,2.

[**] Tarbell, Mallatt, and Wilson, J. Am. Chem. Soc. 64, 2229 (1942); Baker et al., J. Chem. Soc. (1947) 713-726; (1949) 9-31.

[***] Aerojet Report No. 833, p. 45.

[****] Aerojet Report No. 772, Appendix B.

[*****] Aerojet Report No. 482, p. 42.

## TABLE VI

### RATE OF POLYMERIZATION OF POLYURETHANE XIII-J USING TRIETHYLAMINE CATALYST

Initial Concentration: 1 eq/liter (-OH) and (-NCO) in dioxan
Temperature: 50°C

| | Degree of Polymerization | | | | |
|---|---|---|---|---|---|
| Elapsed Time, hr | Control No Catalyst | FeAA* $1 \times 10^{-5}$ mole/liter | Triethylamine $1 \times 10^{-1}$ mole/liter | Triethylamine $1 \times 10^{-2}$ mole/liter | Triethylamine $1 \times 10^{-3}$ mole/liter |
| 0 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| 0.5 | — | 1.01 | 20 | 2.74 | 1.18 |
| 1.0 | — | 1.02 | 40 | 4.39 | 1.34 |
| 2.0 | — | — | — | 8.40 | 1.70 |
| 3.0 | — | 1.04 | — | 12.70 | 2.07 |
| 4.5 | 1.01 | 1.05 | — | 20.0 | 2.68 |
| $k_{35^\circ}$ liter/eq hr = | 0.002 | 0.013<br>(0.35)** | Approximately 40 | 3.8 | 0.35 |
| Comparative rates, | 1 | 6.5<br>(175)** | 20,000 | 1900 | 175 |

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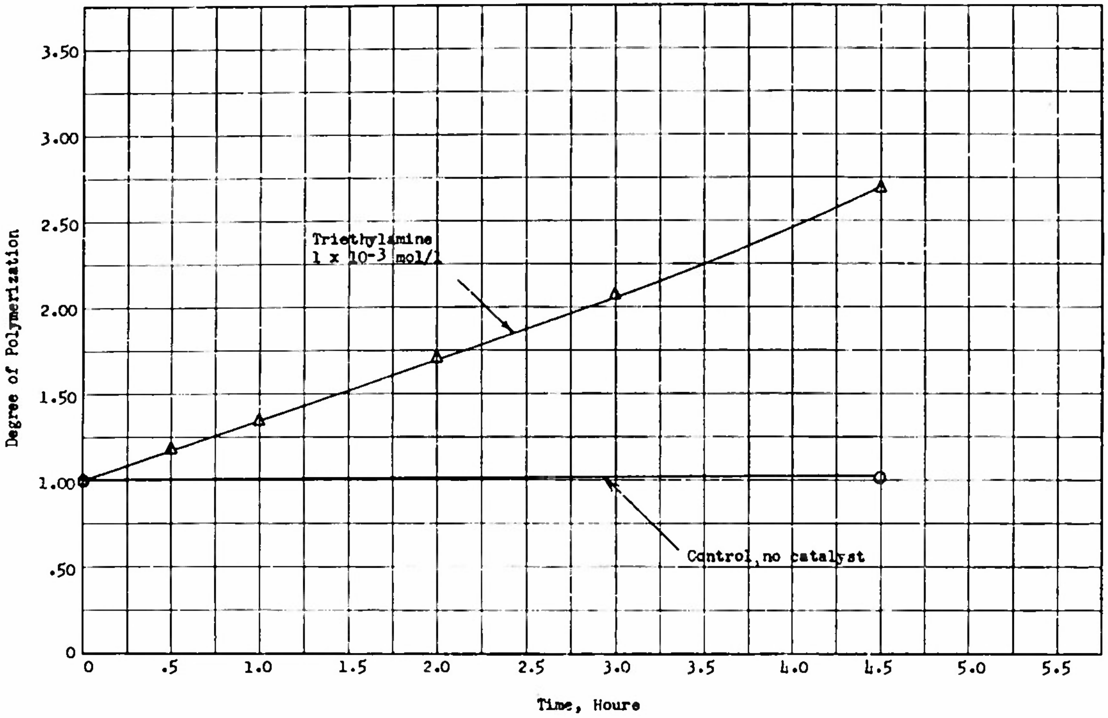
*Ferric acetylacetonate.

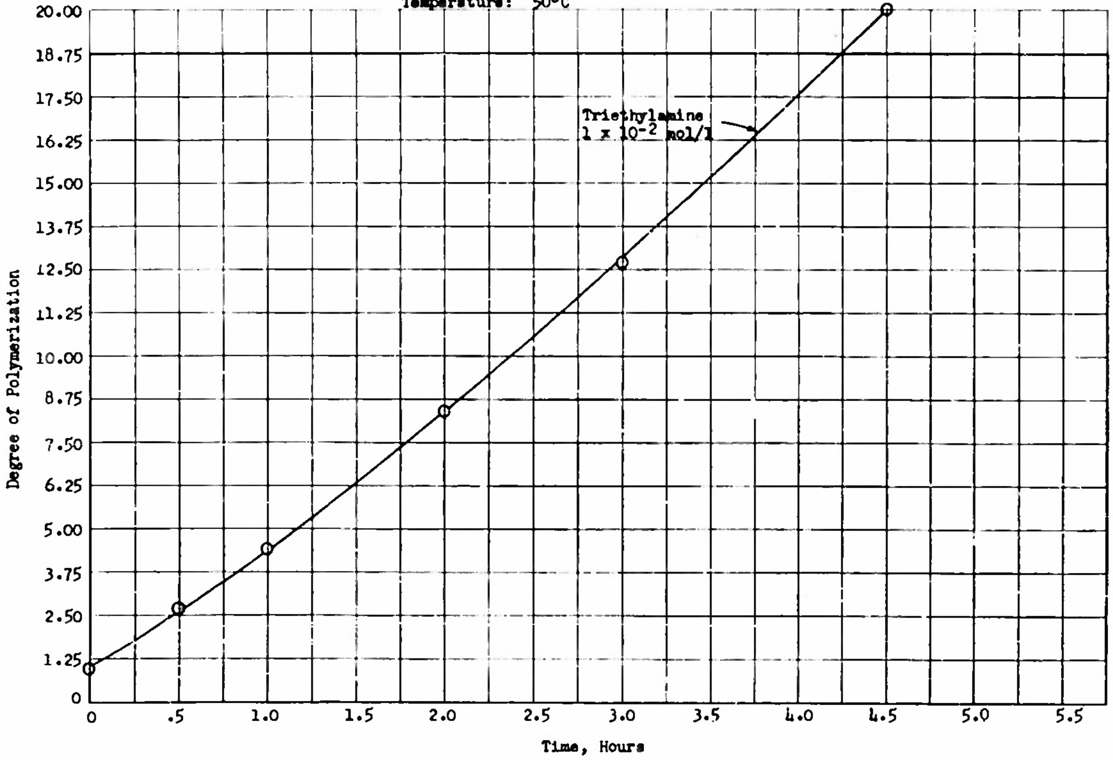
**Aerojet Report No. 740, p. 8.



Rate of Polymerization of Polyurethane XIII-J Using Triethylamine Catalyst

Initial Concentration: 1 eq/liter (-OH) and (-NCO) in dioxan
Temperature: 50°C

Figure 4



Rate of Polymerization of Polyurethane XIII-J Using Triethylamine Catalyst

Initial Concentration: 1 eq/liter (-OH) and (-NCO) in dioxan
Temperature: 50°C

Figure 5

ferric-acetylacetonate-catalyzed run was much lower than that of an identical earlier run in which the rate constant was $k_{50°C}$ = 0.35 liter/eq. hr.[*] Apparently a portion of the iron catalyst was destroyed by impurities in the monomers. The three triethylamine runs indicate that the catalytic effect is directly proportional to catalyst concentration. The solutions did not become discolored, evolve gas, or give any other indication of decomposition.

(c) The rate study with the new XVI diisocyanate, 2,5-dinitraza-1,6-hexane diisocyanate, was made using J diol, 2-nitro-2-methyl-1,3-propanediol. Ferric acetylacetonate catalyst was used at two levels, 1 x $10^{-4}$ and 1 x $10^{-5}$ mole/liter in dioxan solution. The initial monomer concentration was 1 eq./liter. At 1 x $10^{-4}$ mole/liter catalyst concentration the rate was much too fast to measure accurately. At 1 x $10^{-5}$ mole/liter catalyst concentration a straight line was not obtained in a plot of degree of polymerization vs time. The initial rapid rate became much slower after 1 hr. From the slope of the curve after 1 hr a rate constant of $k_{50°}$ = 0.7 liter/eq. hr was obtained. The experimental results are summarized in Tables VII and VIII and Figure 6.

(d) The stability of the 2,5-dinitraza-1,6-diisocyanate in various solvents at 50°C was determined in the usual manner.[**] The experimental results are shown in Table IX.

## TABLE VII

### RATE OF POLYMERIZATION OF POLYURETHANE XVI-J USING FERRIC ACETYLACETONATE CATALYST

Initial Concentration: 1 eq./liter (-OH) and (-NCO) in Dioxan
Temperature: 50°C

| | Degree of Polymerization | |
|---|---|---|
| Elapsed Time hr | Ferric Acetylacetonate 1 x $10^{-4}$ mole/liter | Ferric Acetylacetonate 1 x $10^{-5}$ mole/liter |
| 0 | 1.00 | 1.00 |
| 0.5 | | 2.98 |
| 0.75 | 44 | — |
| 2.0 | | 4.59 |
| 3.0 | | 5.32 |
| 4.0 | | 6.00 |
| $k_{50°}$ liter/eq. hr = | — | 0.7 |

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

[**] Aerojet Reports No. 712, p. 9 and No. 740, p. 9.

## TABLE VIII

### COMPARISON OF NITRO DIISOCYANATE REACTIVITIES WITH 2-NITRO-2-METHYL-1,3-PROPANEDIOL

Initial Concentration: 1 eq./liter (-OH) and (-NCO) in Dioxan
1 x $10^{-5}$ mole/liter Ferric Acetylacetonate
Temperature: 50°C

| Code Number | Diisocyanate | $k_{50^o}$ liter/eq. hr | Relative Rate | Reference |
|---|---|---|---|---|
| I | 3,3-Dinitro-1,5-pentane | 4.3 | 215 | Aerojet Report No. 712, p. 7 |
| XII | 3,6-Dinitraza-1,8-octane | 0.02 | 1 | Aerojet Report No. 712, p. 10 |
| XIII | 3-Nitraza-1,5-pentane | 0.35 | 18 | Aerojet Report No. 740, p. 8 |
| XV | 2-Nitraza-1,4-butane | 2.0 | 100 | Aerojet Report No. 807, p. 14 |
| XVI | 2,5-Dinitraza-1,6-hexane | 0.7 | 35 | This report |

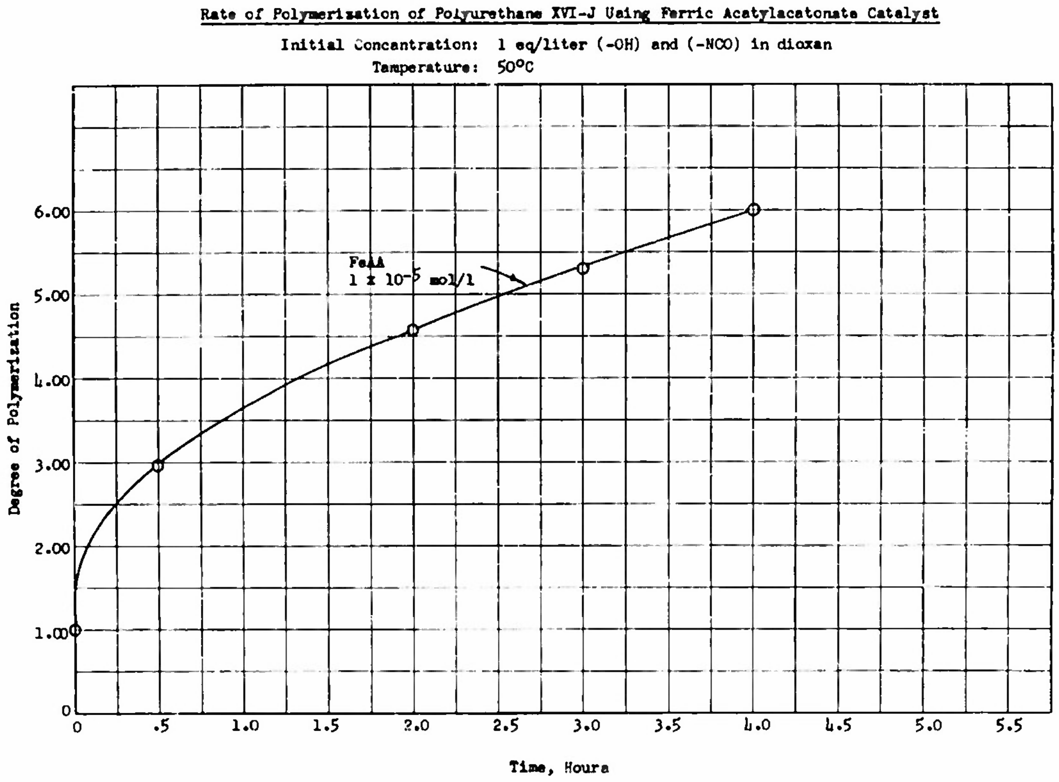

Figure 6

## TABLE IX

## RATE OF LOSS OF 2,5-DINITRAZA-1,6-HEXANE DIISOCYANATE IN VARIOUS SOLVENTS AT 50°C

| | Total Equivalents (-NCO) Present | | | |
|---|---|---|---|---|
| Elapsed Time hr | Dioxan Solution | γ-Butyrolactone Solution | Acetone Solution | Dimethylformamide Solution |
| 0 | 0.100 | 0.100 | 0.100 | 0.100 |
| 1 | 0.995 | 0.998 | 0.984 | 0.865 |
| 2 | 0.983 | — | — | 0.798 |
| 18 | — | 0.965 | 0.831 | — |
| 20 | 0.888 | — | — | 0.174 |
| 43 | 0.825 | — | — | — |
| 96 | -- | 0.935 | — | — |
| 121 | 0.710 | -- | — | — |

### (e) Conclusions

Triethylamine can be used as a catalyst for the formation of Polyurethane XIII-J. A concentration of 1 x $10^{-3}$ mole/liter triethylamine is equivalent to 1 x $10^{-5}$ mole/liter iron acetylacetonate. The new diisocyanate, 2,5-dinitraza-1,6-hexane diisocyanate, reacts rapidly with 2-nitro-2-methyl-1,3-propanediol in the presence of ferric acetylacetonate. The particular batch of diisocyanate used consumed some of the iron catalyst, so that the rate is probably greater than reported. The comparisons shown in Table VIII reveal that the rate previously measured for the XII diisocyanate is unusually low. A re-examination of the experimental rate curves* shows a striking resemblance to the curve (Figure 6) of the XVI diisocyanate. It is concluded that in both XII-J and XVI-J, impurities in the monomers have consumed a portion of the iron catalyst. Dimethylformamide cannot be used as a polymerization solvent for the XVI-series.

### (f) Experimental, XIII-J

The XIII diisocyanate used assayed 100.0% by the standard analytical method. Approximately 1.0 g of the diisocyanate is added to a standard solution of di-n-butyl amine in absolute dioxan. The excess amine is back titrated to a pH of 4.0 with standard hydrochloric acid. A blank determination is used to establish the normality of the amine solution. This method does not differentiate between (-NCO) and acidic or basic impurities in the diisocyanate. Hence, this particular batch may have contained some acidic impurities which consumed a portion of the ferric acetylacetonate catalyst. The J diol was purified via the isopropylidene derivative.** The dioxan was distilled from sodium, then stored over sodium. The triethylamine was distilled from KOH, bp 89.4°/753 mm. A dioxan solution of the monomers containing 1 eq./liter (-OH) and (-NCO) was divided into five portions, and the appropriate amount of catalyst was added. These solutions were maintained at 50°C and periodically analyzed for (-NCO) by the technique described above.

### (g) Experimental, XVI-J

The XVI-diisocyanate assayed 98.8% by the method described above. The J diol and dioxan were purified as described above. The experimental technique was the same as for XIII-J above. All other solvents were purified by distillation from p,p' diphenylmethane diisocyanate.

## b. New Polyurethanes

### (1) Introduction

(a) During this period a new diisocyanate, 2,5-dinitraza-1,6-hexane diisocyanate,*** became available in sufficient quantity and purity for the preparation of a new series of polymers, which will be designated XVI. The structures and estimated specific-impulse values are listed in Table X.

