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30 December 1953
Report No. 772
(Quarterly)
Copy No. 5

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RESEARCH IN

NITROPOLYMERS AND

THEIR APPLICATION TO

SOLID SMOKELESS

PROPELLANTS

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

Aerojet-General CORPORATION   THE GENERAL TIRE

A SUBSIDIARY OF THE GENERAL TIRE & RUBBER COMPANY
AZUSA, CALIFORNIA

54AA-12306

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30 December 1953

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RESEARCH IN NITROPOLYMERS AND THEIR

APPLICATION TO SOLID SMOKELESS PROPELLANTS

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

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Period Covered:-

16 August through 15 November 1953

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Report No. 772

CONTRACT FULFILLMENT STATEMENT

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

I.   SUMMARY

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

B.   The more important results are summarized below:

1.   A study of the emulsion polymerization of 2,2-dinitrobutyl
acrylate revealed that the difficulties in solving this problem appear to be
due to the differences between the normally encountered monomers as compared
with the nitromonomers. These differences are the increased density, chemical
reactivity, and decreased thermal stability of the nitromonomers. The two
best emulsifying agents found to date are Tween 20 and Tween 40, but the
emulsions lack reproducibility and often stability.

2.   Utilizing 3,6-dinitro-3,6-diaza-1,8-octane diisocyanate
and the diols available on this program, a series of new polyurethanes have
been characterized by analysis, relative viscosity, and stability tests. Some
polymers have been investigated by X-ray diffraction to determine crystallinity.
The following new polymers are reported:

Polymer	Diol
XII-M	bis-β-Hydroxyethyl oxamide
XII-MN	bis-β-Hydroxyethyl oxamide
XII-N	Ethylene glycol
XII-NM	Ethylene glycol
XII-O	5,5-Dinitro-1,2-hexanediol
XII-ON	5,5-Dinitro-1,2-hexanediol

3.   The new 3,3,5,7,7-pentanitro-5-aza-1,9-nonane diisocyanate
has been used for the preparation of new polyurethanes. This diisocyanate is
particularly interesting because of the high specific impulse of polyurethanes
which can be formed with it. Two polyurethanes have been prepared, which are
of rather low molecular weight. This may be due to some monofunctional im-
purities in the diisocyanate. During purification studies it was found that
the diisocyanate forms a complex with dioxan in the molar ratio of 1:1.
However, no higher-molecular-weight polymers were obtained using this complex.

4.   The postnitration of several polyurethanes previously
prepared from 3-nitro-3-aza-1,5-pentane diisocyanate has been completed.
Polyurethane XIII-HN, the postnitrated polyurethane obtained from 3-nitraza-
1,5-pentane diisocyanate and 5,5,5-trinitro-1,2-pentanediol, has an excellent
Warburg stability. Another product is Polyurethane XIII-JN, the postnitrated

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

polymer obtained from 3-nitraza-1,5-pentane diisocyanate and 2-nitro-2-methyl-1,3-propanediol. This particular polymer shows a great variation in the relative viscosity, depending on the solvent used in measuring the relative viscosity.

5.   Polyurethane XII-A, prepared from 3,6-dinitraza-1,8-octane diisocyanate and 2,2-dinitro-1,3-propanediol, was previously obtained in an amorphous form (90% yield) and a crystalline form (10% yield) when dioxan was used as the solvent. The relative viscosity of both forms appeared to be rather low. In the search for a good polymerization solvent both acetone and butyrolactone were found to give high-molecular-weight fibrous polymers. However, when these samples were nitrated under identical conditions the polymer prepared in acetone solution was degraded further than that prepared in butyrolactone. Therefore butyrolactone appears to be the preferred solvent.

6.   Considerable effort has been made to obtain a high-molecular-weight Polyurethane XII-H from 3,6-dinitraza-1,8-octane diisocyanate and 5,5,5-trinitro-1,2-pentanediol. However in all cases only low-molecular-weight polymer has been obtained, even though the same samples of monomers have given high-molecular-weight polymers in other systems. As yet no explanation has been offered for this anomaly.

7.   The postnitration of partly cross-linked Polyurethane I-A, obtained from 3,3-dinitro-1,5-pentane diisocyanate and 2,2-dinitro-1,3-propanediol, was of interest in determining the effect of the branching agent on the physical properties of Polyurethane I-AN. The resulting postnitrated polyurethane was of higher molecular weight and better quality than the linear Polyurethane I-AN.

8.   The preparation of new polyureas by the reaction of diisocyanates with water yielded a new polyurea, XII-δ, which was prepared from 3,6-dinitraza-1,8-octane diisocyanate. The new polyurea has a very high softening point and was characterized by analysis, relative viscosity, and X-ray diffraction pattern.

9.   The postnitration of two previously reported polyureas, XIII-γ and I-α, yielded the expected derivatives, as proven by the analysis and heat of combustion. However, both the polyureas suffered considerable chain degradation during the post-nitration, even when the procedure was conducted under scrupulously anhydrous conditions.

10.   4,4-Dinitro-ε-caprolactam, an intermediate for the preparation of nitropolyamides, resisted all attempts at polymerization. Basic materials, the sodium salt of 4,4-dinitrohexanoic acid, and ferric acetylacetonate were used as catalysts. Under very vigorous conditions the reaction mixture fumed off.

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11. The determination of the heat of combustion of a series of compounds containing the nitramino group caused unexpected difficulties. A phenomenon was observed which was named "corrosive burning." Instead of normal combustion, the sample burned in an explosive manner upon ignition, attacking the Parr bomb, with the formation of heavy metal oxides and large amounts of acid. A glass liner for the bomb was designed, and normal combustion was achieved in place of the corrosive burning.

12. The molecular weights of all fractions previously obtained in a fractionation study of Polyurethane I-J have been determined. This work led to the evaluation of the constants of the Staudinger equation and the relationship of intrinsic viscosity and molecular weight.

13. In order to form a propellant grain a process must be developed whereby either the polymerization mixture can be cast into the mold or the grain can be formed by some molding or extrusion process. Efforts have been continuing toward the development of products having desirable physical characteristics and which can be formulated by either a casting or forming process. Branched polyurethanes of both I-A and XIII-A have been prepared using small amounts of nib glycerol as a branching or cross-linking agent. Such branched materials when swollen by solvents or plasticizers are quite rubbery. In the solvent-free form they exhibit a more fibrous character.

14. Where high-energy plasticizers have been used as polymerization solvents the nitroplasticizers have interfered and acted as chain stoppers for the polymerization. Therefore, in order to introduce such plasticizers into a highly branched polymer the technique has been adopted of adding the nitroplasticizer to previously prepared polymer slurried with water in a Waring Blendor. The resulting spongy material, when dried on a roller mill, yields a homogeneous, rubbery product.

15. 3-Nitraza-1,5-pentanediol has been prepared. This is the first diol containing a nitramino group to be used for polyurethane formation on this program. The compound was prepared by two methods, one starting from the explosive DINA, the other by oxidation of the corresponding nitroso compound with trifluoro peracetic acid.