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*Aerojet Report No. 712, p. 11.

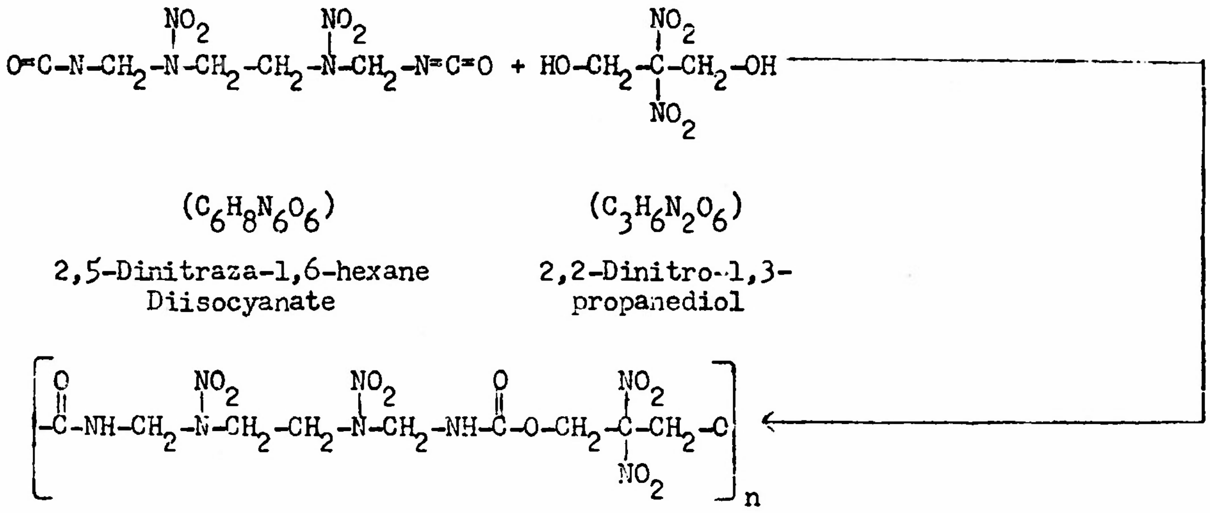
**Aerojet Report No. 686, p. 60.

***Aerojet Report No. 833, p. 45.

## TABLE X

## NEW POLYURETHANES

**Polyurethane XVI-A**



$O{=}C{-}N{-}CH_2{-}\overset{NO_2}{\overset{|}{N}}{-}CH_2{-}CH_2{-}\overset{NO_2}{\overset{|}{N}}{-}CH_2{-}N{=}C{=}O + HO{-}CH_2{-}\overset{NO_2}{\underset{NO_2}{C}}{-}CH_2{-}OH$

$(C_6H_8N_6O_6)$ $(C_3H_6N_2O_6)$

2,5-Dinitraza-1,6-hexane Diisocyanate

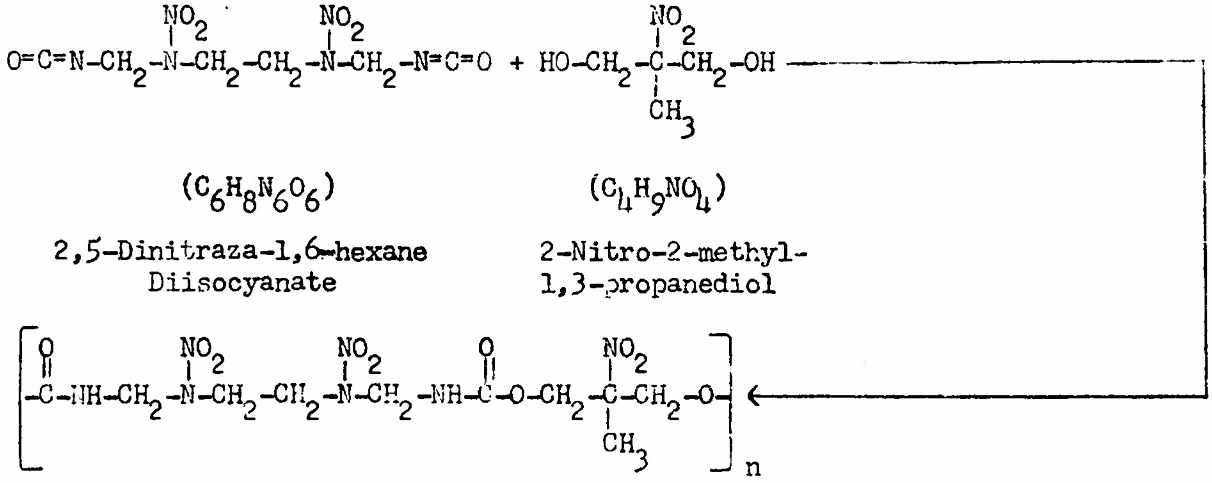
2,2-Dinitro-1,3-propanediol

$\left[\overset{O}{\overset{\|}{C}}{-}NH{-}CH_2{-}\overset{NO_2}{\overset{|}{N}}{-}CH_2{-}CH_2{-}\overset{NO_2}{\overset{|}{N}}{-}CH_2{-}NH{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}\overset{NO_2}{\underset{NO_2}{C}}{-}CH_2{-}O\right]_n$

$(C_9H_{14}N_8O_{12})_n$

Calc'd $I_{sp}$ = 198 lbf sec/lbm

**Polyurethane XVI-J**



$O{=}C{=}N{-}CH_2{-}\overset{NO_2}{\overset{|}{N}}{-}CH_2{-}CH_2{-}\overset{NO_2}{\overset{|}{N}}{-}CH_2{-}N{=}C{=}O + HO{-}CH_2{-}\overset{NO_2}{\underset{CH_3}{C}}{-}CH_2{-}OH$

$(C_6H_8N_6O_6)$ $(C_4H_9NO_4)$

2,5-Dinitraza-1,6-hexane Diisocyanate

2-Nitro-2-methyl-1,3-propanediol

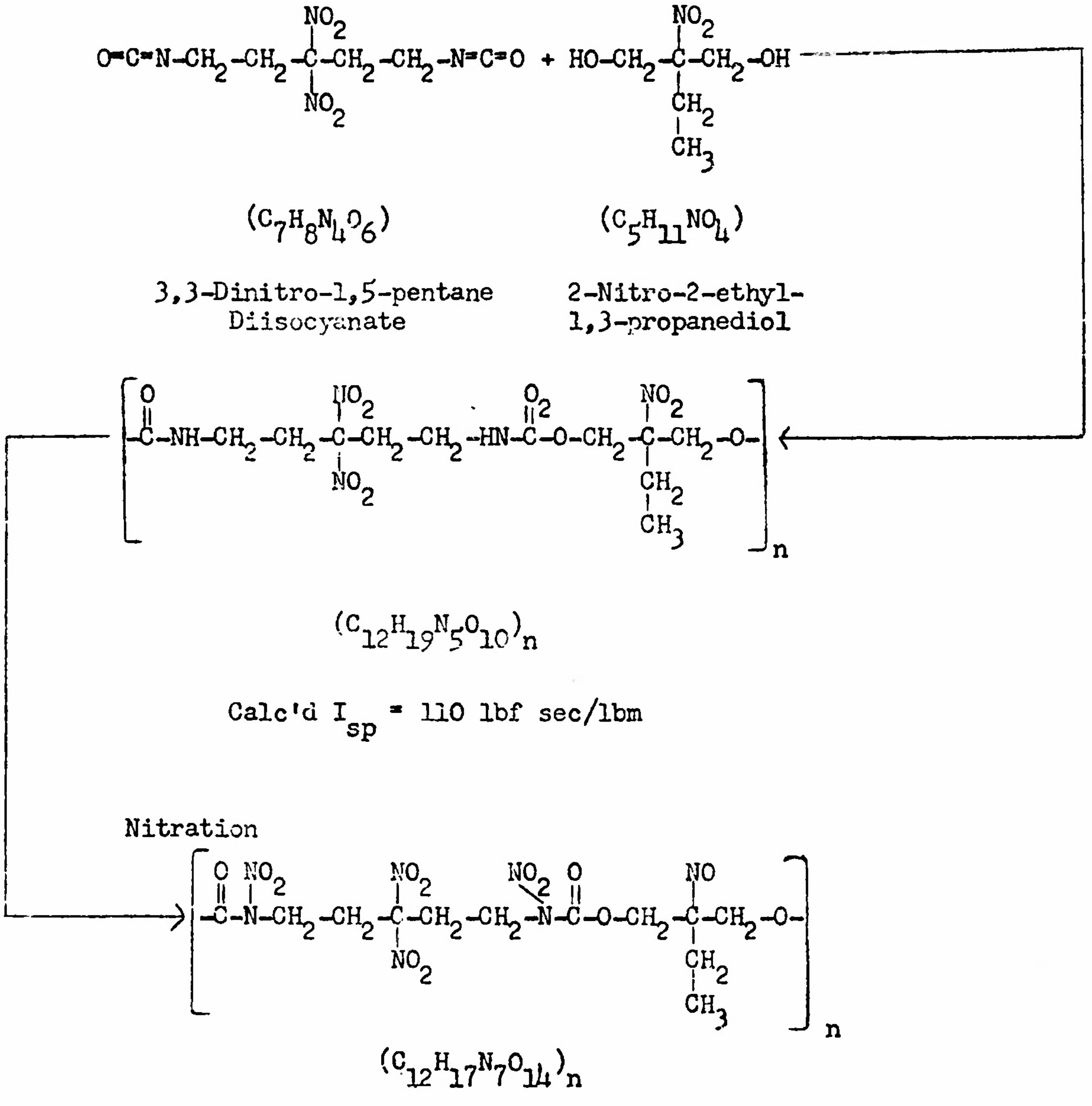
$\left[\overset{O}{\overset{\|}{C}}{-}NH{-}CH_2{-}\overset{NO_2}{\overset{|}{N}}{-}CH_2{-}CH_2{-}\overset{NO_2}{\overset{|}{N}}{-}CH_2{-}NH{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}\overset{NO_2}{\underset{CH_3}{C}}{-}CH_2{-}O\right]_n$

$(C_{10}H_{17}N_7O_{10})_n$

Calc'd $I_{sp}$ = 154 lbf sec/lbm

TABLE X (cont.)

Polyurethane I-C and I-CN



$(C_7H_8N_4O_6)$

3,3-Dinitro-1,5-pentane Diisocyanate

$(C_5H_{11}NO_4)$

2-Nitro-2-ethyl-1,3-propanediol

$(C_{12}H_{19}N_5O_{10})_n$

Calc'd $I_{sp}$ = 110 lbf sec/lbm

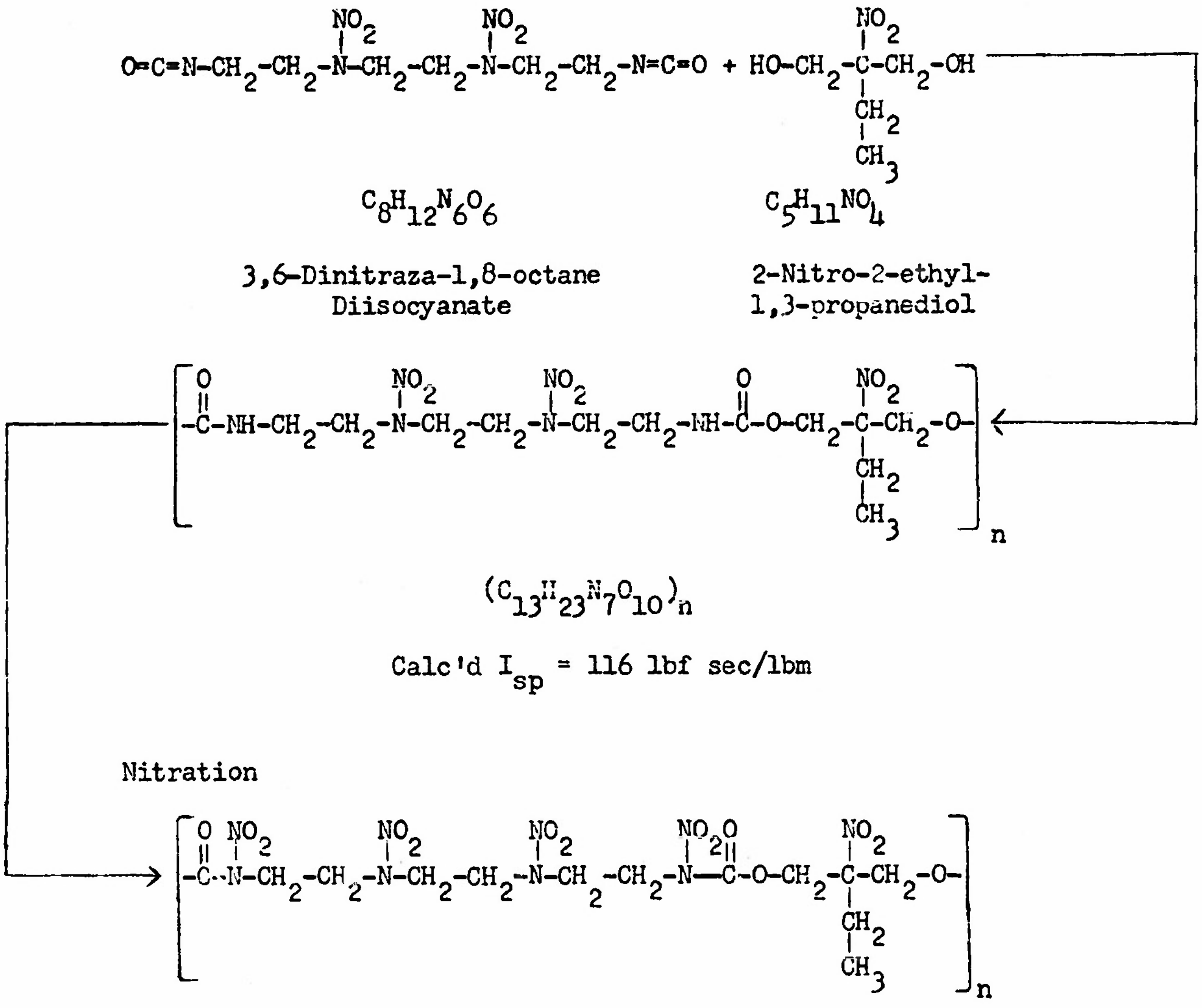
Nitration

$(C_{12}H_{17}N_7O_{14})_n$

Calc'd $I_{sp}$ = 189 lbf sec/lbm

TABLE X (cont.)

**Polyurethanes XII-C and XII-CN:**



$C_8H_{12}N_6O_6$

3,6-Dinitraza-1,8-octane Diisocyanate

$C_5H_{11}NO_4$

2-Nitro-2-ethyl-1,3-propanediol

$(C_{13}H_{23}N_7O_{10})_n$

Calc'd $I_{sp}$ = 116 lbf sec/lbm

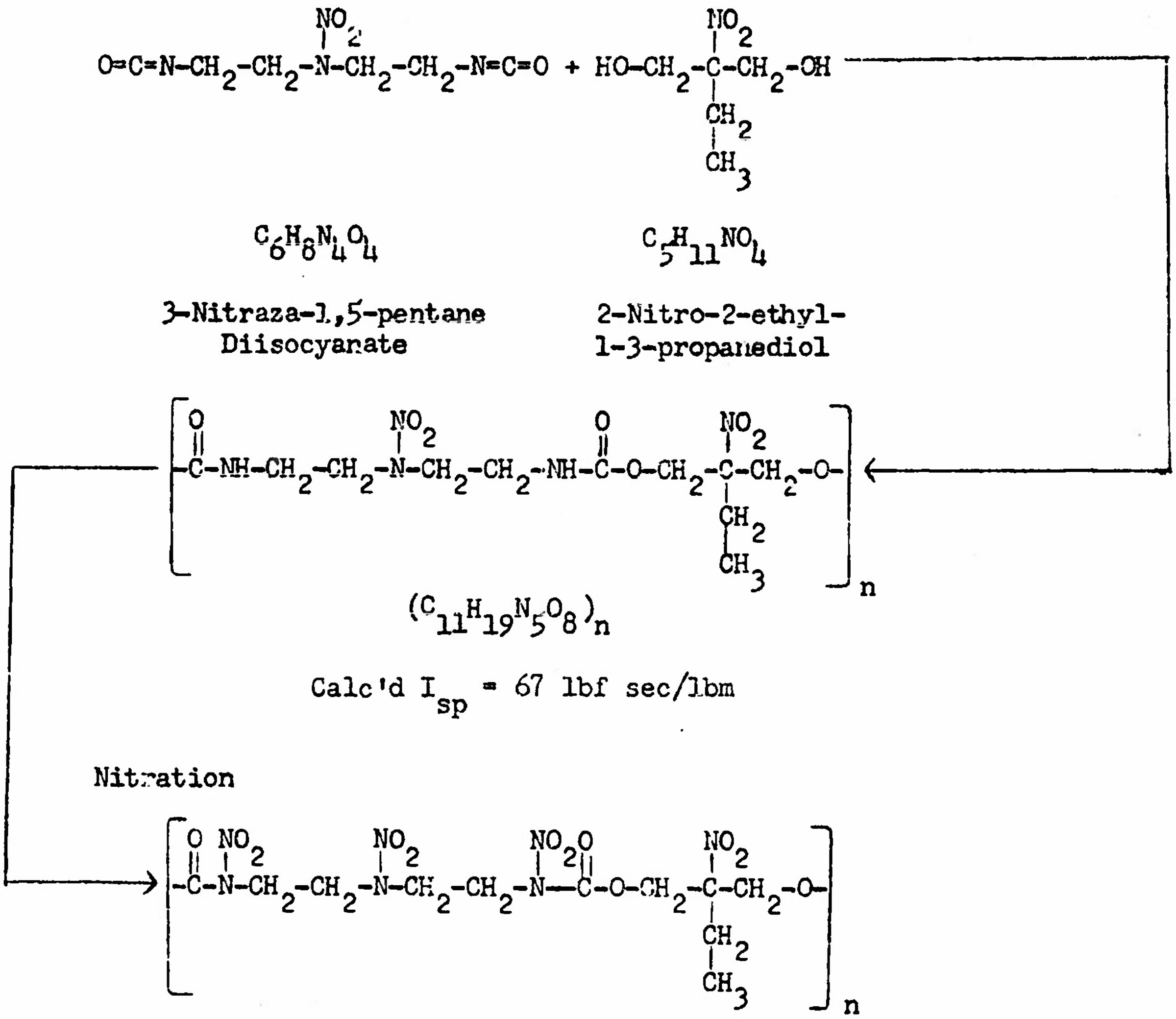
Nitration

$(C_{13}H_{21}N_9O_{14})_n$

Calc'd $I_{sp}$ = 186 lbf sec/lbm

TABLE X (cont.)

Polyurethanes XIII-C and XIII-CN:



$C_6H_8N_4O_4$

3-Nitraza-1,5-pentane Diisocyanate

$C_5H_{11}NO_4$

2-Nitro-2-ethyl-1-3-propanediol

$(C_{11}H_{19}N_5O_8)_n$

Calc'd $I_{sp}$ = 67 lbf sec/lbm

Nitration

$(C_{11}H_{17}N_7O_{12})_n$

Calc'd $I_{sp}$ = 179 lbf sec/lbm

(b) The formulation program now in progress is based on the information obtained from the preparation and physical properties of pure linear nitropolymers.* In the preparation of new polyurethanes an effort is being made to diversify the monomers so that a great variety of products will be available to the formulation program.

(c) During this period a commercially available nitrodiol,** 2-nitro-2-ethyl-1,3-propanediol, was polymerized with available nitro diisocyanates. In accordance with the nomenclature system for condensation polymers, this nitrodiol will be given the code letter C.*** The structures and estimated specific impulse values are shown in Table X.

(2) Preparation of Polyurethane XVI-A from 2,5-Dinitraza-1,6-hexane Diisocyanate and 2,2-Dinitro-1,3-propanediol (JRF-284 and -286)

(a) JRF-284

Equivalent quantities of the monomers, 55 g total weight, were dissolved in 55 ml absolute dioxan. Ferric acetylacetonate, 0.018 g, was added to catalyze polymerization. Heat was evolved and the stirred viscous mass was maintained in the range from 30 to 40°C for 30 min. Suddenly, solid polymer separated from the solution, and within 5 min the slurry could not be stirred. The temperature was maintained at 50°C for 66 hr. The solid polymer was dissolved in acetone, then precipitated by pouring the acetone solution into rapidly stirred ice water. After drying, the product had the following characteristics:

| | |
|---|---|
| Weight: | 52 g = 95% yield |
| Anal. Calc'd for $C_9H_{14}N_8O_{12}$: | %C, 25.35; %H, 3.31; %N, 26.29 |
| Found: | %C, 24.16; %H, 3.02; %N, 24.39 |
| Heat of Combustion Calc'd: | 2663 cal/g |
| Found: | 2806, 2808, 2829, cal/g |
| Relative Viscosity: | $\eta_r'$ = 1.18 (1% in acetone); $\eta_r'$ = 1.31(1% in DMF at 25°C) |
| Stability at 65.5°C, KI-Starch: | 1.5 hr |
| Impact Stability: | >100 cm/2kg |
| Softening Range: | 85 to 95°C |

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*Aerojet Report No. 807, p. 29; No. 833, p. 27.

**Commercial Solvents Corp.

***Aerojet Report No. 772, Appendix C.

(b) JRF-286

The preparation was repeated using acetone as the polymerization solvent. The polymer did not precipitate from solution as in JRF-284 above.

| | |
|---|---|
| Anal. Calc'd for $C_9H_{14}N_8O_{12}$: | %C, 25.36; %H, 3.31; %N, 26.29 |
| Found: | %C, 25.74; %H, 3.67; %N, 25.80 |
| Heat of Combustion Calc'd: | 2663 cal/g |
| Found: | 2767, 2827 cal/g |
| Relative Viscosity: | $\eta_r' = 1.34$ (1% in DMF at 25°C) |
| Stability at 65.5°C, KI-Starch: | 1.5 hr |
| Impact Stability: | 100 cm/2kg |
| Softening Range: | 85 to 95°C |

The poor agreement between the calculated analytical values and those actually obtained requires further study of this promising polymer.

(3) Preparation of Polyurethane XVI-J from 2,5-Dinitraza-1,6-hexane Diisocyanate and 2-Nitro-2-methyl-1,3-propanediol (JRF-282)

Equivalent amounts of the monomers, 46 g total weight, were dissolved in 46 ml absolute dioxan. A total of 0.032 g ferric acetylacetonate was required to give a permanent catalyst color. Heat was evolved, and the solution rapidly increased in viscosity. The reaction temperature was maintained at 50°C for 144 hr. Adjustment of monomer equivalence required the addition of 1% excess diisocyanate. The final solution viscosity was very high. After precipitation and drying the product has the following characteristics:

| | |
|---|---|
| Weight: | 44 g - 95% yield |
| Anal. Calc'd for $C_{10}H_{17}N_7O_{10}$: | %C, 30.38; %H, 4.34; %N, 24.81 |
| Found: | %C, 30.30; %H, 4.47; %N, 25.18 |
| Heat of Combustion Calc'd: | 3314 cal/g |
| Found: | 3274, 3308 cal/g |
| Relative Viscosity: | $\eta_r' = 1.16$ (1% in acetone); $\eta_r' = 1.25$ (1% in dioxan); $\eta_r' = 1.38$ (1% in $\gamma$-butyrolactone); 1.59, DMF at 25°C |
| Stability at 65.5°C, KI-Starch: | 2 hr |
| Impact Stability: | $>$100 cm |
| Softening Range: | 100 to 110°C |

### (4) Preparation of Polyurethane I-C from 3,3-Dinitro-1,5-pentane Diisocyanate and 2-Nitro-2-ethyl-1,3-propanediol (JRF-277)

Equivalent quantities of the monomers, 42 g total weight, were dissolved in 42 ml absolute dioxan. Ferric acetylacetonate, 0.0075 g, was added to catalyze polymerization. After 75 hr at 50°C the product was diluted with acetone and precipitated by pouring into rapidly stirred ice water. The dried product weighed 40 g and had the following characteristics:

| | |
|---|---|
| Anal. Calc'd for $C_{12}H_{19}N_5O_{10}$: | %C, 36.64; %H, 4.87; %N, 17.81 |
| Found: | %C, 37.20; %H, 5.22; %N, 17.67 |
| Heat of Combustion Calc'd: | 3887 cal/g |
| Found: | 3918 cal/g |
| Relative Viscosity: | $\eta_r' = 2.05$ (1% in acetone) at 25°C |
| Impact Stability | > 100 cm/2kg weight |
| Softening Range: | 55 to 65°C |

### (5) Preparation of Polyurethane XII-C from 3,6-Dinitraza-1,8-octane Diisocyanate and 2-Nitro-2-ethyl-1,3-propanediol (JRF-279)

#### (a) Experimental

Equivalent quantities of the monomers, 67 g total weight, were dissolved in absolute dioxan. Ferric acetylacetonate, 0.0110 g, was added to catalyze polymerization. Inasmuch as the reaction was very slow at this catalyst concentration ($1 \times 10^{-4}$ mole catalyst/eq.-NCO or -OH) the quantity was increased to 0.0550 g ($5 \times 10^{-4}$ mole/eq.). After 1 hr at 50°C, polymer began to separate from solution. After 50 hr at 50°C the thick polymer slurry was diluted with acetone, which dissolved most of the dioxan-insoluble material. The diluted product was centrifuged free of 4 g of insoluble material, then poured into rapidly stirred ice water. The dry polymer weighed 60 g and had the following characteristics:

| | |
|---|---|
| Anal. Calc'd for $C_{13}H_{23}N_7O_{10}$: | %C, 35.70; %H, 5.30; %N, 22.42 |
| Found: | %C, 35.70; %H, 5.38; %N, 22.75 |
| Heat of Combustion Calc'd: | 4068 cal/g |
| Found: | 4113 cal/g |
| Relative Viscosity: | $\eta_r' = 1.41$ (1% in DMF) at 25°C |
| Impact Stability: | >100 cm/2 kg weight |
| Softening Range: | 75 to 85°C |

(b) The 4 g of insoluble material had the following characteristics:

Relative Viscosity: $\eta_r' = 1.07$ (1% DMF) at 25°C
Softening Range: 100 to 120°C

### (6) Preparation of Polyurethane XIII-C from 3-Nitraza-1,5-pentane Diisocyanate and 2-Nitro-2-ethyl-1,3-propanediol (JRF-276)

Equivalent quantities of the monomers, 93 g total weight, were dissolved in 93 ml absolute dioxan. Ferric acetylacetonate, 0.187 g, was added to catalyze polymerization. After 95 hr at 50°C, the product was diluted with acetone and precipitated by pouring into rapidly stirred ice water. The dried product weighed 90 g and had the following characteristics:

Anal. Calc'd for $C_{11}H_{19}N_5O_8$: %C, 37.82; %H, 5.48; %N, 20.05
Found: %C, 37.67; %H, 5.28; %N, 20.04
Heat of Combustion Calc'd: 4167 cal/g
Found: 4119 cal/g
Relative Viscosity: $\eta_r' = 2.33$ (1% in DMF) at 25°C
Impact Stability $>$100 cm/2 kg weight
Softening Range: 60 to 70°C

### c. Further Work on Previously Described Polyurethanes

### (1) Preparation of Polyurethane XIV-J from 3,3,5,7,7-Pentanitro-5-aza-1,9-nonane Diisocyanate and 2-Nitro-2-methyl-1,3-propanediol (JRF-280 and -281)

(a) Earlier attempts to prepare polymers from this high-impulse diisocyanate have given only low-molecular-weight products.[*] At that time it was concluded that the diisocyanate contained impurities that limited the molecular weight. Work has been resumed on this system, using carefully purified diisocyanate and a lower reaction temperature. An improvement in the relative viscosity has been achieved, and it is believed that this high-impulse series of polymers can now be fully exploited.

### (b) Experimental (JRF-280)

The diisocyanate was carefully purified via the dioxan complex,[**] then recrystallized twice from ethylene dichloride

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[*] Aerojet Report No. 772, p. 14.

[**] Ibid.

(mp 110 to 110°C). This diisocyanate cannot be assayed by the standard method, inasmuch as the di-n-butylamine solution causes decomposition.[*] Equivalent amounts of the monomers, 41 g total weight, were dissolved in 41 ml absolute dioxan. At the beginning, 0.005 g ferric acetylacetonate catalyst was added, more being added during the polymerization whenever the catalyst color was discharged. Monomer equivalence was adjusted by adding a total of 2% excess diisocyanate. The reaction temperature was maintained at 30°C for 21 days. The precipitated product had the following relative viscosity:

$\eta_r$ = 1.38 (1% in acetone) at 25°C

$\eta_r$ = 1.34 (1% in dioxan) at 25°C

$\eta_r$ = 1.52 (1% in $\gamma$-butyrolcatone) at 25°C

$\eta_r$ = 1.66 (1% in dimethylformamide) at 25°C

The osmometric molecular weight was found to be in the range of 28,000 to 29,000 with 6.5% diffusion through the membrane. The highest relative viscosity obtained previously was $\eta_r$ = 1.24 (1% in acetone) at 25°C.

(c) Experimental (JRF-281)

This run was identical with (JRF-280) described above, except that boron trifluoride etherate was used as catalyst. A total of 4.5 equivalent % was used in three separate additions. The product had the following relative viscosity:

$\eta_r$ = 1.23 (1% in dimethylformamide) at 25°C

(2) Preparation of Polyurethane XIII-N from 3-Nitraza-1,5-pentane Diisocyanate and Ethylene Glycol (JRF-278)

(a) In the formulation program now in progress[**] the study of a high-molecular-weight polycrystalline nitropolymer is desired. Polyurethane XIII-N has been selected from the available polycrystalline nitropolyurethanes[***] for further study. In an earlier preparation using absolute dimethylformamide as polymerization solvent[****] at 50°C, the polycrystalline product separated from solution early in the polymerization, thus limiting the

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[*] Aerojet Report No. 740, p. 70.

[**] Aerojet Report No. 807, p. 29.

[***] Aerojet Report No. 817, pp. 27-28.

[****] Aerojet Report No. 740, p. 26.

molecular weight. Recently it was observed that XIII-N is moderately soluble in γ-butyrolactone at elevated temperatures. A preparation using γ-butyrolactone at 150°C as polymerization solvent shows a definite improvement in the molecular weight.

### (b) Experimental (JRF-278)

A solution of 71.68 g (0.358 mole) 3-nitraza-1,5-pentane diisocyanate in γ-butyrolactone, previously distilled from p,p'diphenylmethane diisocyanate, was added dropwise with cooling to 22.23 g (0.358 mole) ethylene glycol in γ-butyrolactone containing 0.0126 g ferric acetyalcetonate catalyst. The ultimate concentration was 25 wt %. Solids began to separate just as the addition was completed. The mixture was placed in an oil bath at 125°C, and the temperature was gradually raised to 150°C to effect almost complete solution. (A small portion that adhered to the wall of the vessel was worked up separately.) After 1 hr at 150°C the solution was cooled to room temperature, resulting in separation of a solid polymer phase. The solids were washed repeatedly with acetone, then dried <u>in vacuo</u> at 100°C.

Relative Viscosity: $\eta_r' = 1.36$ (1% solution in formic acid) at 25°C

The portion that adhered to the vessel was worked up in the same manner.

Relative Viscosity: $\eta_r' = 1.39$ (1% solution in formic acid) at 25°C

The preparation reported previously had a relative viscosity of $\eta_r' = 1.21$ (1% solution in formic acid) at 25°C.

### (c) Conclusions

There is a definite imporvement in molecular weight, but perhaps some degradation and/or reaction with the solvent occurred at the higher temperature, since the portion that did not go into solution had a slightly higher relative viscosity.

### (3) Preparation of Copolymer Polyurethane XII-A-XIII-A from Mixtures of 3,6-Dinitraza-1,8-octane Diisocyanate, 3-Nitraza-1,5-pentane Diisocyanate, and 2,2-Dinitro-1,3-propanediol (RDH-37 and -50)

(a) Polyurethane XIII-A is a typical high-molecular-weight amorphous polymer that can be cross-linked and plasticized to give a rubbery product suitable for propellant fabrication.* Polyurethane

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*Aerojet Reports No. 772, p. 21, No. 807, p. 50, and No. 817, pp. 12, 27, 29.

XII-A exhibits various degrees of crystallinity but has poor physical properties for use as a propellant.* It was of interest therefore, to study the preparation and physical properties of copolymers of these two systems.