16. 3-Nitraza-1,6-hexanedioic acid has been prepared, starting from glycine and acrylonitrile. It has been successfully converted to the new 2-nitraza-1,4-butane diisocyanate. The new diisocyanate was characterized by conversion to a methyl urethane.

17. Stress-relaxation data obtained on Polyurethane I-J (195-P1) have been fitted to a Wiechert rheological model, which is a parallel array of Maxwell elements. Each Maxwell element in turn consists of a Newtonian dashpot characterized by a relaxation time τ_i and a Hookean spring characterized by a Young's modulus E_i. The results of this analysis reveal that the maximum density of relaxation processes on the absolute time scale at 116°F occurs at a value of $\tau = 27$ sec and extends over a range from 2 to 16,000 seconds. Physically, this means that if a given stress is applied to a high-

molecular-weight, linear, amorphous nitropolymer at its distinctive tempera-
ture, 116°F in the case of Polyurethane I-J (195, P-1), within 16,000 sec,
then the tensile strength of the polymer must exceed the given stress in
order to avoid rupture. The generalization from the specific case of
Polyurethane I-J, 195, P-1, to any high-molecular-weight, linear, amorphous
nitropolymer is based on the fact that the data are reduced in terms of
dimensionless parameters. In the case of plasticized, crosslinked nitro-
polymers, stress-relaxation data show that these materials behave like real
rubbers.

18.   Ballistic studies have been carried out on various nitro-
polymers in the absence and in the presence of ballistic modifiers. For
example, a mixture of 90:10 Polyurethane I-AN and the sodium salt of dini-
troacetonitrile in the presence of lead salicylate had a burning rate of
0.8 in/sec at 1000 psi. Polyurethanes such as XII-A and XIII-A, containing
nitramino groups, gave values of 0.11 and 0.12 in./sec as compared with
Polyurethane I-A, which gave a value of 0.10 in./sec.

19.   A Beken dispersion blade-mixer has been installed. This
will allow polymerization mixtures to be studied under conditions comparable
to those encountered during actual manufacturing operations. A photograph
of the machine is shown in the appendix of this report.

II.   TECHNICAL PROGRESS: NITROPOLYMERS (Contract N7onr-46201)

A.   VINYL POLYMERIZATION

1.   2,2-Dinitrobutyl Acrylate

a.   Discussion

(1)   The polymerization of small quantities of vinyl
nitropolymers in small sealed tubes presents no problem. The dissipation of
the heat of polymerization is rapid, due to the small mass and rapid heat
transfer. However, if one wishes to prepare large quantities of polymer,
the exothermic reaction becomes increasingly important. Of the three methods
of polymer formation (i.e., bulk, emulsion, and suspension), the last two
provide the best control of the polymerization temperature. It was decided
to investigate the possibility of using the emulsion technique in the
polymerization of the nitroalkyl acrylates.

(2)   There are several differences between nitro-
monomers and known vinyl monomers which make the task of emulsion poly-
merization somewhat more difficult:

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      (a) The difference in the density of the nitromonomer and the aqueous phase is greater. This increases the difficulty of emulsification, and gives rise to less stable emulsions.

      (b) The chemical reactivity of the monomers toward base renders the usual emulsifying agents useless. Anionic and cationic emulsifying agents give aqueous solutions with pH values which are deterimental to nitro compounds. Accordingly, the non-ionic agents appear most desirable.

      (c) Nitromonomers require a lower polymerization temperature to reduce possible decomposition.

      (3) Previous work carried out on the explosives program indicated that the product Tween 40 (Atlas Powder Co.), in conjunction with the use of polyvinyl alcohol as a stabilizer, gave the best emulsions. This work has been repeated, and it has been found that this formulation does not yield reproducible results. Complete emulsification is often not achieved and the stability of the emulsion which is obtained is not always satisfactory. Another disadvantage to this formulation is the occasional precipitation of the polyvinyl alcohol along with the polymer when the emulsion is poured into methanol. This would necessitate an extra step for the removal of the stabilizer.

      (4) Screening tests on a test tube scale have been carried out on a number of non-ionic emulsifying agents produced by the Atlas Powder Co. The stability of the emulsions was observed qualitatively, using the monomeric mixture. It was found that Tween 20 is equal to, or better than, Tween 40 as an emulsifying agent. It was also observed that these non-ionic agents appeared to be quite sensitive to small quantities of dissolved salts. For example, the addition of 0.25% (based on the aqueous phase) of ammonium or potassium persulfate catalyst destroyed the emulsion.

      (5) Several emulsion polymerizations were attempted, using hydrogen peroxide as catalyst. Although the original monomeric mixture seemed unaffected by the addition of this catalyst, two phases were obtained upon polymerization. It seems that sometime during the polymerization process the particles are tacky enough to cause agglomeration of the organic phase. The addition of polyvinyl alcohol is beneficial but does not completely stop the agglomeration of the organic phase. Perhaps the use of an inorganic suspending agent such as Bentonite or talc would solve the problem.

      (6) It was necessary to prepare a larger quantity of 2,2-dinitrobutyl acrylate for use in rheological studies. Eighty grams of monomer was polymerized in bulk in sealed evacuated tubes at $50^{\circ}C$, using 0.25% azo-bis-isobutyronitrile as initiator. The polymer had a relative viscosity, η_r of 2.84 (2% in acetone) when purified, and will be compared with poly 3,3-dinitrobutyl acrylate.

b.   Experimental

Emulsion polymerizations were carried out in 4-oz round bottles which had been cleaned in chromic acid solution, then rotated at about 30 rpm in a 45°C water bath. The bottles were filled first with the aqueous phase, then with the monomer, and finally with the catalyst. They were then purged with nitrogen and sealed with a screw-cap containing a Teflon liner. The samples were run in duplicate. The formulations tried are given in Table I. All formulations contained 15.0 g of dinitrobutyl acrylate monomer and 0.150 g of ammonium persulfate initiator (1% based on monomer weight). The percentages listed in Table I are based on monomer weight.

TABLE I

EMULSION POLYMERIZATION OF 2,2-DINITROBUTYL ACRYLATE

Formulation	Ingredients	Remarks
I	8.0% Tween 40 30.0 ml of distilled water	No emulsification, separates into two phases.
II	8.0% Tween 40 3.0% Elvanol 52-22 30.0 ml of distilled water	Some emulsification, but not complete; more separation on standing
III	8.0% Tween 40 3.0% Elvanol 52-22 0.5% Lecithin 30.0 ml of distilled water	Same as II
IV	20.0% Tween 40 30.0 ml of distilled water	No emulsification
V	10.0% Elvanol 52-22 30.0 ml of distilled water	Very thick, barely pours

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B.   ADDITION AND CONDENSATION POLYMERS

1.   Polyurethanes

a.   New Polyurethanes

(1)   Introduction

(a)   The new nitro diisocyanate, 3,3,5,7,7-pentanitro-5-aza-1,9-nonane diisocyanate,* has been made in quantities sufficient for polymerization studies. Hereafter it will be assigned the Roman numeral XIV for convenience in discussion.