(b) Experimental (RDH-37, 50 eq % XII and 50 eq. % XIII)

A solution of 47.335 g 3-nitraza-1,5-pentane diisocyanate and 68.070 g 3,6-dinitraza-1,8-octane diisocyanate in 100 ml of dry acetone was slowly added to a slurry of 76.971 g 2,2-dinitro-1,3-propanediol and 67 mg of ferric acetylacetonate in 60 ml of dry acetone. The temperature during the addition was held below 50°C by the intermittent application of a water-ice bath. After completion of the diisocyanate addition, the addition funnel was washed with the remainder (32 ml) of the acetone, and the washings were added to the reaction mixture. The ultimate monomer concentration was 50 wt % with a calculated excess of 2.276% diisocyanate. The reaction mixture was then placed in a 50°C oil bath, and the reaction mixture was followed by measurements of solution viscosity. After 18 hr a solid phase began to separate. After 60 hr at 50°C the efflux time was 220 sec. A sample, worked up in the usual way, had a relative viscosity of 1.42 (1% in acetone) at 25°C. After 175 hr the solution viscosity had not changed appreciably, and the reaction mixture was removed from the bath and precipitated into water using the Waring blendor. The precipitated polymer was washed with water and dried <u>in vacuo</u>. The dried polymer had the following relative viscosity:

$\eta_r$ = 1.45 (1% in acetone) $\eta_r$ = 2.06 (1% in DMF)

(c) A similar batch was made using a mixture of 20% 3,6-dinitraza-1,8-octane diisocyanate, 80% 3-nitraza-1,5-pentane diisocyanate, and an equivalent amount of 2,2-dinitro-1,3-propanediol, using dioxan as a solvent.

(d) Experimental (RDH-50)

The polymer was made in the same manner as described above for RDH-37, using 26.672 g 3,6-dinitraza-1,8-octane-diisocyanate, 75.810 g 3-nitraza-1,5-pentane diisocyanate, 78.098 g 2,2-dinitro-1,3-propanediol, 66 mg ferric acetylacetonate, and 179 ml absolute dioxan. An insoluble phase appeared almost immediately. Monomer equivalence was adjusted by the addition of 2.1437 g 3-nitraza-1,5-pentane diisocyanate, making a total excess of 2.392% diisocyanate. When the solution viscosity had reached 148 sec the reaction mixture was removed from the 50°C bath, diluted with acetone, and precipitated into water using the Waring Blendor. The polymer was next washed five times with water and dried <u>in vacuo</u>. The dry polymer had the following relative viscosity:

$\eta_r$ = 1.21 (1% in acetone) $\eta_r$ = 1.43 (1% in DMF)

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*Aerojet Reports No. 712, p. 17, and No. 817, p. 9 and 10.

### (e) Conclusions

The physical properties of the 50-50 eq. % copolymer (RDH-37) will be compared with other potential propellants, inasmuch as the molecular weight appears to be high, judging by the relative viscosity. Polyurethane XII-A had been prepared with a relative viscosity of $\eta_r = 1.7$ (1% DMF). Polyurethane XIII-A has $\eta_r = 2.5$ (1% in DMF). The 80-20 eq. % copolymer (RDH-50) is not suitable for comparisons because of low molecular weight.

### (4) Preparation of Cross-Linked Polyurethane XIII-A from 3-Nitraza-1,5-pentane Diisocyanate, 2,2-Dinitro-1,3-propanediol, and tris-Hydroxymethyl Nitromethane

In order to continue further the studies of physical characteristics of cross-linked nitropolyurethanes in the program for development of a nitropolymer propellant, a series of batches of Polyurethane XIII-A was run. These products will be used for swelling experiments in various solvent plasticizers. A summary of the experimental details is given in Table XI. Dioxan was used as solvent in all runs along with ferric acetylacetonate as catalyst.

TABLE XI

SUMMARY OF RUNS ON CROSS-LINKED POLYURETHANE XIII-A

| | | Branching Agent | | | Cure | |
|---|---|---|---|---|---|---|
| Run No. | Polymer | Type | eq. % | Gel Time min | at 50°C hr | Remarks |
| RDH-50 | XIII-A | NG* | 2 | 90 | 200 | Soft gel |
| RDH-52 | XIII-A | NG | 4 | 60 | 200 | Medium gel |
| RDH-53 | XIII-A | NG | 6 | 10 | 200 | Gelled almost immediately |
| RDH-54 | XIII-A | NG | 8 | 70 | 200 | Hard gel |
| RDH-42 | XIII-A | NG | 10 | 20 | 28 | Hard gel |

*NG is nitroglycerol.

### d. Attempted Stabilization of Post-Nitrated Polyurethanes

All previous attempts* have failed to produce post-nitrated polyurethanes having acceptable thermal stability. The metal acetylacetonates react with mineral acids, yielding the metal salt and

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*Aerojet Reports No. 712, p. 12; 740, p. 10; and 807, p. 24.

acetylacetone. Incorporation of a small amount of a metal acetylacetonate with a post-nitrated polyurethane might act as a scavenger of nitric acid and prevent further degradation. However, incorporation of Aluminum III acetylacetonate or other acid neutralizers such as calcium carbonate, magnesium oxide, or activated alumina failed to increase thermal stability or prevent degradation of Polyurethanes I-AN and XIII-AN in solution.* In fact, with Aluminum III acetylacetonate, no polymeric product was recovered after 24 hr in dioxan solution. A shorter time in solution resulted in partial recovery of product with no improvement in thermal stability.

## II. TECHNICAL PROGRESS: FORMULATION STUDIES

### A. INTRODUCTION

For some time an investigation has been in progress to produce useful propellant materials having rubbery characteristics. Such materials have been produced by proper formulation of the nitropolymers with nitroplasticizers. Two procedures have been used in the preparation of test samples for mechanical property and ballistic evaluations. The first procedure used is a casting process. In this method all the ingredients are mixed, degassed and polymerized to yield cross-linked, rubbery shapes. The second process involves the preliminary preparation of a linear or slightly branched polyurethane. With this product plasticizers and other components are incorporated on the roller mill, yielding a thermoplastic material. In each of the processes studied several problems still require solution. During the past quarter considerable emphasis was placed on attempts to incorporate inorganic oxidizers in the plastic matrix in order to produce propellant materials with desirable energy content. However it was found that this new variable produced by the introduction of an insoluble inorganic salt did not allow gelation to occur during the casting operation. Apparently the catalyst was inactivated. When the less active vanadyl acetyl acetonate was substituted for the more labile ferric acetyl acetonate the new catalyst was not inactivated, thus providing a solution to the problem. In the case of the thermoplastic formulations, considerable effort has been directed toward the achievement of a second-stage cross-linking reaction which can be used to insure high-temperature structural stability. The previously described studies have been continued, and have led to investigations of the behavior of nitropolyurethanes at elevated temperatures. It has been found that in addition to branched-soluble polyurethanes, most linear polyurethanes can also be caused to become insoluble by the application of high temperature.

### B. CASTING STUDIES

#### 1. Discussion

a. Previous studies of the basic processes available for the formulation of a nitropolymer propellant grain have shown that the

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*I-AN is the nitrated reaction product of 3,3-dinitro-1,5-pentane diisocyanate and 2,2-dinitro-1,3-propanediol. XIII-AN is the nitrated reaction product of 3-nitraza-1,5-pentane diisocyanate with the same nitrodiol.

nitropolymer systems are amenable to a wide variety of processing techniques. In particular, emphasis was given to the development of a one-stage and two-stage nitropolymer-nitroplasticizer casting. During the past quarter these basic studies have been extended, and a process for the casting of nitropolyurethanes in the presence of inorganic oxidizers has been developed. The first experiments undertaken utilized sodium chloride as the inorganic salt, ferric acetylacetonate catalyst, and the Polyurethane XIII-A or XIII-J system as the binder. In no instance was a gelled casting obtained. As previously reported, excellent castings were obtained in the absence of inorganic oxidizers.* The negative experiments are presented in Table XII.

## TABLE XII

### ATTEMPTED POLYURETHANE CASTINGS IN THE PRESENCE OF SODIUM CHLORIDE, FERRIC ACETYLACETONATE CATALYZED

| | Composition, wt % | | | Nib Glyc. | Catalyst[1] | | |
|---|---|---|---|---|---|---|---|
| Run | Polymer | Plasticizer | Salt | Conc. (eq. %) | Conc. (eq. FeAA/eq. NCO) | Cure 50°C | Results |
| 295 | XIII-J<br>26.7 | γ-BL,[2]<br>13.3 | NaCl<br>60.0 | 2.0 | $3 \times 10^{-5}$ | 3<br>days | Phase separation. No gel. |
| 296 | XIII-J<br>22.4 | MNV,[3]<br>7.6 | NaCl<br>70.0 | 2.0 | $5 \times 10^{-5}$ | 16<br>hr | Slight stiffening. No gel. |
| 297 | XIII-A<br>22.4 | MNV<br>7.5 | NaCl<br>70.0 | 2.0 | $1 \times 10^{-4}$ | 16<br>hr | Slight initial exotherm. Obtained hard but non-gelled casting. |
| 298 | XIII-A<br>20.0 | MNV<br>10.0 | NaCl<br>70.0 | 2.0 | $1 \times 10^{-4}$ | 16<br>hr | Vigorous exotherm. No gel |

[1] Initial catalyst concentration. In each run the catalyst color was discharged within 5 minutes. Further catalyst was added in each case, except in Run 298, which thickened too rapidly to allow further addition.

[2] γ-Butyrolactone

[3] Methyl 4-nitrazavalerate

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*Aerojet Reports No. 807, p. 29 and 833, p. 27.

b. Experimental

The diisocyanate, diol, nib glycerol, and plasticizer were combined in a round-bottomed flask, and vacuum degassed at 50°C for 1 to 16 hr. Anhydrous sodium chloride was added to the monomer solution, and after thorough mixing, ferric acetylacetonate catalyst was added in solution (acetone or plasticizer). Further vacuum degassing was conducted at 50°C, followed by curing at 50°C. The catalyst color in each run was almost immediately discharged, and an attempt was made in each case to add further catalyst. At no time was it possible to add sufficient catalyst to give a persistent coloration.

## 2. Ferric Acetylacetonate Decomposition Studies

a. Discussion

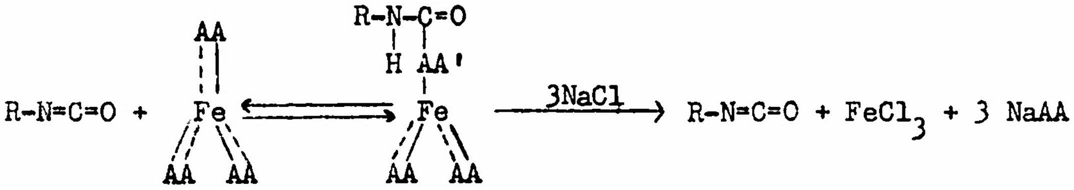
(1) It became obvious early in the above group of experiments that the catalyst was being decomposed and that the polymerization was being interrupted early in its progress, thus preventing gel formation. It seemed likely that the sodium chloride was responsible for this decomposition, but mixtures of catalyst, sodium chloride, and acetone failed to show any loss of catalyst color intensity with time. Further experiments showed that in order to reproduce this catalyst decomposition in acetone solution the presence of sodium chloride and the diisocyanate was a necessary and sufficient condition. The generality of this phenomenon was established when it was found that four other salts (KCl, $Na_2SO_4$, $NH_4NO_3$, and $NH_4ClO_4$), three other isocyanates (different Batch XIII, I, and phenyl isocyanate) and two other solvents (dioxan, methyl 4-nitrazavalerate) also showed the same behavior, though in varying rates. The addition of water or the application of heat greatly increased the decomposition rate. The A diol showed no such effect, and the catalyst color persisted for more than 24 hr in the presence of the diol and sodium chloride.

(2) It was also found that when a few drops of an aqueous solution of potassium thiocyanate were added to a mixture of acetone, 3-nitraza-1,5-pentane diisocyanate, sodium chloride and ferric acetylacetonate, in which the iron complex color had been completely discharged, an intense red-orange coloration arose immediately. In a control experiment, in the absence of the diisocyanate and in the presence of the undecomposed catalyst, 2 hr was required to produce the same intensity of red-orange coloration.

(3) It was also found that above a certain critical concentration, the iron catalyst was stable in the presence of sodium chloride and 3-nitraza-1,5-pentane diisocyanate. This critical concentration level is about $1 \times 10^{-3}$ molar. The fact that the reactants and products of this decomposition are at such a low concentration level has precluded further investigations by means of standard macro-analytical methods for the determination of the isocyanate group as a function of time.

### b. Conclusions

It is believed that the catalyst decomposition proceeds as follows: A molecule of ferric acetylacetonate complexes with an isocyanate group, probably involving a proton transfer. This complexing breaks the symmetry of the stable chelate molecule, and partially exposes the central metal atom to attack. Then, under the influence of the small amount of inorganic salt dissolved in the solvent or plasticizer, the chelate molecule undergoes a metathetical reaction with the salt. The presence of free ferric ions in a solution of the decomposed catalyst has been shown by means of the qualitative thiocyanate test. The low reactant concentrations support the belief that the driving force in the decomposition reaction is the small but finite solubility of the salt in the organic solvent. (The solubility of sodium chloride in absolute acetone is about 6 x $10^{-6}$ mole per liter at room temperature, and increases rapidly with small additions of water.) The variation in decomposition rate with salt and solvent is attributed to differences in solubility of the various salts in the solvents. These reactions are represented by the following equations (AA is enolate of acetylacetone, AA' is same less a hydrogen atom):



$$\text{R-N=C=O} + \text{Fe(AA)}_3 \rightleftarrows \text{(R-N(H)-C(=O)-AA')Fe(AA)}_2 \xrightarrow{\text{3NaCl}} \text{R-N=C=O} + \text{FeCl}_3 + 3\ \text{NaAA}$$

These experiments, in addition to suggesting the mechanism of catalyst decompositions, also shed light on the mechanism of the catalyzed urethane formation. It seems certain that the catalyst first complexes with the isocyanate; then, perhaps, the diol is complexed by the catalyst, and in such a spatial position that the formation of the urethane grouping requires very little further energy input.

### 3. Further Castings Using Ferric Acetylacetonate

### a. Discussion

(1) Because the critical catalyst concentration level was found to be reasonably low, an attempt was made to use the iron catalyst in a sodium-chloride-containing casting at a level where the catalyst was stable. Accordingly, a casting of Composition XIII-J-4x-10MNV-70NaCl was made using FeAA at a level of 1 x $10^{-5}$ mole catalyst per equivalent diisocyanate. (In this same system the catalyst is decomposed when used at a level of 1 x $10^{-4}$.) The polymerization proceeded rapidly to completion in this case and a hard, rubbery gel containing very few bubbles and still colored with catalyst was obtained in 16 hr at 45°C. However, the initial exotherm was vigorous, and within 5 min after the catalyst was added the temperature of the mix had reached a maximum of about 50°C. This obviously represented too fast a rate of reaction for practical use, particularly on a larger scale.

(2) Attempts were then made to utilize the two-stage casting process developed for the two-component systems (nitropolymer-plasticizer), wherein high initial rates of polymerization can be more easily tolerated. It was found that the presence of the inorganic salt in the prepolymer solution, even at low DP, made transfer operations virtually impossible, because of the very low fluidity. In two attempts to apply the two-stage process to the XIII-J-4x-20MNV-60 NaCl system, the transfer to the test-tube molds was extremely difficult, even when a vacuum transfer technique was used.

b. Conclusions

The use of the iron catalyst at higher concentrations in order to avoid decomposition has not thus far proved practical. The need for a less active catalyst, as well as a more stable one, becomes very apparent. It also appears that inorganic-salt-containing castings are not amenable to the two-stage casting process involving a transfer operation.

### 4. Castings Catalyzed by Tertiary Amines

a. Discussion

(1) Tertiary amines have been known as active catalysts for urethane formation, but their use in nitropolyurethane work has been restricted because of the general sensitivity of the nitromonomers to basic materials. Following the failure of ferric acetylacetonate as a catalyst in inorganic salt-containing castings, the use of tertiary amines was again considered.* It was believed that the amine catalysts would be of value if suitable monomers were found that were stable toward bases.

(2) As expected, the XIII-A monomers, 3-nitraza-1,5-pentane diisocyanate and 2,2-dinitro-1,3-propanediol, behaved violently on the addition of a small amount of pyridine. The monomer solution immediately heated, began gassing, and charred rapidly. On the other hand, the XIII-J monomers, 3-nitraza-1,5-pentane diisocyanate and 2-nitro-2-methyl-1,3-propanediol, were found to be very stable toward such bases as dimethylaniline, pyridine, and triethylamine; and furthermore, small-scale polymerization experiments showed that each of the three amines catalyzed the XIII-J system to a good degree. The triethylamine was the most active catalyst, judging from exotherms and viscosity increases.