(b)   Three new polyurethanes have been prepared and characterized using the monomer 3,6-dinitro-3,6-diaza-1,8-octane diisocyanate (XII). The problem of obtaining high-molecular-weight polyurethanes containing the nitraza grouping is still unresolved in many of the systems studied, because of the extreme insolubility of these polymers in the available polymerization solvents.

(c)   Polyurethanes of the XII and XIII series described in Aerojet Report No. 740 have been post-nitrated to raise the specific impulse. The nitration technique described in Aerojet-General Report No. 712, p. 12, was applied to these polymers. Table II shows the structures of the new polymers.

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*For preparation see Aerojet Report No. 740, p. 70.

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TABLE II

NEW POLYURETHANES

Polyurethanes XIV-J and XIV-JN
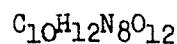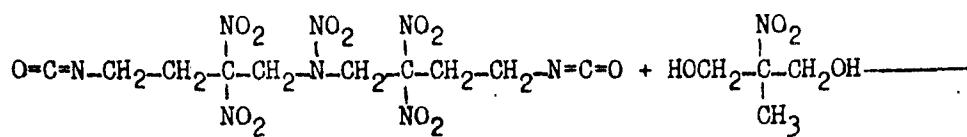
$$O=C=N-CH_2-CH_2-\underset{\underset{NO_2}{|}}{\overset{\overset{NO_2}{|}}{C}}-CH_2-\underset{\underset{}{\overset{NO_2}{|}}}{N}-CH_2-\underset{\underset{NO_2}{|}}{\overset{\overset{NO_2}{|}}{C}}-CH_2-CH_2-N=C=O \quad + \quad HOCH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{NO_2}{|}}{C}}-CH_2OH$$

$$C_{10}H_{12}N_8O_{12} \qquad\qquad\qquad\qquad C_4H_9NO_4$$

3,3,5,7,7-Pentanitro-5-aza-1,9-nonane   2-Nitro-2-methyl
Diisocyanate   1,3-propanediol

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

$$(C_{14}H_{21}N_9O_{16})_n$$
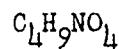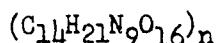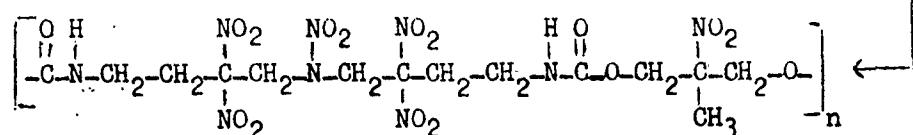
Theoretical I_{sp} = 189 lbf sec/lbm

Nitration

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

$$(C_{14}H_{19}N_{11}O_{20})_n$$
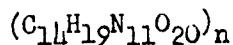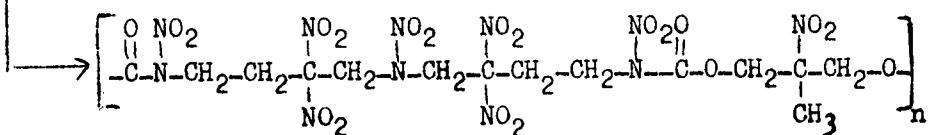
Theoretical I_{sp} = 222 lbf sec/lbm

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TABLE II (cont.)

Polyurethane XIV-A and XIV-AN

$$O=C=N-CH_2-CH_2-\underset{\underset{NO_2}{|}}{\overset{\overset{NO_2}{|}}{C}}-CH_2-\underset{NO_2}{N}-CH_2-\underset{\underset{NO_2}{|}}{\overset{\overset{NO_2}{|}}{C}}-CH_2-CH_2-N=C=O + HO-CH_2-\underset{NO_2}{\overset{\overset{NO_2}{|}}{C}}-CH_2-OH$$
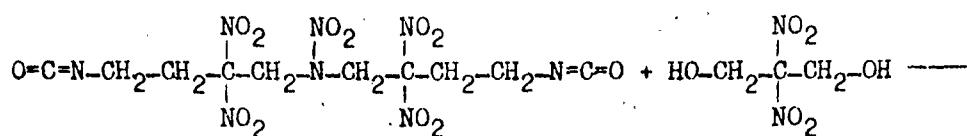
3,3,5,7,7-Pentanitro-5-aza-1,9-nonane   2,2-Dinitro-
           Diisocyanate   1,3-propanediol

$$C_{10}H_{12}N_8O_{12} \qquad\qquad C_3H_6N_2O_6$$

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

$$(C_{13}H_{18}N_{10}O_{18})_n$$
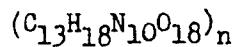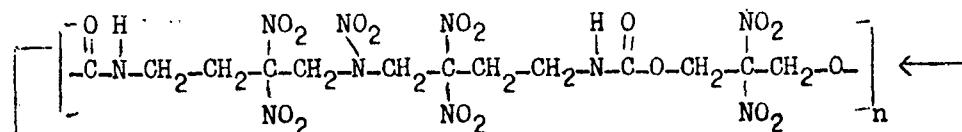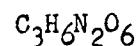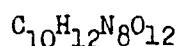
Theoretical I_{sp} = 212 lbf·sec/lbm

Nitration

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

$$(C_{13}H_{16}N_{12}O_{22})_n$$
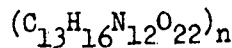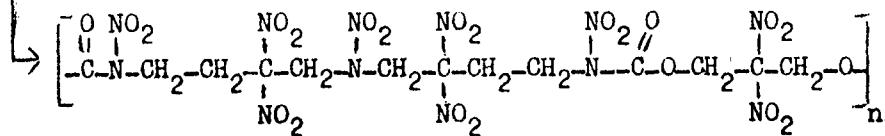
Theoretical I_{sp} = 237 lbf·sec/lbm

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TABLE II (cont.)

Polyurethanes XII-M and XII-MN
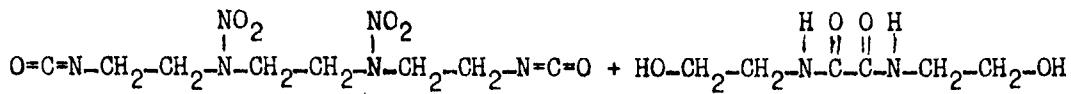
$$O=C=N-CH_2-CH_2-\overset{\overset{\displaystyle NO_2}{|}}{N}-CH_2-CH_2-\overset{\overset{\displaystyle NO_2}{|}}{N}-CH_2-CH_2-N=C=O \; + \; HO-CH_2-CH_2-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{||}}{C}-\overset{\overset{\displaystyle O}{||}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-CH_2-CH_2-OH$$

3,6-Dinitro-3,6-diaza-1,8-octane	N,N'-bis(2-hydroxyethyl)
Diisocyanate	Oxamide
$C_8H_{12}N_6O_6$	$C_6H_{12}N_2O_4$

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

$$(C_{14}H_{24}N_8O_{10})_n$$

Nitration

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

$$(C_{14}H_{20}N_{12}O_{18})_n$$
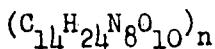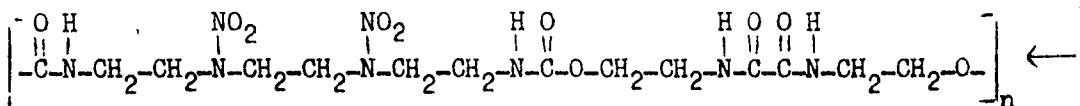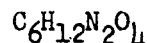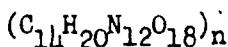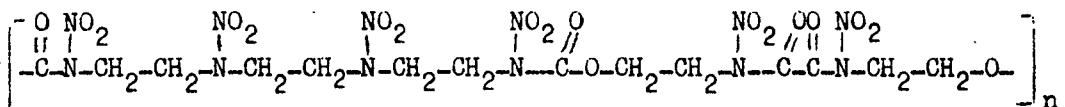
Theoretical I_{sp} = 207 lbf·sec/lbm

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TABLE II (cont.)