(3) Triethylamine, TEA, was then used in a standard polymer system to evaluate its behavior under normal casting conditions in the absence of inorganic salts. When the System XIII-J-2x-25MNV was catalyzed with TEA at a level of $1 \times 10^{-3}$ mole/eq. -NCO, the rate of polymerization was so fast that the monomer solution heated immediately to 70°C, began gassing

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*See early studies of triethylamine as catalyst, Aerojet Report No. 482, p. 38.

violently, and gelled within 5 min after the catalyst was added. When the run was repeated at a catalyst level of 1 x $10^{-4}$ mole/eq. -NCO no initial exotherm was observed, and after 2 weeks at 50°C only a soft, weak, bubble-filled, DMF-insoluble gel was obtained.

b. Conclusions

It has been shown that the Polyurethane XIII-J system can be catalyzed to a gel point with triethylamine. TEA appears almost as active as FeAA, and in this regard is undesirable since the reaction rate is too sensitive to small changes in catalyst concentration. TEA possesses the added liability of being so volatile that no vacuum degassing is possible after the catalyst is added to the monomers. It is possible that a higher molecular weight, solid, tertiary amine might overcome these disadvantages of TEA. The fact still remains, however, that only a few of the currently available nitromonomers can be polymerized in the presence of a base, and in this respect the tertiary amines cannot be considered as general catalysts for nitropolyurethanes.

## 5. Castings Catalyzed by Chromium Acetylacetonate

a. Previous studies of urethane catalysts have shown that chromium acetylacetonate, CrAA, possesses a lower catalytic activity in polyurethane systems than FeAA. Continuing the search for a suitable catalyst in nitropolyurethane casting systems, CrAA was investigated in this regard.

b. In the absence of inorganic salts two runs of XIII-J-2x-25MNV were made using CrAA at a level of 1 x $10^{-3}$ mole/eq. -NCO and 1 x $10^{-2}$ mole/eq. -NCO, respectively. The latter concentration represents close to a saturated solution in the system used. Both runs were cured for four days at 45°C, and only slight increases in viscosity were observed. The castings after the cure were both fluid enough to be poured from the molds. It is concluded that the catalytic activity of CrAA is far too low for it to be of practical use in polyurethane casting systems.

## 6. Castings Catalyzed by Vanadyl Acetyl Acetonate

a. Discussion

(1) Previous rate studies showed that vanadyl acetyl acetonate was a fair catalyst for polyurethane formation.* In the search for a catalyst which would withstand decomposition in formulations containing inorganic salts, vanadyl acetyl acetonate was investigated in the presence and absence of inorganic oxidizers. It was found that vanadyl acetyl acetonate was not only a very stable catalyst but was also sufficiently active at a concentration of 2 x $10^{-4}$ to give good polymerization rates in formulations, and yielded satisfactory gelled specimens.

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*Aerojet Report No. 833, p. 13.

(2) In the absence of the inorganic salts the following experiment demonstrated the usefulness of vanadyl acetyl acetonate in cross-linked formulations.

(a) A XIII-H-2x-25MNV system was polymerized in the presence of VOAA at a concentration of $2 \times 10^{-4}$ mole/eq. -NCO. A good exotherm was observed, and within 15 minutes a temperature maximum of about 80°C was attained. The high temperature caused a slight darkening of the solution. After curing for 2 days at 45°C, a soft, rubbery gel was obtained which contained no gassing bubbles.

(b) A composition of XIII-J-2x-25 dinitrohexanone was polymerized in the presence of vanadyl acetyl acetone at a level of $2 \times 10^{-4}$ mole/eq. -NCO. Within 10 min after the catalyst was added, the temperature of the monomer solution had risen to about 60°C. After curing for 16 hr at 45°C, the mix had gelled to a soft, flexible rubber, with a faint odor of the plasticizer detectable.

(3) After these encouraging experiments it was of interest to determine whether VOAA was stable in a casting system containing sodium chloride. Accordingly, a composition of XIII-J-4x-20MNV was prepared and mixed with 60% sodium chloride, and VOAA was added at a level of $1 \times 10^{-4}$ mole/eq. -NCO. After curing for 68 hours at 50°C, a flexible, rubbery, bubble-free, gelled casting was obtained. In a repeat of this run under identical conditions, the same successful casting was obtained. These experiments indicated that the problem of developing a casting process utilizing 2-nitro-2-methyl-1,3-propanediol is solved.. However, in an attempt to utilize 2,2-dinitro-1,3-propanediol, in a sodium chloride casting catalyzed with VOAA, only a weak, bubble-filled, yellow-colored casting was obtained. Further study on methods of stabilizing 2,2-dinitro-1,3-propanediol in casting systems is required before this or other high-energy diols can be considered as a utilizable monomer.

(4) The casting process using VOAA catalyst was then extended to systems containing inorganic oxidizers. Using a XIII-J-4x-15MNV binder, ammonium nitrate and ammonium perchlorate were successfully cast at a catalyst level of $7 \times 10^{-5}$ mole/eq. -NCO and an oxidizer level of 60 wt %. Strong, rubbery, bubble-free castings were obtained after a 16-hr cure at 45°C. The propellant castings burned readily at 1 atm, producing no smoke or appreciable residue.

b. Experimental

(1) The experimental procedure used for the inorganic-salt-filled castings catalyzed by VOAA is as follows: diisocyanate, diol, nib glycerol and plasticizer were combined in a 125-ml Erlenmeyer flask and vacuum-degassed at 50°C for 1 to 16 hr in order to remove all gas-producing impurities. In the castings using the J diol, 2-nitro-2-methyl-1,3-propanediol, it was

necessary to add a small amount of acetone to the system after degassing in order to completely dissolve the diol, which is incompletely soluble in the plasticizers used. To the degassed monomer solution was then added the inorganic salt, followed by an acetone solution of catalyst. The mix was transferred to the casting mold, test tube, or flat-bottomed dish, the acetone was vacuum-stripped off. and the run was cured at 45 to 50°C. Using silicone high-vacuum grease on the molds, the cured castings readily released from the mold surfaces.

(2) In a series of further experiments designed for mechanical-property studies the casting technique will be improved, and attempts will be made to eliminate the addition of acetone.

## C. SECOND-STAGE CROSS-LINKING STUDIES

### 1. High-Temperature Studies on Linear Polyurethanes

### a. Discussion

(1) In the process starting from linear or slightly branched polyurethanes with subsequent incorporation of the plasticizer and inorganic salts, the primary disadvantage is that a thermoplastic material is obtained. In order to prevent cold flow of the composition a second stage cross-linking should be effected to obtain a final product with the required strength. In previously described experiments on second-stage cross-linking it was found that soluble polyurethanes branched with 0.5% nib glycerol became insoluble after high-temperature treatment.* It was concluded at that time that at elevated temperatures the urethane linkage was split and reformed in an "abspalter" reaction, allowing a redistribution of the branching points. This redistribution during the high-temperature treatment led to an equilibrium and hence a more uniform distriubtion of the cross-links; and with this more uniform distribution came the insolubility. It is now believed that this is false, since linear nitropolyurethanes under more vigorous conditions also have been made to become insoluble.

(2) In the course of other second-stage cross-linking experiments, a control run was made wherein a linear Polyurethane I-A sample was maintained at 150°C for 1 hr. It was found that the polymer was not soluble in acetone after the heat treatment. Following this discovery, other polymer systems were investigated with respect to solubility after various degrees of exposure at 150°C. Table XIII shows the results of these experiments.

### b. Conclusions

Most of the polymer systems studied became insoluble after the high-temperature treatment. With the exception of the XV series,

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*Aerojet Report No. 833, p. 29.

certain consistent trends appear in the data. The A and H polymers became insoluble faster than the J polymers; and the A polymers showed by color changes and a fume-off a greater thermal instability than the other polymer systems. These differences in rates are in rough proportion to the thermal stabilities of the diol monomers, the J diol being the most stable, the H diol being less stable by virtue of the trinitromethyl group, and the A diol being unstable because of high-temperature deformylation, which leads to a terminal dinitromethyl group. It is believed that the following mechanism accounts for all these facts: At a temperature of 150°C the polyurethanes exhibit "abspalter" characteristics and hence give rise to a large number of free, reactive end-groups in unit time. The diols, being much less stable than the diisocyanates, are relatively easily decomposed when they exist as free end-groups at the elevated temperature. This disparity in monomer decomposition rate favors a rise in excess diisocyanate, which is then free to react with urethane hydrogens, thus giving rise to branching and eventually insolubility. It is important to note that the cross-linking is being obtained at the expense of an irreversibly broken urethane linkage, and that decomposition products increase with time within and above the polymer mass. Since a branch point is formed only after a break in the linear chain there is a lower molecular weight limit below which this type of degradative cross-linking would fail to produce an insoluble polymer. It is believed that the XV series listed in Table XIII have molecular weights below this limit, as suggested by their low relative viscosities. It is not likely that these reactions may have practical use in second-stage curing techniques due to the very high temperatures involved and the attendant decomposition reactions. It has also been previously shown that these "abspalter" reactions are inhibited by most additives and diluents, particularly those containing isocyanate-reactive groupings or impurities.

TABLE XIII

HIGH-TEMPERATURE STUDIES ON LINEAR NITROPOLYURETHANES

| Polymer | Relative Viscosity | Solvent | Solubility<br>After 15 min at 150°C | <br>After 75 min at 150°C |
|---|---|---|---|---|
| I-A | 1.61 | acetone | slowly sol. | insol. |
| I-H | 1.60 | acetone | insol. | insol. |
| I-J | 1.77 | acetone | sol. | sol. |
| XII-A | 1.85 | DMF | insol. | decomp. |
| XII-H | 1.26 | acetone | sol. | insol. |
| XII-J | 1.62 | DMF | sol. | insol. |
| XIII-A | 1.45 | acetone | slowly sol. | fumed off |
| XIII-H | 1.53 | acetone | insol. | insol. |
| XIII-J | 2.32 | DMF | sol. | insol. |
| XV-A | 1.47 | acetone | sol. | sol. |
| XV-H | 1.22 | acetone | sol. | sol. |
| XV-J | 1.78 | DMF | sol. | sol. |
| XV-N | 1.30 | DMF | sol. | sol. |

## III. TECHNICAL PROGRESS: MANUFACTURING STUDIES

### A. INTRODUCTION

The scale-up of polymerization experiments from small laboratory apparatus to larger quantities requires the solution of many problems. During the past quarter emphasis has been placed on problems encountered in the scale-up of nitropolyurethanes in the Beken dispersion-blade mixer, with particular attention to problems of manufacturing time, work-up procedures, and uniformity and reproducibility of the product. The polymers have been characterized by measurements of relative viscosity, thermal stability, softening points, and impact stability.

### B. DISCUSSION

1. Previously all manufacturing studies have been conducted with slightly branched nitropolyurethanes.* During the past period the linear nitropolyurethanes have been investigated. Some new problems have been encountered with linear nitropolymers which were not present with the branched nitropolymers. The major problem concerns the failure of pilot batches for determination of true monomer equivalence in the master batches. With branched nitropolymers the mix time was cut from 72 hr, with no pilot batch, to an average of 5 hr by use of pilot batches. However, with the linear nitropolymers further adjustment of monomer equivalence has been necessary in order to produce a polymer with satisfactory molecular weight. This has resulted in a far greater mix time than had been expected on the basis of experience with the branched nitropolymers. Further studies will be necessary in order to shorten the reaction time.

2. Additional work dealt with a suitable method for following the course of polymerizations in the Beken mixer. At present a rough determination is made by measurements of solution viscosity. However, this method is far from exact and needs much improvement before the results are reproducible and reliable. The use of the infrared spectrophotometer for determination of monomer equivalence has been investigated. It was hoped that the (-OH) or (-NCO) groups would show up if either one were in excess and that the absorption peaks would disappear when true equivalence had been reached. Measurements of solution viscosity were used as a standard for comparison, but all signs of the monomer functional groups disappeared in the infrared absorption peaks before an appreciable change in solution viscosity had been effected.

3. All of the linear nitropolymers have been worked up in the conventional manner in the Morehouse mill. The branched nitropolymers have a high density when precipitated from a non-solvent. An attempt was made to produce the branched product in the granular form by conducting the polymerization in a homogeneous solvent such as acetone or dioxan, and on completion of

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*Aerojet Report No. 833, p. 33.

the polymerization to leach out the solvent with a heterogeneous solvent and grind the resultant polymer in the Beken mixer. This was tried, on small scale, with a wide variety of solvents at temperatures down to -78°C, but the crude nitropolymer-acetone system remained plastic in all cases. Attempts were also made to precipitate an acetone solution of nitropolymer into a similar group of heterogeneous solvents at temperatures from -20 to 30°C. Methylene chloride at 30°C yielded a product which was slightly denser than the water-precipitated polymer, but it still remained somewhat plastic and would therefore be unsuitable for further applications. It has been found that the crude polymer, when diluted with acetone to a concentration of 2 to 5%, was precipitated into water using the Morehouse mill in a time of about 2 hr per kg polymer. This compares with previous precipitations of 10 to 15% solutions of 1 kg of polymer, for which 10 hr were needed. Physical measurements and thermal stability tests of the final product were used to evaluate reproducibility and uniformity. In the linear polymers these tests have shown that end products are reproducible even though the time and equivalence factors might differ from batch to batch.

4. One major difference between the pilot batch and the master batch has been the rate of the addition of diisocyanate to the diol. Whereas addition times of 0.25 hr were common in pilot runs, the rate of addition in master batches has been held at 2 to 3 hr so as to be certain the reaction could be kept under full control. Recently the addition time has been decreased to as low as 0.5 hr, and the batch temperatures easily maintained below 50°C. However, it has been found that complete dispersion of the heat exchange medium to all parts of the external jacket of the mixer requires considerable time. This problem is being solved by tapping in another exit line into the opposite side of the mixer from the existing line. By the placement of a valve on each exit line the heat exchange medium can then be controlled so as to keep all portions of the mixer at a uniform temperature.

5. In the experimental section is shown a representative batch of linear nitropolyurethane. A summary of the Beken runs is given in Table XIV, showing differences in operating technique and physical characteristics.

## C. EXPERIMENTAL

### 1. Polyurethane XIII-A, from 3-nitraza-1,5-pentane Diisocyanate and 2,2-Dinitro-1,3-propanediol

#### a. Pilot Batch

Prior to the master batch a laboratory polymerization was conducted in order to determine the true monomer equivalence. The Beken mixer run was based on this pilot plant run.

## TABLE XIV

SUMMARY OF BEKEN MIXER RUNS FOR LINEAR NITROPOLYURETHANES

| Run No. | Type Polymer | Solvent Type | Solvent Conc. | Addition Time, hr | Mixing Time hr | Mix Temp. °C | Work-up Procedure | Relative Viscosity 1% in Acetone |
|---|---|---|---|---|---|---|---|---|
| RDH-39 | Polyurethane XIII-A* | Acetone | 50 wt % | 2.5 | 44 | 50 | ppt into Morehouse mill | 1.66 |
| RDH-41 | Polyurethane XIII-A | Acetone | 50 wt % | 2.5 | 21.5 | 50 | ↓ | 1.63 |
| RDH-47 | Polyurethane I-A** | Dioxan | 50 wt % | 2.5 | 70 | 50 | | 1.91 |
| RDH-49 | Polyurethane XIII-A | Dioxan | 50 wt % | 0.75 | 40 | 50 | | 1.64 |

| Run No. | Warburg Stability ml gas/100 g/hr | KI-Starch Stability min to Fail | Softening Point °C | Yield g | Yield % | Impact Stability cm/2 kg | Remarks |
|---|---|---|---|---|---|---|---|
| RDH-39 | -.019 | 60 | 80-85 | 1070 | 96.3 | >100 | Required adjustment of monomers before equivalence was reached. |
| RDH-41 | -.023 | 60 | 80-85 | 856 | 95.1 | >100 | Polymer seems on verge of insolubility. |
| RDH-47 | -.0499 | 65 | 75-80 | 850 | 97.7 | >100 | Very white, fibrous polymer. |
| RDH-49 | -.0390 | >180 | 75-85 | 780 | 98.7 | >100 | Very white, fibrous polymer with no brown discoloration which was present in previous runs. |

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*Polyurethane XIII-A is 3-nitraza-1,5-pentane diisocyanate + 2,2-dinitro-1,3-propanediol.

**Polyurethane I-A is 3,3-dinitro-1,5-pentane diisocyanate + 2,2-dinitro-1,3-propanediol.

b. Master Batch

(1) A solution of 610.36 g 3-nitraza-1,5-pentane diisocyanate (assay 99.0%) and 650 ml of dry acetone was slowly added to a slurry of 494.84 g 2,2-dinitro-1,3-propanediol (assay 99.03%) and 430 mg of ferric acetylacetonate in 400 ml of dry acetone. Temperature of the reaction mixture during the diisocyanate addition was held between 40 and 45°C by the intermittent use of the heat exchange unit and adjustment of the rate of addition. On completion of the addition the remainder of the acetone was used to wash the addition funnel, and the washings were added to the reaction mixture. Addition time was 2.5 hr. Ultimate monomer concentration was 50 wt %, with a calculated excess of 2.276% diisocyanate. The temperature of the mix was then raised to 50°C and held at that point during mixing periods. Further additions of monomers were required before true monomer equivalence was reached. Final monomer equivalence was at an excess of 1.859% diisocyanate. Heating and mixing were continued intermittently for 42 hr, and the solution viscosity rose from 2 sec to 2000 sec. When the reaction mixture had reached this point it was diluted with 12 liters of acetone and precipitated into water, using the Morehouse mill. The polymer was then ground in successively finer grinds until the finest grind on the mill had been reached. It was next washed with hot (40 to 50°C) water and ground again in the finest grind. The polymer was then air-dried and finally dried in vacuo. Attempts to improve the physical characteristics of the final product by changes in work-up procedures met with no success, and the principal method for final work-up is still precipitation into water using the Morehouse mill.

(2) Table XIV is a summary of all Beken runs for the past period. In all cases a pilot batch was run prior to the master batch for determination of monomer equivalence, but in every instance further adjustment of monomers was required. Care was taken to duplicate batches as much as possible with monomers, solvents, and operational procedures.

c. Conclusions

Linear Polyurethanes I-A and XIII-A have been successfully produced in the Beken mixer. Reaction times have been much longer than for the corresponding polymers using 0.5% branching agents. The pilot batch method for determination of monomer equivalence has failed in all cases with the linear runs, and further adjustment to reach monomer equivalence in the master batches has been necessary. However, the pilot batch is still useful inasmuch as it still shows whether a successful batch of polymer can be made from the corresponding monomers. The past quarter has shown that the linear nitropolyurethanes can be reproduced with respect to physical characteristics and stability measurements of the final product.

## IV. TECHNICAL PROGRESS: PHYSICAL STUDIES

### A. HEATS OF COMBUSTION

The determination of the heat of combustion is used for the calculation of the specific impulse. N-Nitromorpholine was found to be an excellent plasticizer for nitropolyurethanes and its specific impulse is of interest for formulating compositions. A series of determinations of the heat of combustion of nitromorpholine, prepared according to the method of Wright et al,* gave an average value of 4225 cal/g, while 4568 cal/g is calculated. From these values a contribution factor of 6 kcal/mole is calculated for the six-member aminoether ring. Using this value for the heat of combustion the estimated specific impulse of nitromorpholine is 146 lbf sec/lbm.

### B. OSMOMETRIC MOLECULAR-WEIGHT DETERMINATIONS

Approximate molecular weights were determined by the osmometric methods on several preparations of poly 2,2-dinitropropyl acrylate. Runs were performed at three concentrations and, since all three determinations gave negative slopes, a numerical average was used as the estimation. The results are compiled in the following table:

| Code | Molecular Weight | % Diffusion |
|---|---|---|
| Bulk Polymer $IV_2$ | 50,000 | not determined |
| Emulsion Polymer L.T.C. 4/30 | 120,000 | 1.6 |
| Emulsion Polymer L.T.C. 5/12 | 105,000 | 0.9 |

## V. TECHNICAL PROGRESS: ORGANIC SYNTHESIS

### A. INTRODUCTION

The development of new monomers for both radical-induced polymerization and addition-type polymerization is fundamental for improved nitropolymers. Furthermore, the synthesis of plasticizers and special modifiers is essential for the solution of various problems in formulation. During the past quarter, emphasis in synthesis was placed on the exploration of new means for developing new high-energy diisocyanates. Other work dealt with the synthesis of plasticizers and diols containing functional groups suitable for modifying polymers by postcuring processes.

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*Can. J. Research 26B, 114 (1948).

## B. NITRODIOLS

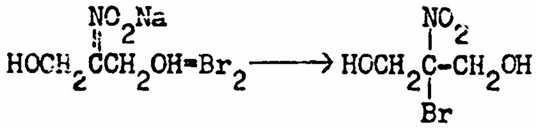
### 1. Monomers for Second-Stage Cross-Linking

#### a. Introduction

Several means are being investigated for the cross-linking of nitropolymers. This may be accomplished during polyurethane formation by polymerization in the presence of a trifunctional monomer. There are some advantages, however, to effecting the cross-linking at a second stage, after the linear polymer has been prepared. In order to study this process monomers are being prepared which contain sites for reaction other than in urethane formation. The two monomers being reported here, 2-bromo-2-nitro-1,3-propanediol and 2-nitro-1,3-propanediol, meet this requirement, in one case by containing halogen and in the other an acidic hydrogen atom.

#### b. 2-Bromo-2-nitro-1,3-propanediol

(1) The synthesis of 2-bromo-2-nitro-1,3-propanediol was carried out by the bromination of the sodium salt of 2-nitro-1,3-propanediol, as shown below:



$$HOCH_2\overset{NO_2Na}{\overset{\|}{C}}CH_2OH + Br_2 \longrightarrow HOCH_2\overset{NO_2}{\underset{Br}{C}}-CH_2OH$$

This material is reported to melt at 120 to 122°C after recrystallization from a mixed ethyl acetate and chloroform solvent.* The diol prepared in these laboratories melted at 133 to 134.5°C after recrystallization from ethylene dichloride and gave an elemental analysis corresponding to that of the desired compound.

(2) Experimental

The damp salt obtained from the reaction of nitromethane, formaldehyde, and sodium hydroxide on a 4.5 mole scale was stirred in 2.5 liters of chloroform and, with stirring and cooling to maintain the temperature at 10°C, a solution of bromine in chloroform was added until a permanent bromine color was obtained. A total of 528 g (3.3 moles) of bromine in 575 ml of chloroform was required. The solution was then filtered and the residue was washed with about 200 ml of acetone. The combined filtrates were evaporated to dryness *in vacuo*, and the residue was stirred with 1 liter of dry ethyl acetate at 50°C. After filtration, 2 liters of chloroform were added to the ethyl acetate solution, and the crystalline

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*E. Schmidt and R. Wilkendorf, Ber. 52, 389 (1919).

product separated on cooling. After three more recrystallizations from this mixed solvent the diol melted at about 115°C, and still contained some colored impurity. Two recrystallizations from ethylene dichloride then raised the melting point to 133 to 134.5°C and gave 187 g of the colorless product.

Anal. Calc'd for $C_3H_6NO_4Br$: %C, 17.84; %H, 2.99; %Br, 39.56; %N, 6.94

Found: %C, 18.43; %H, 3.[illegible]2; %Br, 39.44; %N, 6.92

c. 5,5,5-Trinitro-1,2-pentanediol

5,5,5-Trinitro-1,2-pentanediol was originally obtained as a viscous oil, and has been used for some time in polymerization reactions.* A recent batch, prepared in the usual manner, crystallized and showed a melting point of 54 to 55°C. Samples of previous preparations also solidified upon seeding. The diol can be recrystallized from ethylene dichloride.

Anal. Calc'd for $C_5H_9N_3O_8$: %C, 25.11; %H, 3.79; %N, 17.57

Found: %C, 24.68; %H, 3.82; %N, 18.03

## C. NITRO DICARBOXYLIC ACIDS

### 1. 3-Nitraza-1,5-pentanedioic Acid

a. Discussion

Attempts have been made to prepare 3-nitraza-1,5-pentanedioic acid (nitriminodiacetic acid), an intermediate in the proposed preparation of 2-nitraza-1,3-propane diisocyanate. The methods used have involved (1) the nitration of iminodiacetic acid, (2) the oxidation of nitromorpholine, and (3) the hydrolysis of nitriminodiacetonitrile.

(1) The nitration of iminodiacetic acid by anhydrous nitric acid was reported by Franchimont and Dubsky in 1912.** Using this method, a crude nitriminodiacetic acid was obtained when the nitration was carried out on a very small scale, but increasing the size of the batch yielded an unstable product. An attempt to nitrate iminodiacetic acid using an acetic anhydride and nitric acid mixture in the presence of a chloride catalyst was unsuccessful.

(2) Unsuccessful attempts were made to oxidize nitromorpholine using 50% and 70% nitric acid and using sodium dichromate in a 50%

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*Aerojet Report No. 540, p. 38.

**Centralblatt 1912 II, 1428; Beil. EI4, 488.

sulfuric acid solution. In all cases, essentially quantitative recoveries of the nitromorpholine were made. This stability of the nitromorpholine structure to oxidation is in marked contrast with the ease with which cyclohexanone, tetrahydrofuran, and tetrahydropyran were oxidized.

(3) The hydrolysis of nitriminodiacetonitrile appears to have yielded the desired nitriminodiacetic acid, but the initial experiment indicates a more complex reaction than the hydrolysis of 4-nitraza-1,7-heptane dinitrile, 3,6-dinitraza-1,8-octane dinitrile, and other previously reported dinitriles. Nitriminodiacetonitrile was first reported by Franchimont and Dubsky.* The Aerojet preparation of this material is a modification (use of the pre-formed nitric acid salt of iminodiacetonitrile) of the chloride-catalyzed nitration of iminodiacetonitrile reported by Wright et al.** Iminodiacetonitrile was obtained by the action of 10% hydrocyanic acid on hexamethylene tetramine following the method described by Dubsky.***

### b. Experimental

#### (1) Hydrolysis of Iminodiacetonitrile

To a solution of 500 g (3.57 moles) hexamethylene tetramine in a mixture of 850 ml (600 g; 22.2 moles) anhydrous hydrocyanic acid and 5400 ml water was added 250 ml (1.87 moles) 23% hydrochloric acid with stirring while the temperature was held at 20°C. The addition was completed in 1 hr and stirring was continued for 2 hr. The solution was stored for 21 to 24 hr in a bath of running tap water. The bulk of the product crystallized from solution during this time. Additional product was obtained on chilling the mixture to 0 to 5°C. The product was collected by filtration, washed sparingly with ice water, and dried in a vacuum desiccator over potassium hydroxide pellets. The yield was 398 to 451.5 g, corresponding to 39.2 to 44.4% of the theoretical. The yields were on the high side when the storage period was increased an additional 24 to 36 hr, but the product was highly colored in such cases.

#### (2) Nitric Acid Salt of Iminodiacetonitrile

To a solution of 34.2 g (0.36 mole) iminodiacetonitrile in 250 ml methanol was added 24 ml (0.38 mole) 70% nitric acid during a 5-min period at 25°C. The mixture was chilled to 0°C, and the salt was collected by filtration, washed with chilled methanol, then with absolute ether, and dried. The product weighed 50.5 g, corresponding to an 88.9%

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*Centralblatt 1912 II, 1428; Beil. EI4, 488.

**Can. J. Research 26B, 124 (1948).

***Ber. 54, 2659 (1921).

yield, and melted at 128 to 132°C. An analytical sample was prepared by recrystallization of the salt from methanol and treatment of the solution with charcoal.

Anal. Calc'd for $C_4H_6O_3N_4$: %C, 30.38; %H, 3.82; %N, 35.44

Found: %C, 30.35; %H, 3.72; %N, 34.80

### (3) Nitriminodiacetonitrile

A nitrating solution was prepared by the successive addition of 2 ml (0.048 mole) anhydrous nitric acid and 1 ml (0.012 mole) 37% hydrochloric acid to 41.5 ml (0.438 mole) acetic anhydride at 20°C. To this solution was added 39 g (0.246 mole) of the nitric acid salt of iminodiacetonitrile in portions during a 15 to 20-min period at 20°C. The salt dissolved in the nitrating medium, and product began to precipitate from solution before the addition of the salt was completed. Stirring was continued for 20 min at 20°C. The slurry was chilled to 5°C, diluted with 100 ml ice water, and filtered. The product was washed with ice water, washed sparingly with chilled methanol, and finally washed with ether. The last traces of solvent were removed in a vacuum desiccator over potassium hydroxide pellets. The nitriminodiacetonitrile (faint cream color) weighed 30.7 g, corresponding to an 89.1% yield, and melted at 95 to 96.5°C. An analytical sample was prepared by recrystallization from anhydrous benzene. However, this solvent is not satisfactory for the recrystallization of large quantities of the product due to the rather low solubility. The colorless nitriminodiacetonitrile melted at 95.5 to 96.5°C.

Anal Calc'd for $C_4H_4O_2N_4$: %C, 34.29; %H, 2.88; %N, 39.99

Found: %C, 34.48; %H, 2.86; %N, 39.58

### (4) Nitriminodiacetic Acid

A mixture of 15 g (0.107 mole) nitriminodiacetonitrile and 50 ml 37% hydrochloric acid was heated on the steam bath for 1 hr and stored at room temperature overnight. The reaction was extremely rapid during the initial stage. The dinitrile dissolved without warming the mixture, followed by an immediate and vigorous evolution of hydrogen chloride with an accompanying temperature rise and rapid darkening of the solution. The mixture (at room temperature) was filtered, and the solid was dried (8.2 g) and identified as ammonium chloride. The filtrate was stripped to dryness in vacuo to yield a colored solid weighing 18.5 g. The latter material was treated with hot acetone, and the undissolved portion (ammonium chloride, 2.4 g) was removed by filtration. The acetone filtrate was evaporated to dryness to yield a black, viscous residue weighing 15 g which crystallized on standing at room temperature. This material (mp 80 to 130°C, dec.), was dissolved in 100 ml hot absolute ethyl acetate and filtered from the undissolved tar. The filtrate was reheated, and treatment with charcoal removed the greater portion of the color. The yellow solution was stripped to dryness to yield 12 to 12.5 g of solid melting at 130 to 145°C (dec). The product was redissolved in 35 ml absolute ethyl acetate but could not be crystallized from this solvent by chilling, scratching, or seeding. The product was reprecipitated by the addition of methylene chloride. The initial material precipitated as oil, carrying most of the remaining color. The supernatant liquid was decanted, and 5 g of product crystallized, melting at 140 to 146°C (dec). The filtrate was evaporated to dryness to yield the remaining 2.5 g of product, melting at 145 to 150°C (dec). A suitable solvent could not be found for the recrystallization of this material. The product was soluble in water, methanol, ethanol, isopropanol, ethyl acetate, dioxan, and acetone, and was apparently quite insoluble in chloroform, methylene chloride, ether, and benzene. A sample of the higher-melting fraction was submitted for analysis for the purpose of identification.

Anal. Calc'd for $C_4H_6O_6N_2$: %C, 26.97; %H, 3.40; %N, 15.73

Found: %C, 28.56, %H, 4.28; %N, 15.74

The product has an impact stability greater than 100 cm/2 kg.

## D. NITRO PLASTICIZERS

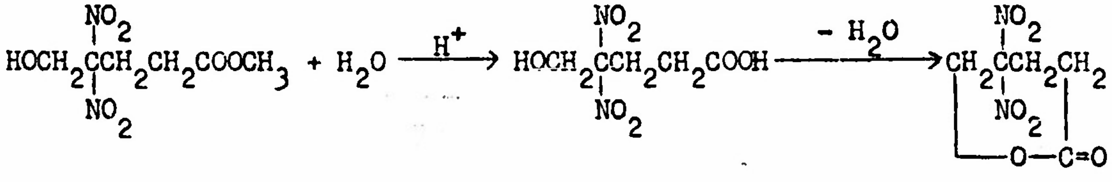
### 1. Introduction

A number of high-energy compounds are being examined for their effectiveness as plasticizers for nitropolymers. In order to obtain some correlation between structure and plasticizing properties, materials are being used for this study which contain a variety of functional groups. Among the materials under investigation are esters, amides, ethers, lactones, and ketones containing nitro groups.

### 2. 4,4-Dinitro-valerolactone

#### a. Discussion

(1) It has previously been reported that the methyl ester of 5-hydroxy-4,4-dinitro pentanoic acid cyclizes to give 4,4-dinitro valerolactone in about a 42% yield by hydrolysis with hydrochloric acid and subsequent vacuum distillation.*



$$HOCH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2COOCH_3 + H_2O \xrightarrow{H^+} HOCH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2COOH \xrightarrow{-H_2O} \underbrace{CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2}_{O-C=O}$$

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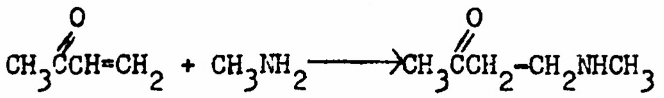
*Aerojet Report No. 404, 12 September 1949, p. 31; K. Klager, J. Org. Chem. 16, 163 (1951).