Polyurethanes XII-N and XII-NN

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

3,6-Dinitro-3,6-diaza-1,8-octane   Ethylene Glycol
        Diisocyanate

$C_8H_{12}N_6O_6$ $C_2H_6O_2$

$$\left[-\overset{\overset{\displaystyle O}{||}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-CH_2-CH_2-\overset{\overset{\displaystyle NO_2}{\uparrow}}{N}-CH_2-CH_2-\overset{\overset{\displaystyle NO_2}{\uparrow}}{N}-CH_2-CH_2-\overset{\overset{\displaystyle H}{|}}{N}\overset{\overset{\displaystyle O}{||}}{C}-O-CH_2-CH_2-O- \right]_n$$

$$(C_{10}H_{18}N_6O_8)_n$$

Nitration

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

$$(C_{10}H_{16}N_8O_{12})_n$$
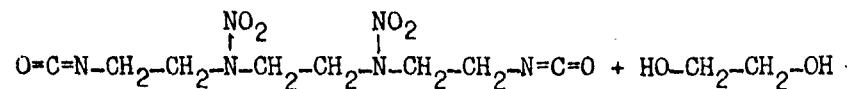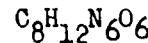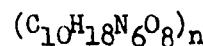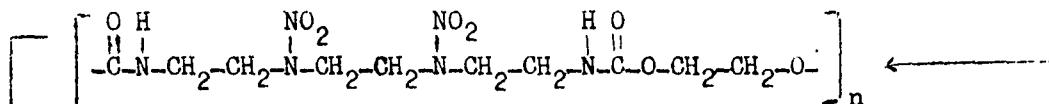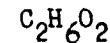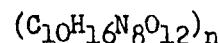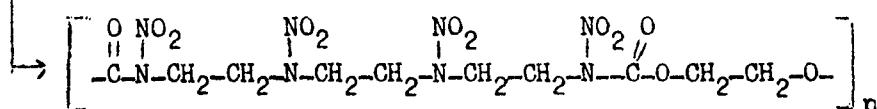
Theoretical I_{sp} = 197 lbf·sec/lbm

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TABLE II (cont.)

Polyurethanes XII-O and XII-CN

$$O=C=N-CH_2-CH_2-\underset{\underset{NO_2}{|}}{N}-CH_2-CH_2-\underset{\underset{NO_2}{|}}{N}-CH_2-CH_2-N=C=O \quad + \quad HO-CH-CH_2OH$$

3,6-Dinitro-3,6-diaza-1,8-octane
Diisocyanate

$$C_8H_{12}N_6O_6$$

5,5-Dinitro-1,2-
hexanediol

$$C_6H_{12}N_2O_6$$

Side chain of diol:
$$-CH-CH_2OH$$
$$|$$
$$CH_2$$
$$|$$
$$CH_2$$
$$|$$
$$O_2N-C-NO_2$$
$$|$$
$$CH_3$$

$$\left[-\underset{\underset{O}{\parallel}}{C}-\underset{\underset{H}{|}}{N}-CH_2-CH_2-\underset{\underset{NO_2}{|}}{N}-CH_2-CH_2-\underset{\underset{NO_2}{|}}{N}-CH_2-CH_2-\underset{\underset{H}{|}}{N}-\underset{\underset{O}{\parallel}}{C}-O-CH-CH_2-O- \right]_n$$

$$CH_2$$
$$CH_2$$
$$O_2N-C-NO_2$$
$$CH_3$$

$$(C_{14}H_{24}N_8O_{12})_n$$

Nitration

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

$$CH_2$$
$$CH_2$$
$$O_2N-C-NO_2$$
$$CH_3$$

$$(C_{14}H_{22}N_{10}O_{16})_n$$
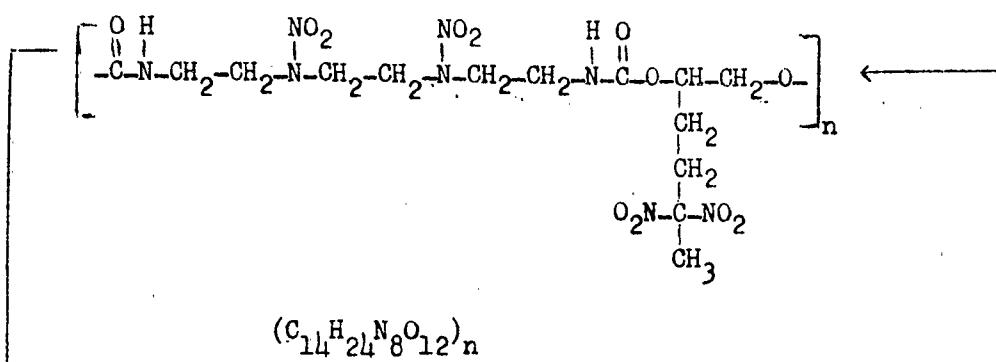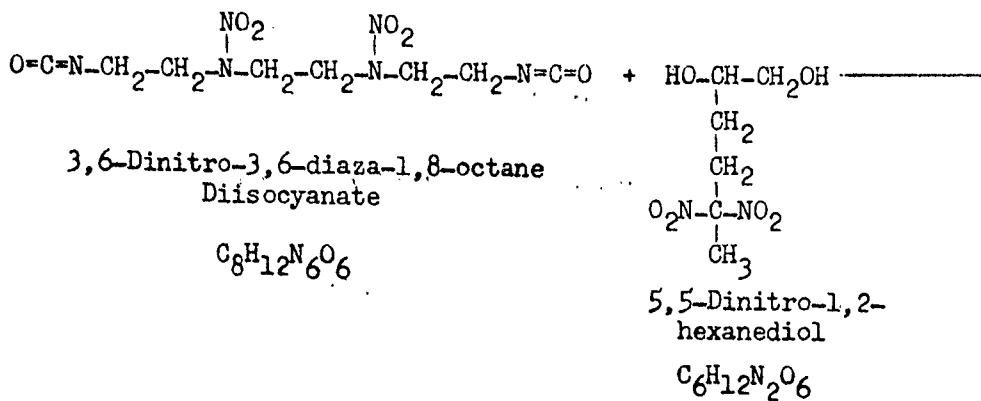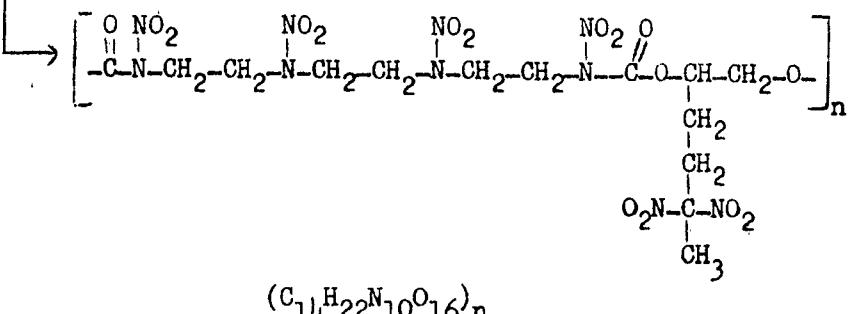
Theoretical I_{sp} = 200 lbf·sec/lbm