This procedure has been modified to increase the yield of the lactone by treating the crude mixture of lactone and acid obtained from the hydrolysis reaction with thionyl chloride. The use of this reagent resulted in a more efficient lactonization, and the distillation of the lactone, previously required, could be eliminated. The nitration of 1-methylamino-3-butanone was considered the most feasible method of synthesizing 5-nitraza-2-hexanone. The preparation of this β-aminoketone was therefore attempted by the Michael reaction of methylamine with methyl vinyl ketone:



$$CH_3\overset{O}{\overset{/\!/}{C}}CH{=}CH_2 + CH_3NH_2 \longrightarrow CH_3\overset{O}{\overset{/\!/}{C}}CH_2{-}CH_2NHCH_3$$

This type of reaction is known to be subject to some limitations since further reaction of the desired secondary amine with the unsaturated compound to give a tertiary amine cannot always be prevented.* In order to minimize this possibility the Aerojet reaction was performed with a large excess of aqueous methylamine. The product from the reaction was a dark liquid which was unstable to heat. No solid salt could be obtained from this material, and an attempt to nitrate the crude product was unsuccessful. Distillation under a high vacuum yielded a small amount of oil believed to be the aminoketone, but which was not stable on standing. Instability to heat and acids is reportedly not uncommon with these compounds.** This synthesis is thus more complex than anticipated, and further work will be postponed until the synthesis of other promising plasticizers can be completed.

(2) In applying this method it was found that in several runs only low yields of the lactone could be obtained. In these instances the crude product was found to be contaminated with 4,4-dinitroheptanedioic acid. This acid would most likely arise as a by-product from the synthesis of the starting 5-hydroxy-4,4-dinitrovalerate from potassium dinitroethanol and methyl acrylate. There are some indications, however, that the amount of acid obtained on lactonization increases with the age of the starting ester. It may be concluded that this synthesis should be carried out rapidly and with 5-hydroxy-4,4-dinitropentanoate prepared from sodium 4,4-dinitrobutyrate and formaldehyde, and thus free of the dinitroheptanedioate.

b. Experimental

A mixture of 22 g (1 mole) of methyl 5-hydroxy-4,4-dinitropentanoate and 400 ml of concentrated hydrochloric acid was refluxed for 2 hr. The solution was cooled, diluted with 400 ml of water, and extracted

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*R. B. Wagner and H. D. Zook, Synthetic Organic Chemistry, Chapman and Hall, New York, 1953, p. 673.

**N. H. Cromwell, Chem. Revs., 38, 83, (1946).

three times with 200-ml portions of ether. After the extracts were dried over sodium sulfate, the ether was removed in vacuo to leave 211 g of a dark-brown oil. This crude acid was dropped into 300 ml of thionyl chloride with stirring at 50°C over a period of 2 hr. The mixture was refluxed for another hour, and the excess thionyl chloride was removed in vacuo. The crude, oily product was dissolved in 200 ml of ether and cooled in a dry ice and acetone bath. The solid lactone crystallized from the ether solution and could be recrystallized from methylene chloride or ether to melt at 78.5 to 79.5°C (75% yield).

### 3. Attempted Preparation of 5-Nitraza-2-hexanone

The observation that the plasticizing efficiency of methyl 4-nitraza pentanoate was far greater than that of methyl 4,4-dinitropentanoate suggested a comparison of other similar structures. 5,5-Dinitro-2-hexanone has been used as a nitro plasticizer for some time with good success. If the analogous 5-nitraza-2-hexanone could be synthesized another excellent nitroplasticizer would be available.

## PART II

## DEVELOPMENT OF A NITROPOLYMER PROPELLANT
(Contract NOas 54-399-c)

### I. TECHNICAL PROGRESS: RHEOLOGICAL STUDIES

### A. INTRODUCTION

1. The ultimate goals of this contract are to evaluate the compounds synthesized on the nitropolymer program in terms of rheological and ballistic properties, and to formulate a nitropolymer propellant of high performance and burning rate, which is expected to be applicable to booster and sustainer rockets. These two goals are referred to hereafter as Phase I and Phase II of this contract.

2. The evaluation phase has several immediate goals. One of these is to characterize the solubility properties of nitropolymers. The practical value of such characterization is that it defines a range of chemical structures from which permanent, efficient, and compatible plasticizers may be chosen for a given nitropolymer. The results of these studies are presented and discussed in Sections B, C, and D.

3. Another immediate goal of the evaluation phase is the determination of the rheological properties of both oxidizer-filled and non-filled plasticized nitropolymer binders. The practical value of this study lies in the determination of the concentrations of plasticizer and oxidizer which lead to optimum tensile strength, ultimate strain, and impact strength. Initial results are presented in Section E.

4. In order to produce a propellant with desirable ballistic properties, it is necessary to modify the basic composition by incorporating a small amount ($<5\%$) of one or more additives. Initial results are presented in Section II,A.

### B. THERMODYNAMICS OF POLYMER-SOLVENT MIXTURES

1. In order to understand why some solvents display a marked affinity for a polymer while others do not, it is necessary to define the tendencies which cause a polymer to dissolve or swell in a solvent. These tendencies arise from two sources: statistical and energetic. The "statistical tendency" arises from the number of configurations available to the polymer molecules distributed among solvent molecules. It is measured by the change in entropy which results when $n_1$ solvent molecules and $n_2$ polymer molecules, each of average chain length $\bar{x}$, are mixed in a volume V. The increase in entropy* is given by

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*P. J. Flory, J. Chem Phys. 13, 453 (1945).

$$\Delta S_M = -k\,(n_1 \ln v_1 + n_2 \ln v_2) \tag{1}$$

where $v_1$, equal to $n_1/(n_1 + \bar{x}n_2)$, and $v_2$, equal to $\bar{x}n_2/(n_1 + \bar{x}n_2)$, are the volume fractions of solvent and polymer respectively. Similarly, it can be shown* that the heat of mixing is given by

$$\Delta H_M = B_{12}\,(V_1/N)\,n_1\,v_1 \tag{2}$$

where $B_{12}$ is known as the cohesive energy density of the mixture, $V_1$ is the molar volume of the solvent, and N is Avogadro's number. The quantity $B_{12}$ $V_1/N$ is equal to $Z\Delta W_{12}$, where Z (approximately equal to 6) is the coordination number of the quasi-crystalline lattice upon which the polymer and solvent molecules are mixed, and $\Delta W_{12}$ is the heat of the reaction $1/2\ [1,1] + 1/2\ [2,2] = [1,2]$. The term $[1,1]$ represents a solvent-solvent bond, etc. The overall tendency of the polymer and solvent to mix is known as the free energy of mixing and is merely the sum of $\Delta H_M$ and $-T\Delta S_M$, so that

$$\Delta F_M = B_{12}\,(V_1/N)\,n_1v_2 + kT(n_1 \ln v_1 + n_2 \ln v_2) \tag{3}$$

2. For the purpose of relating the thermodynamic properties of a polymer-solvent mixture to experimentally measured quantities such as vapor pressure, osmotic pressure, swelling ratio, and phase equilibria in general, it is convenient to work with the chemical activity $a_1$ of the solvent, defined by

$$kT \ln a_1 = \frac{\partial\,\Delta F_M}{\partial n_1} = B_{12}\,(V_1/N)\,v_2^2 + kT \ln(1-v_2) + v_2(1-1/\bar{x}) + (2/Z)\,v_2^2 \tag{4}$$

Equation (4) may be rewritten more simply:

$$\ln a_1 = \ln(1 - v_2) + v_2\,(1 - 1/\bar{x}) + \chi_{12}\,v_2^2 \tag{5}$$

where

$$\chi_{12} = \frac{2}{Z} + \frac{B_{12}V_1}{RT} \tag{6}$$

Equation (5) states that, if $a_1$ can be measured as a function of $v_2$, both $\bar{x}$, the degree of polymerization, and $\chi_{12}$, the interaction parameter, may be calculated. Note that $a_1$ is so defined that, as $v_2$ approaches 0, $a_1$ approaches 1.

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*Ibid.

3. In the case of a solution of a linear polymer of low molecular weight in a volatile solvent, it is convenient to measure the vapor-pressure lowering; the activity is given by

$$a_1 = P_1/P_1^o \tag{7}$$

In the case of a solution of linear polymer of high molecular weight in a volatile or non-volatile solvent, it is convenient to measure the osmotic pressure ($\pi$); the activity is given by

$$a_1 = \exp\left[-\pi V_1/RT\right] \tag{8}$$

In the case of dilute solutions, Equations (7) and (8) simplify respectively to

$$\frac{P_1^o - P}{P_1^o\, v_2} = \frac{1}{\bar{x}} + v_2(1/2 - \chi_{12}) \tag{9}$$

and

$$\frac{\pi V_1}{v_2 RT} = \frac{1}{\bar{x}} + v_2\,(1/2 - \chi_{12}) \tag{10}$$

Mixing a cross-linked polymer with a volatile or non-volatile solvent results in the formation of a swollen gel. By a rather lengthy analysis it can be shown* that, for swelling ratios larger than 10,

$$1/2 - \chi_{12} = \frac{GV_1}{RT}\, q^{5/3} = \frac{\nu_e V_1}{V_o}\, q^{5/3} \tag{11}$$

where G is the shear modulus of the swollen gel; $q = 1/v_2 = V/V_o$ is the ratio of the volume of the swollen gel to that of the unswollen material; and $\frac{G}{RT} = \frac{\nu_e}{V_o}$ is equal to the number of elastic chains per unit volume of unswollen material.

C. SOLUBILITY AND THE COHESIVE ENERGY DENSITY (C.E.D.)

1. The quantity $B_{12}$ has the dimensions of energy per unit volume and, as such, is a measure of the heat evolved when one half of a polymer-polymer bond and one half of a solvent-solvent bond reform to one polymer-solvent bond. By definition, then, $B_{12}$ may be decomposed into three terms:

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*P. J. Flory, J. Chem. Phys. 18, 108 (1950).

$$B_{12} = B_1 + B_2 - 2K\sqrt{B_1 B_2} \tag{12}$$

where

$B_1$ is the c.e.d. of the pure solvent

$B_2$ is that of the pure polymer

K is a measure of departure from the general rule that the energy of heterodipolar bonds is the root mean of the energies of the homodipolar bonds

A value of K greater than unity indicates the presence of specific interactions between the polymer and solvent such as may be due to hydrogen bonding or crystallization. A value of K less than unity indicates the presence of specific repulsions between the polymer and solvent such as may be due to steric effects.

2. Some implications of Equation (12) may be seen by reference to Figure 7, which shows the predicted behavior of a polymer with c.e.d. equal to 150 cal/cm$^3$ in various types of solvents. Regardless of the value of K, $B_{12}$ is a minimum when $B_1$ equals $K^2B_2$ (equal to $(1-K^2)\ B_2$). And because $B_{12}$ is directly proportional to the heat of mixing, the enthalpy or potential energy of the polymer-solvent mixture can be minimized by proper choice of solvent or of $B_1$. This principle of the minimization of the potential energy of the solution, together with the principle of maximization of the configurational entropy (Equation 1) of the solution, are the criteria that define the optimum solvent. Thus, it becomes important to determine the c.e.d. of both the pure solvent and the pure polymer.

3. From Figure 7 it is seen that for a polymer with a c.e.d. of 150 cal/cc, the optimum solvent may possess an energy density between 130 and 170 cal/cc, depending on the precise value of K. Experience dictates that a solvent whose c.e.d. deviates from that of the polymer by more than 20 cal/cc is usually not a good one, unless K also deviates markedly from unity. Thus a rough rule of thumb equates the c.e.d. of the solvent with that of the polymer for optimum solution tendency.

4. The c.e.d. of a pure solvent is readily determined from its latent heat of vaporization. By definition the energy per unit volume needed to break all the solvent-solvent bonds is simply the energy of vaporization divided by the specific volume.

$$B_1 = (L - RT)/V_1 \tag{13}$$

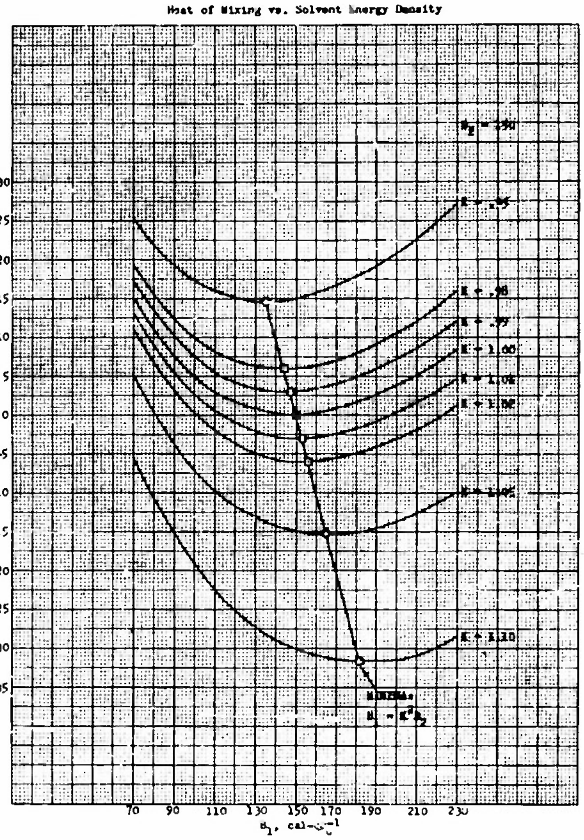

Figure 7

If the data are not available, the latent heat of vaporization can be determined by the modified Trouton's rule, using an appropriate value for the entropy of vaporization. Correlations also exist* between the latent heat of vaporization and the boiling point of the pure substance.

5. The c.e.d. of a bulk polymer is not readily obtained. The material usually has an extremely high boiling point, provided that it does not decompose before boiling. The c.e.d. must therefore be obtained either by estimating it from a table of group contributions, or by calculating it from the measured c.e.d. of a mixture whose K is known to be unity. Both methods have been used.

6. Small** has shown that a quantity F, which has the dimensions of cal$^{1/2}$ cc$^{1/2}$ is an additive function of the various chemical groupings within a molecule. The c.e.d. of a substance is thus estimated from the relation

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*E. E. Walker, J. Applied Chem. 2, 474 (1952).

**P. A. Small, J. Applied Chem. 3, 71 (1953).

$$B = (\Sigma F/V)^2 \tag{14}$$

in which V is the molal volume.

7. Table XV shows the measured and estimated values of the c.e.d. of six solvents and three nitropolymers. The agreement, where comparison is available, is good.

### TABLE XV

MEASURED AND ESTIMATED COHESIVE ENERGY DENSITIES (C.E.D.) AT 20°C

| Solvent | $t_B$, °C | L, kcal/mole | L-RT | $V_1$, cc/mole | $B_1$ (from L) | $B_1$ (est) |
|---|---|---|---|---|---|---|
| Acetone | 56.2 | 7.76 | 7.18 | 73.5 | 97.7 | 91.5 |
| Dioxan | 101.4 | 8.90 | 8.32 | 85.25 | 97.6 | 83.0 |
| DMF* | 152.6 | 11.90 | 11.32 | 76.8 | 148 | 148 |
| MDNV | 300** | 20.9 | 20.3 | 159 | 127 | 127 |
| MNV | 285** | 19.7 | 19.1 | 132 | 145 | 146 |
| TNB | 330** | 23.2 | 22.6 | 134 | 169 | 162 |

| Nitropolymer | $V_2$ | $B_2$ (est) | B (measured in solvents with K=1) |
|---|---|---|---|
| I-A | 280 | 160 | 164 |
| XIII-A | 280 | 145 | 148 |
| DNPA | 138.2 | 135 | |

---

*Symbols for solvents are defined in Table XVII.

**Estimated from the boiling points at reduced pressure, using an entropy of vaporization of 33 cal/mole.

## D. EXPERIMENTAL

1. Equation (11) reveals that the shear modulus, G, must be known in order to evaluate the c.e.d. of polymer-solvent mixtures from swelling measurements. Rather than assume that the value of G, determined by modulimetry for XIII-A-40D, was representative of the swollen gel, G was calculated indirectly (Equations 5, 7, 11) by first determining $\chi_{12}$ for solutions of Nitropolymers XIII-A and I-A in acetone from vapor-pressure measurements, and then determining q by swelling the corresponding cross-linked polymers in acetone. The results of these measurements are shown below and compared with the result obtained by modulimetry.

| Polymer | $v_2$ | $a_1$ | $\chi_{12}$ | q | $\nu_e/V_o$ | G, dynes $cm^{-2}$ | E, dynes $cm^{-2}$ |
|---|---|---|---|---|---|---|---|
| XIII-A | 0.145 | 0.970 | -0.93 | 26.4 | $8.36 \times 10^{-5}$ | $2.04 \times 10^6$ | $6.1 \times 10^6$ |
| I-A | 0.200 | 0.954 | -0.61 | 22.6 | $8.31 \times 10^{-5}$ | $2.02 \times 10^6$ | $6.1 \times 10^6$ |

The fact that the measured value of Young's modulus E is the same for both polymers at different concentrations of solvent indicates that it is truly characteristic of the binder alone. This is confirmed by the excellent agreement of the value, $6.1 \times 10^6$, with the value obtained from modulimetry, $8.3 \times 10^6$.[*]

2. Substitution of the measured value of the shear modulus into Equation (11), along with measured swelling ratios, permits calculation of the c.e.d. and K values for a large number of solvent-polymer combinations. Results to date are shown in Table XVI. In calculating $B_{12}$ from $\chi_{12}$ (Equation 6) the value 0.3 is assigned to the lattice parameter $2/Z$. This conforms with available data and corresponds to a coordination number, Z, slightly less than 7. The tabulated values of K are obtained with the aid of Figure 7, which is based on a value of $B_2 = 150$, which corresponds pretty nearly to the estimated value for Nitropolymer XIII-A, which is being used in many swelling experiments.

### TABLE XVI

### INTERACTION CONSTANTS OF VARIOUS SOLVENTS WITH XIII-A AND I-A

Nitropolymer XIII-A

| Solvent | q | $\chi_{12}$ | $\Delta B_{12}$ | $B_1$ | K |
|---|---|---|---|---|---|
| Acetone | 26.4 | -0.935 | -9.78 | 97.7 | 1.07 |
| Dioxan | 11.0 | +0.113 | -1.28 | 97.6 | 1.03 |
| DMF | 29.0 | -1.253 | -11.76 | 148 | 1.04 |
| MDNV | 3.3 | +0.566 | +0.97 | 127 | 1.00 |
| MNV | 17.6 | -0.80 | -3.5 | 145 | 1.01 |
| TNB | 5.3 | +0.431 | +0.57 | 169 | 1.00 |

Nitropolymer I-A

| Solvent | q | $\chi_{12}$ | $\Delta B_{12}$ | $B_1$ | K |
|---|---|---|---|---|---|
| Acetone | 22.6 | -0.607 | -7.18 | 97.7 | 1.05 |
| Dioxan | 15.2 | -0.163 | -3.16 | 97.6 | 1.04 |
| DMF | 27.1 | -1.066 | -10.35 | 148 | 1.04 |
| DMNV | 10.5 | -0.168 | -1.71 | 127 | 1.01 |
| MNV | 21.9 | -1.387 | -7.43 | 145 | 1.02 |
| TNB | 9.05 | +0.061 | -1.04 | 169 | 1.01 |

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[*] Aerojet Report No. 817, p. 26.

3. The interaction constant K may also be calculated from vapor-pressure measurements by means of Equations (5), (6), and (12). Values of K obtained from further vapor pressure and swelling measurements are summarized in Table XVII for a large number of solvents. Because Figure 7 is based on $B_2 = 150$, whereas the estimated value of $B_2$ for Nitropolymer I-A is 164, the values of K obtained by swelling this material in various solvents will be high by about 0.01, and the summarized values in Table XVII have been lowered accordingly.

### TABLE XVII

### INTERACTION CONSTANTS OF VARIOUS SOLVENTS WITH A NITROPOLYURETHANE BINDER OF C.E.D. = 150

| Solvent | K, Interaction Constant |
|---|---|
| Nitromethane | 1.00 |
| Nitroethane | 1.00 |
| Trinitrobutane (TNB) | 1.00 |
| Methyl-4,4-dinitrovalerate (MDNV) | 1.00 |
| Methyl-4-nitrazavalerate (MNV) | 1.00 |
| Ethyl acetate | 1.02 |
| Acetic anhydride | 1.03 |
| Maleic anhydride | 1.03 |
| Dioxane | 1.04 |
| Dimethylformamide (DMF) | 1.04 |
| Methyl ethyl ketone | 1.04 |
| $\gamma$-Butyrolactone | 1.05 |
| Acetone | 1.05 |

4. The values of K presented in Table XVII have been calculated from data obtained on both pure and mixed solvents. Thus, for example, since experiments with pure solvents show that both TNB and MNV are characterized by K of unity, it should be possible to calculate the expected swelling ratio for a mixture of the two solvents. Conversely, the agreement of the measured swelling ratio with the estimated values lends further support to the definition of the interaction constants presented in Table XVII. Calculations were carried out, and in all cases agreement was excellent. This means, in the simplified picture of nitropolymers in nitrosolvents, that maximum swelling is achieved when $B_2$ equals $B_1$, when $V_1$ equals 1. Thus trinitropentanone (TNP) has been reported to be incompatible with Nitropolymer XIII-A but not with Nitropolymer I-A. This means simply that the c.e.d. of trinitropentanone is probably between 165 and 170, just right for I-A but too high for XIII-A. This prediction will be checked when the density and boiling point of TNP become available. As another example, it is predicted that methyl dinitrovalerate (c.e.d. = 127) should be a good solvent for poly-2,2-dinitropropylacrylate (DNPA) (c.e.d. = 135).

5. This simplified picture (K = 1) allows a more accurate determination of $B_2$ for Nitropolymers I-A and XIII-A, by means of Equations (11) and (12), with K = 1. The average values of B for XIII-A and I-A are listed in Table XV and are slightly lower than the estimated values.

6. Now that the solubility phenomena of nitropolymers in nitrosolvents is beginning to fit into a reasonably simple and accurate picture, it is necessary to assess the practical value of this treatment. This is the ability to predict a good solvent with a high impulse. The four logical candidates are displayed in Figure 8, where density impulse is plotted against c.e.d. The optimum combination should be a mixture of trinitrobutane (TNB) with whatever amount of methyl dinitrovalerate (MDNV) or nitromorpholine (NMPN) is needed to adjust the c.e.d. to a value within 20 units of the c.e.d. of the polymer binder. Other candidates for which data are not yet available are trinitropentanone ($I_{sp}$ = 228), and butylene glycol dinitrate ($I_{sp}$ = 233). This completes the study of plasticizer efficiency.

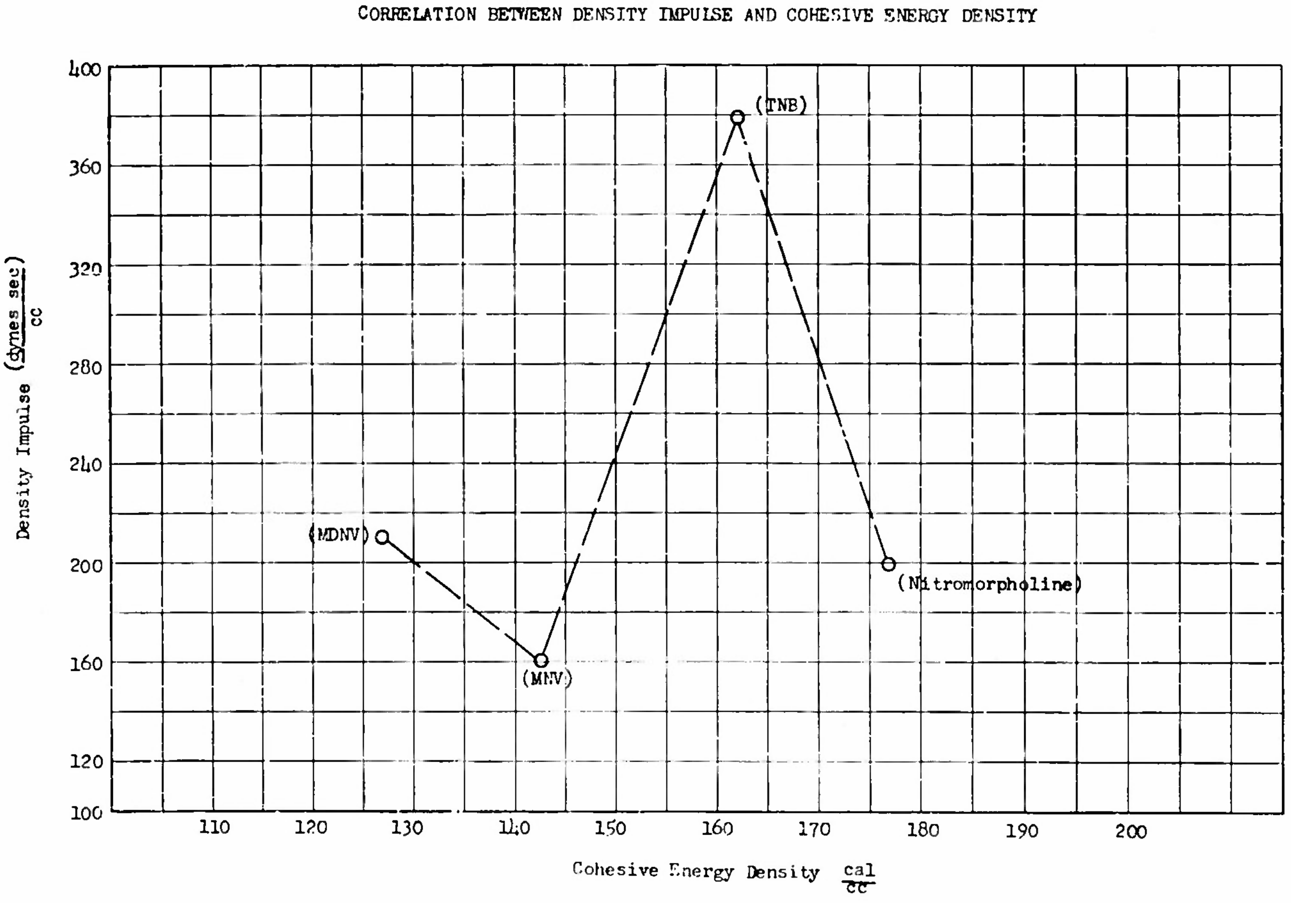

Figure 8

## E. RHEOLOGY OF NITROPOLYMERS

1. Four solutions of linear Nitropolymer XIII-A in acetone were prepared containing respectively 6, 10, 18, and 24% MNV. After digestion the mixtures were roll-milled to constant weight at 150°F. Partly by design, the 18% mixture was worked on the mill for a period of 3 hr, at the end of which time it became exceedingly tough and horny. The inference is that cross-linking occurs slowly at higher temperatures.

2. The four milled samples were compression-molded into sheets 0.2 in. thick. Tensile specimens 0.25 in. wide were cut from the 6, 12, and 24% sheets. Although each of the strands was stretched about 1000% on the Scott tensile tester, no appreciable stress was registered. Strands of large cross-sectional area are being prepared.

3. In order to obtain some characterization of the available materials, the strands were hung vertically parallel to a meter stick, a weight was tied to the bottom of the gage length, and the length of the deformed strand was recorded at three or four intervals of time. Figure 9 reveals a fortuitously good correlation between 5-sec Young's modulus, 1-min Newtonian viscosity, and plasticizer content. No significance is yet attached to the slopes of the plot.

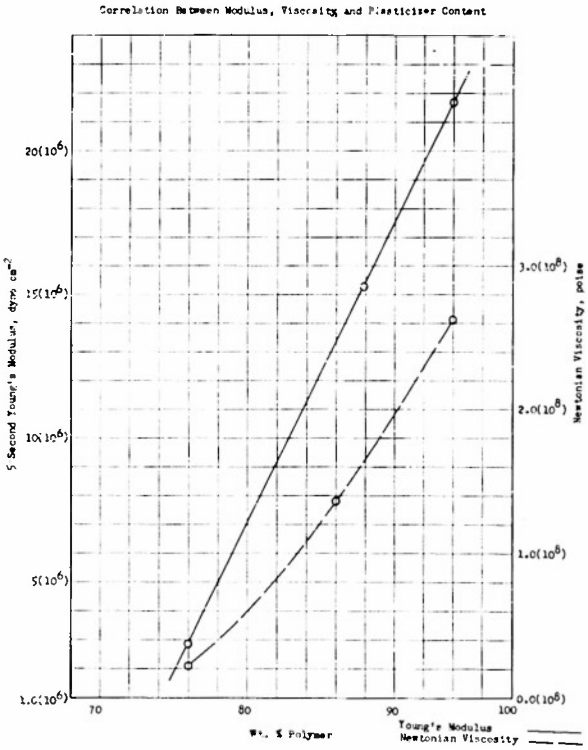

Figure 9

## II. TECHNICAL PROGRESS: BALLISTIC STUDIES

### BURNING-RATE STUDIES

A stoichiometric mixture of $NH_4ClO_4$ and XIII-A (1.925/1 by wt) was prepared by ball-mill procedure. The burning rate vs pressure curve is shown in Figure 10. The value of 0.73 in. $sec^{-1}$ at 1000 psi is considerably lower than that* obtained from a stoichiometric mixture of $NH_4ClO_4$, XIII-A, and DNH (dinitrohexanone), prepared by roll-mill procedure. The ball-milled material was then roll-milled with added plasticizer and oxidizer to yield a final stoichiometric composition of 12.6 parts XIII-A, 15.2 parts MNV, and 72.2 parts $NH_4ClO_4$. The burning rate vs pressure curve of this mixture is shown in Figure 10. The "super-rate" phenomenon exhibited between 1000 and 1500 psi may be attributed to residual acetone (ca 5%) in the roll-milled composition.

BURNING RATE - PRESSURE CHARACTERISTICS OF A STOICHIOMETRIC MIXTURE OF

XIIIA - 15.2 MNV - 72.2 $NH_4ClO_4$

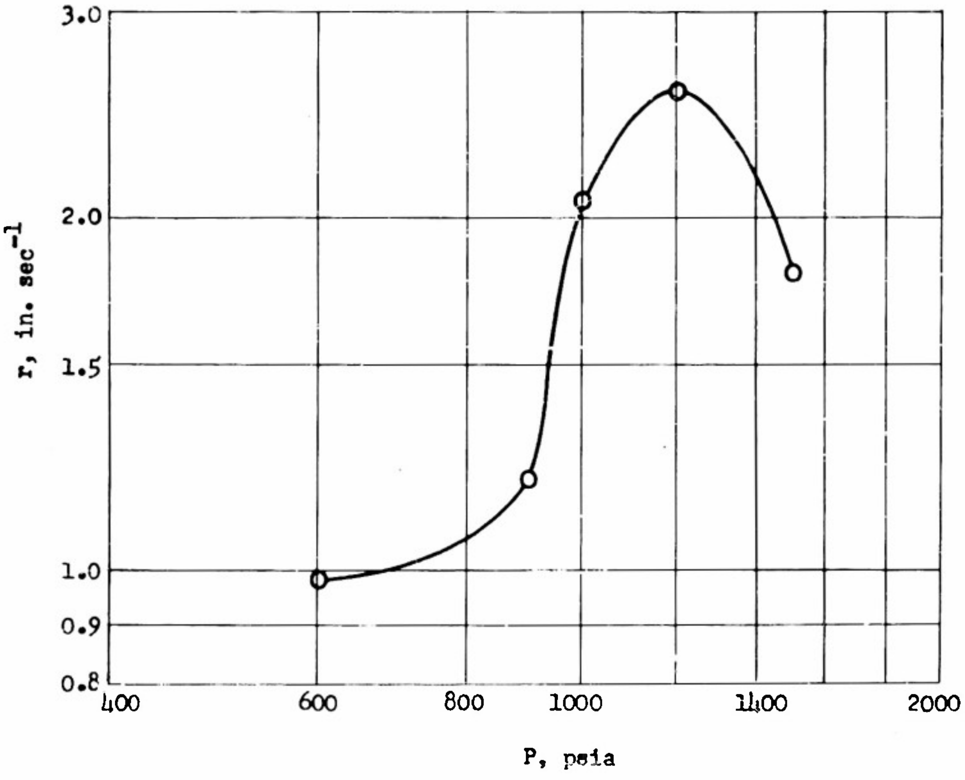

Figure 10

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*Aerojet Report No. 817, 3 May 1954, Table IV, 1.6 in. $sec^{-1}$.

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