(2)   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

(a)   Inasmuch as the standard isocyanate analytical technique could not be applied to this isocyanate, the material, mp 103 to 105°C, was assumed to be pure in calculating monomer equivalence for the first preparation, JRF-242. Purified dioxan, 50 wt %, was used as the polymerization solvent, and ferric acetylacetonate catalyst was used at the rate of 5×10^{-4} mol/equivalent diol. Heat was evolved, and the solution became more viscous during the first half hour. The mixture was placed in a 50°C bath but failed to increase in viscosity. Attempts to increase the viscosity by adjusting monomer equivalence failed. The addition of more catalyst likewise failed to increase the molecular weight. A portion was placed in a 65°C bath but no further polymerization occurred, $\eta_r^{1\%}$ acetone = 1.09. After 44 hr at 50°C the polymer was worked up. The relative viscosity of a 1% solution in acetone at 25°C was 1.11.

(b)   The XIV-diisocyanate was recrystallized from anhydrous chlorobenzene. The product, mp 105 to 106°C, was used for a small-scale polymerization, JRF-246. There was no improvement in molecular weight, $\eta_r^{1\%}$ acetone = 1.12.

(c)   It was believed that the XIV-diisocyanate might be dimeric, resulting in a great disparity in monomer equivalence. A small-scale polymerization, JRF-248, was made using double the weight of XIV-diisocyanate mp 103 to 105°C. There was no increase in molecular weight; in fact, more heat was evolved when additional diol was added ($\eta_r^{1\%}$ acetone = 1.13).

(d)   The XIV-diisocyanate was recrystallized from purified 1-chloro-1-nitroethane. The product had a higher mp, 110°C. A small scale polymerization, JRF-249, was made using dioxan as solvent. The worked-up polymer was somewhat fibrous, softened in the range 80 to 90°C, and had a relative viscosity of 1.24 (1% in acetone at 25°C). The X-ray diffraction pattern showed that the polymer was amorphous.

Anal. Calc'd for $C_{14}H_{21}N_9O_{16}$:   %C, 29.43; %H, 3.70; %N, 22.07
   Found: %C, 30.91; %H, 4.01; %N, 21.10

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(e)   A portion of the diisocyanate, mp 103
to 105°C, was recrystallized from purified dioxan, yielding material of
mp 83 to 84°C.

Elementary analysis found: %C, 32.36; %H, 3.99; %N, 22.14

Calc'd for $C_{10}H_{12}N_8O_{12}$ (isocyanate): %C, 27.53; %H, 2.77; %N, 25.69

Calc'd for $C_{14}H_{20}N_8O_{14}$ (+ dioxan):   %C, 32.07; %H, 3.84; %N, 21.37

Calc'd for $C_{18}H_{28}N_8O_{16}$ (+ 2 dioxan): %C, 35.30; %H, 4.61; %N, 18.30

A small-scale polymerization, JRF-251, using the complex of mp 83 to 84°C,
yielded polyurethane XIV-X($\eta r^{1\%}$ acetone = 1.24).

(f)   Conclusions

The diisocyanate may contain some mono-
functional impurities that are difficult to remove by recrystallization.
These mono-functional molecules terminate growing polymer chains, resulting
in low-molecular-weight product. The work will be continued with emphasis
on obtaining purer 3,3,5,7,7-pentanitro-5-aza-1,9-nonane diisocyanate.

(3)   Preparation of Polyurethane XIV-A (JKE-192)
from 3,3,5,7,7-Pentanitro-5-aza-1,9-nonane Diisocyanate and 2,2-Dinitro-
1,3-propanediol

To a 500-ml resin flask containing 28.13 g
2,2-dinitro-1,3-propanediol, 60 mg ferric acetylacetonate, and 20 ml anhydrous
dioxan, was added dropwise a solution of 73.88 g 3,3,5,7,7-pentanitro-
5-aza-1,9-nonane diisocyanate, mp 103 to 105°C, in 75 ml hot, anhydrous
dioxan. After the initial heat of polymerization had subsided, the reaction
vessel was placed in a 50°C bath, and remained there for a week, during
which time 2.8% excess diisocyanate was added in small increments. The
viscosity of the reaction solution showed no increase during the run over
the initial low value. The polymer was worked up by diluting with acetone,
filtering, and precipitating in water. After vacuum drying, the following
physical data were obtained: yield, 99 g (95%); softening range, 75 to
85°C; relative viscosity, 1.09 (1% in acetone); impact stability, 40
cm/2 kg; solubility, soluble in acetone, dimethylformamide, and dioxan.

Anal. Calc'd for $(C_{13}H_{18}N_{10}O_{18})n$: %C, 25.92; %H, 3.01; %N, 23.26

Found: %C, 28.42; %H, 3.73; %N, 21.74

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   (4)   Preparation of Polyurethane XII-M (JKE-189)
from 3,6-Dinitro-3,6-diaza-1,8-octane Diisocyanate and N,N'-bis(2-hydroxyethyl)
Oxamide

                        To 14.02 g 3,6-dinitro-3,6-diaza-1,8-octane
diisocyanate, assay 97.4%, in a 500-ml flask was added an equivalent quantity,
8.34 g, of N,N'-bis(2-hydroxyethyl) oxamide and 3.3 mg ferric acetylacetonate
(10^{-4} mole catalyst per equivalent diol). To the monomers was added a mixed
solvent system consisting of 22 ml dioxan, 10 ml dimethylformamide, and 400
ml acetone. The diol was not completely soluble in this system even when
heated to 100°C. The mixture was ground in a Waring Blendor until the particle
size of undissolved solids was small. The reaction mixture was then placed
in a 50°C bath for 186 hr, during which time a slight increase in viscosity
was observed. The polymer was worked up by slurrying with acetone in a blendor
and vacuum drying. The following physical data were obtained: yield, 17.5 g
(78%); relative viscosity, 1.30 (1% in formic acid); softening range, 190 to
200°C; impact stability >100 cm/2 kg; soluble in hot formic acid, 100% nitric
acid; insoluble in acetone, dimethylformamide, dioxan; X-ray diffraction,
polycrystalline.

Anal. Calc'd for $(C_{14}H_{24}N_8O_{10})_n$:   %C, 36.21; %H, 5.21; %N, 24.13

        Found: %C, 35.99; %H, 5.57; %N, 24.15

                        (5)   Preparation of Polyurethane XII-MN (JKE-193)
by Nitration of Polyurethane XII-M, obtained from 3,6-Dinitro-3,6-diaza-1,8-
octane Diisocyanate and N,N'-bis(2-hydroxyethyl) Oxamide

                        To 8.00 g polyurethane XII-M (JKE-189) in a
125-ml Erlenmeyer flask was added 80 ml cold 100% nitric acid. The polymer
dissolved rapidly. The solution remained 1 hr at 50°C and was then poured
into ice-water, precipitating the post-nitrated polymer. After being washed
free of excess acid with water, the polymer was vacuum dried. The following
physical data characterized the new polymer: yield, 8.7 g (78%); relative
viscosity, 1.03 (1% acetone); softening range, 65 to 70°C; impact stability,
90 cm/2 kg; X-ray diffraction, amorphous; soluble in acetone, dimethylformamide,
insoluble in dioxan.

Anal. Calc'd for $(C_{14}H_{20}N_{12}O_{18})n$:   %C, 26.09; %H, 3.13; %N, 26.09
    Found: %C, 26.41; %H, 3.23; %N, 25.44

    Heat of Combustion, Calc'd: 2773 cal/g
                    Found: 2799 cal/g

(6)   Preparation of Polyurethane XII-N (JKE-184)
from 3,6-Dinitro-3,6-diaza-1,8-octane Diisocyanate and Ethylene Glycol

To a 500-ml resin flask containing 4.94 g
purified ethylene glycol (bp 104°C/18 mm, n_D^{25} = 1.4300) and 0.028 g ferric
acetylacetonate (5 x 10⁻⁴ mole catalyst per equivalent diol) in 10 ml
absolute dimethylformamide was added dropwise a solution of 23.36 g (1%
excess) of 3,6-dinitro-3,6-diaza-1,8-octane diisocyanate (assay 99.2%)
in a mixture of 20 ml absolute dimethylformamide and 20 ml absolute acetone.
With ice-bath cooling, the reaction temperature during the diisocyanate
addition was maintained at 50 to 60°C. During the addition a solid phase
began to separate, and within 1 hr, the reaction solution had set up to a
hard solid. After remaining 100 hr at 50°C, the polymer was slurried with
acetone in a Waring Blendor until washed free of dimethylformamide and
catalyst. Acetone was removed from the polymer using a vacuum of <1 mm.
Yield, 24 g (86%); relative viscosity, 1.08 (1% formic acid); softening
range, 165 to 170°C; impact stability >100 cm; solubility, soluble in
hot formic acid; insoluble in acetone, dimethylformamide, and dioxan;
X-ray diffraction, polycrystalline.

Anal. Calc'd for $(C_{10}H_{18}N_6O_8)_n$:   %C, 34.28; %H, 5.18; %N, 24.00

Found: %C, 34.86; %H, 5.49; %N, 24.44

Heat of Combustion, Calc'd: 3892 cal/g

Found: 3833 cal/g

(7)   Preparation of Polyurethane XII-NN (JKE-194)
by Nitration of Polyurethane XII-N, obtained from 3,6-Dinitro-3,6-diaza-1,8-
octane Diisocyanate and Ethylene Glycol

To 10.0 g polyurethane XII-N (JKE-184) in a
125 ml Erlenmeyer flask was added 100 ml of cold 100% nitric acid. The
polymer dissolved rapidly, and the solution was immediately poured into
ice-water, precipitating the post-nitrated product. After the polymer
was washed free of excess acid with water, it was vacuum dried. The
polymer was characterized by the following physical data: yield, 11.6 g
(92%); relative viscosity, 1.08 (1% DMF); softening range, 60-65°C; impact
stability, 75 cm/2 kg; X-ray diffraction, amorphous; soluble in dimethyl-
formamide; insoluble in acetone, dioxan.

Anal. Calc'd for $(C_{10}H_{16}N_8O_{12})_n$:   %C, 27.28; %H, 3.66; %N, 25.45

Found: %C, 26.63; %H, 4.33; %N, 25.18

Heat of Combustion, Calc'd: 3008 cal/g

Found: 2979 cal/g

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                    (8)   Preparation of Polyurethane XII-0 (JKE-190) from
3,6-Dinitro-3,6-diaza-1,8-octane Diisocyanate and 5,5-Dinitro-1,2-hexanediol

                    Equivalent quantities of diol and diisocyanate
were combined in a 250-ml Erlenmeyer flask with dioxan and ferric acetylace-
tonate. The total monomer weight was 39.09 g, the monomer concentration was
50 wt %, and the catalyst concentration was 10^{-3} mole per equivalent diol.
After remaining 186 hr at 50°C, the slightly viscous polymer solution was
diluted with acetone, filtered, and precipitated into water. After vacuum
drying the following physical data were obtained: yield, 38 g (97%); relative
viscosity, 1.13 (1% in acetone); softening range, 90 to 100°C; impact sta-
bility >100 cm/2 kg; X-ray diffraction, polycrystalline; soluble in acetone,
dimethylformamide; insoluble in dioxan.

Anal. Calc'd for $(C_{14}H_{24}N_8O_{12})_n$:   %C, 33.87; %H, 4.87; %N, 22.58
                        Found: %C, 34.01; %H, 4.91; %N, 23.26

                    (9)   Preparation of Polyurethane XII-ON (JKE-195)
by Nitration of Polyurethane XII-0 from 3,6-Dinitro-3,6-diaza-1,8-octane
Diisocyanate and 5,5-Dinitro-1,2-hexanediol

                    To 10.0 g polyurethane XII-0 (JKE-190) in a
125 ml Erlenmeyer flask was added 100 ml of cold 100% nitric acid. After
dissolving readily, the solution was immediately poured into ice-water,
precipitating the post-nitrated product. The polymer was washed free of
excess acid with water and vacuum dried. Yield, 11.0 g (93%); relative
viscosity 1.11 (1% in acetone); softening range, 85 to 95°C; impact stability,
90 cm/2 kg; X-ray diffraction, amorphous; soluble in acetone, dimethylformamide;
insoluble in dioxan.

Anal. Calc'd for $(C_{14}H_{22}N_{10}O_{16})_m$:   %C, 28.67; %H, 3.78; %N, 23.89
                        Found: %C, 28.88; %H, 3.87; %N, 24.15

        Heat of Combustion, Calc'd: 3147 cal/g
                        Found: 3148 cal/g

                    (10)   Preparation of Polyurethane XII-AN (JRF-239)
by Nitration of Polyurethane XII-A, prepared from 3,6-Dinitro-3,6-diaza-
1,8-octane Diisocyanate and 2,2-Dinitro-1,3-propanediol

                    (a)   Discussion

                    Polyurethane XII-A exists in two forms,
amorphous and crystalline.* For the first nitration experiments, amorphous
XII-A, JRF-227, $\eta \frac{1\%}{r}$ DMF = 1.69, was chosen. The resulting post-nitrated

polymer exhibited different properties, depending on the work-up procedure.

*Aerojet Report No. 712, p. 17 and this report, p. 26.

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(b)   Experimental (JRF-234)

To 15 g of polyurethane XII-A, JRF-227,
$\eta \frac{1\%}{r}$ DMF = 1.69, was added 150 ml of 100% nitric acid at 0°C. After the

polymer was completely dissolved the excess acid was removed by distillation
at reduced pressure. The resulting viscous mass was dissolved in acetone.
After standing 15 min a solid phase separated and was removed by filtration.
It was characterized as follows:

Anal. Calc'd for $C_{11}H_{16}N_{10}O_{16}$:   %C, 24.27; %H, 2.96; %N, 25.74
                          Found: %C 24.97; %H, 3.14; %N, 22.60 25.59
    Heat of Combustion, Calc'd: 2584 cal/g
                          Found: 2712, 2741 cal/g (corresponding to 3.1%
                                                    acetone)

$\eta \frac{1\%}{r}$ DMF = 1.28; impact stability 80 cm/2 kg (RDX = 30 cm/2 kg); KI-starch
test at 65.5°C, 15 min to failure; softening range, 75 to 90°C; X-ray
crystalline; Warburg stability at 65.5°C, gassing too fast to measure.
Soluble in DMF, slightly soluble in acetone.

(c)   Experimental (JRF-239)

To 20 g of polyurethane XII-A, JRF-227,
$\eta \frac{1\%}{r}$ DMF = 1.69 was added 250 ml of 100% nitric acid at 0°C. After the poly-

mer was completely dissolved the excess acid was removed by distillation at
reduced pressure. The resulting viscous mass was dissolved in acetone, and
the polymer was precipitated immediately by pouring the acetone solution
into methylene chloride. JRF-239-A was characterized as follows:

Anal. Calc'd for $C_{11}H_{16}N_{10}O_{16}$:   %C, 24.27; %H, 2.96; %N, 25.74
                          Found: %C, 24.55; %H, 3.00; %N, 25.84
        Heat of Combustion, Calc'd: 2584 cal/g
                          Found: 2596, 2611 cal/g.
Warburg Stability at 65.5°C = 0.34 ml/100 g/hr

$\eta \frac{1\%}{r}$ DMF = 1.83   Impact Stability 100 cm/2 kg (RDX = 30 cm/2 kg)

Soluble in DMF and in acetone. Softening range 30 to 40°C when first
prepared. Softening range 65 to 75°C after standing one month at room
temperature. X-ray diffraction amorphous, after standing one month at
room temperature. Acetone was added to JRF-239-A, and the slurry was
permitted to stand at room temperature for 30 min. The product was
filtered, washed with acetone, and dried, giving JRF-239-B.

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Heat of Combustion Calc'd: 2584 cal/g
                    Found: 2669, 2670 cal/g (corresponding to 1.6% acetone)

$\eta_r^{1\%}$ DMF = 1.36; softening range 90 to 110°C; soluble in DMF, slightly soluble in acetone.

(d)   Conclusions

The behavior of XII-AN in acetone is similar to that of I-AN and I-JN in acetone.* I-AN is the post-nitrated polyurethane prepared from 3,3-dinitro-1,5-pentane diisocyanate and 2,2-dinitro-1,3-propanediol. I-JN is the post-nitrated polyurethane obtained from 3,3-dinitro-1,5-pentane diisocyanate and 2-nitro-2-methyl-1,3-propanediol. All three of these polymers, when treated with acetone, form crystalline products that contain various amounts of acetone and are much less soluble and higher melting than the original polymer. It is not understood at present why the relative viscosity of the polymer containing acetone is so much lower than that of polymer alone.

(11)   Preparation of Polyurethane XII-JN: Nitration of Polyurethane XII-J, prepared from 3,6-Dinitro-3,6-diaza-1,8-octane Diisocyanate and 2-Nitro-2-methyl-1,3-propanediol

(a)   The preparation of polyurethane XII-J was described in Aerojet Report No. 740, p. 22. This polymer was nitrated with 100% nitric acid in the usual manner. The low relative viscosity of the nitrated polymer indicates that degradation occurred.

(b)   Experimental (JRF-235-A)

To 15 g of polyurethane XII-J, JRF-230, $\eta_r^{1\%}$ DMF = 1.62, was added 150 ml of 100% nitric acid at 0°C. After vacuum stripping excess acid at room temperature the polymer was dissolved in dimethylformamide and precipitated by pouring the solution into methylene chloride. Softening range 60 to 70°C; $\eta_r^{1\%}$ DMF = 1.17; KI-Starch test at 65.5°C, 5 min to failure; JRF-235-A was dissolved in DMF and again precipitated giving JRF-235-B; X-ray diffraction pattern, amorphous.

Anal. Calc'd for $C_{12}H_{19}N_9O_{14}$:   %C, 28.07; %H, 3.73; %N, 24.56
                        Found: %C, 28.78; %H, 4.28; %N, 24.71

Softening range, 55 to 65°C; Impact Stability, 50 cm/2 kg; $\eta_r^{1\%}$ DMF = 1.17; KI-Starch test at 65.5°C, 12 min to failure; Warburg Stability at 65.5°C, 0.17 ml/100 g/hr;

Heat of Combustion Calc'd: 3085 cal/g
                    Found: 3102 cal/g

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*Aerojet Report No. 663, p. 35.

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(12)   Preparation of Polyurethane XIII-HN by Nitration of Polyurethane XIII-H, prepared from 3-Nitro-3-aza-1,5-pentane Diisocyanate and 5,5,5-Trinitro-1,2-pentanediol

(a)   The preparation of polyurethane XIII-H was described in Aerojet Report No. 740, p. 24. The nitration was accomplished with only a small decrease in relative viscosity, and the resulting post-nitrated product has excellent Warburg stability.

(b)   Experimental (JRF-232)

To 15 g of polyurethane XIII-H, JRF-221-B, $\eta_r^{1\%}$ acetone 1.53, was added 150 ml of 100% nitric acid at 0°C. After vacuum stripping excess acid at room temperature, the polymer was dissolved in acetone and precipitated by pouring the solution into methylene chloride. (JRF-232-A), $\eta_r^{1\%}$ acetone, 1.44; softening range 80 to 90°C; KI-starch test at 65.5°C, 10 min to failure; X-ray diffraction pattern, amorphous; (JRF-232-A) was dissolved in acetone and again precipitated, giving (JRF-232-B), $\eta_r^{1\%}$ acetone, 1.38; softening range, 75 to 85°C; KI-starch test at 65.5°C = 5 min to failure; Warburg stability at 65.5°C, 0.12 ml/100 g/hr; impact stability, 30 cm/2 kg

Anal. Calc'd for $C_{11}H_{15}N_9O_{16}$:   %C, 24.96; %H, 2.85; %N, 23.82

Found: %C, 24.78; %H, 3.10; %N, 23.79

Heat of Combustion Calc'd: 2602 cal/g

Found: 2601 cal/g

(13)   Preparation of Polyurethane XIII-JN by Nitration of Polyurethane XIII-J, Prepared from 3-Nitro-3-aza-1,5-pentane Diisocyanate and 2-Nitro-2-methyl-1,3-propanediol

(a)   The preparation of polyurethane XIII-J was described in Aerojet Report No. 740, p. 24. Nitration in the usual manner gave product having a low relative viscosity as measured in acetone, but higher in DMF. The relative viscosity as measured in γ-butyrolactone had an intermediate value.

(b)   Experimental (JRF-231)

To 15 g of Polyurethane XIII-J, JRF-218-B, $\eta_r^{1\%}$ DMF 2.32, was added 150 ml of 100% nitric acid at 0°C. After vacuum stripping excess acid at room temperature, the polymer was dissolved in acetone and precipitated by pouring into methylene chloride. (JRF-231-A) $\eta_r^{1\%}$ acetone, 1.22; softening range, 70 to 80°C; KI-starch test at 65.5°C, 8 min to failure.   JRF-231-A was dissolved in acetone and again

precipitated in methylene chloride, giving JRF-231-B. $\eta_r^{1\%}$ acetone 1.20; softening range, 70 to 80°C; impact stability, 83 cm/2 kg; KI-starch test at 65.5°C, 10 min to failure; X-ray diffraction pattern, amorphous.

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

Found: %C, 27.92; %H, 3.80 %N, 23.37

Heat of Combustion Calc'd: 2964 cal/g

Found: 2994 cal/g

(c)   Experimental (JRF-256)

To 20 g of polyurethane XII-J, JRF-218-B, $\eta_r^{1\%}$ DMF = 2.32, was added 400 ml of 100% nitric acid at 0°C. The excess acid was vacuum stripped at 10°C, the residue dissolved in purified DMF, and the polymer precipitated by pouring the DMF solution into rapidly stirred methylene chloride. $\eta_r^{1\%}$ acetone, 1.26, $\eta_r^{1\%}$ DMF, 1.80. $\eta_r^{1\%}$ butyrolactone, 1.66 at 25°C.

b.   Further Work on Previously Described Polyurethanes

(1)   Preparation of Polyurethane XIII-A from 3-Nitro-3-aza-1,5-pentane Diisocyanate and 2,2-Dinitro-1,3-propanediol

(a)   Discussion

The preparation of polyurethane XIII-A, described in Aerojet Report No. 740, p. 23 has been repeated with the objective of improving molecular weight and thermal stability. By using a slight excess of the diisocyanate monomer, an improved polymer was obtained. In the previously described preparation of Polyurethane XIII-A, the monomers were combined in calculated equivalence, and since the solution viscosity rose to an extremely high value, no further adjustment of monomer ratio was attempted. The fact that in the latest preparation an even higher molecular weight and greater thermal stability was obtained, again demonstrates the necessity of using excess diisocyanate in polyurethane preparations.

(b)   Experimental (JKE-186)

To a 500-ml resin flask containing 45.06 g of 2,2-dinitro-1,3-propanediol and 0.095 g ferric acetylacetonate in 50 ml absolute dioxan was added dropwise a solution of 54.17 g of 3-nitro-3-aza-1,5-pentane diisocyanate in 50 ml absolute dioxan. Using an icebath, the reaction temperature during the addition was maintained at 40 to 50°C. The reaction flask was placed in a 50°C bath, and the polymerization was followed by means of solution viscosity measurements.* At suitable intervals small increments

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*Aerojet Report No. 686, p. 24.

of diisocyanate were added. After 100 hours at 50°C and after a total of
1.6% excess diisocyanate had been added, the polymer solution was too
viscous to stir. The reaction was removed from the bath after 240 hours,
diluted with acetone, filtered, and the polymer was precipitated by pouring
the solution dropwise into water in a Waring Blendor. After vacuum drying
over phosphorous pentoxide, the following data were obtained: relative
viscosity, 1.60 (1% acetone); KI-starch stability at 65.5°C, >5 hours;
Warburg stability at 65.5°C, <0.01 ml/100g/hr.

        (2)   Preparation of Polyurethane XII-A from 3,6-
Dinitro-3,6-diaza-1,8-octane Diisocyanate and 2,2-Dinitro-1,3-propanediol

        (a)   The preparation of this polymer was
described in Aerojet Reports No. 663, p. 15; 712, p.17, and 740, p. 28.
Dioxan, DMF, and γ-butyrolactone were investigated as polymerization
solvents. During this period the use of dry acetone has been studied.
The resulting polymer was very fibrous and had a relative viscosity of
2.07 (1% solution in DMF). The highest previous value was $\eta_r^{1\%}$ DMF =

1.69, using γ-butyrolactone as polymerization solvent. However when
nitrated under identical conditions, the polymer prepared in acetone
solution was degraded more than that prepared in γ-butyrolactone.

        (b)   Although high-molecular-weight products
have been obtained, all were amorphous. During the past period efforts to
induce crystallization in amorphous XII-A have been partially successful.
A maximum of 10% of the amorphous form was converted into the crystalline
form by cooling an acetone solution of XII-A to -80°C for several hours,
then allowing it to stand at room temperature for several days. Warming
to 50°C after first cooling to -80°C increased the rate, but not the
ultimate yield of crystalline polymer. Solid polymer cooled to -80°C,
then held at 50°C for several days, showed no increase in crystallinity.

        (c)   Experimental (JRF-243)

        Equivalent quantities of 3,6-dinitraza-
1,8-octane diisocyanate and 3,3-dinitro-1,2-propanediol were combined in
dry acetone. Ferric acetylacetonate catalyst at the rate of 2.5×10^{-4}
mol/eq diol was used, and a reaction temperature of 50°C was maintained for
280 hr. Final adjustment of monomer equivalence required 1.66% more
diisocyanate. The worked-up polymer was brown in color, and had a relative
viscosity of 2.07 at a concentration of 1% in purified DMF at 25°C.

Nitration with 100% nitric acid at 0°C resulted in Polyurethane XII-AN, $\eta_r^{1\%}$

DMF = 1.48. However, nitration of XII-A (JRF-227), $\eta_r^{1\%}$ DMF = 1.69,

prepared in γ-butyrolactone, resulted in $\eta_r^{1\%}$ DMF = 1.83.*

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*This report, p. 18.

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(d)   Conclusions

γ-Butyrolactone is the preferred solvent for preparing Polyurethane XII-A. A low yield of the crystalline modification of XII-A can be obtained from the amorphous form. Acetone seems to favor the formation of the crystalline material.

(3)   Preparation of Polyurethane XII-H from 3,6-Dinitraza-1,8-octane Diisocyanate and 5,5,5-Trinitro-1,2-pentanediol

(a)   The preparation of XII-H was repeated using higher-purity diisocyanate in an effort to obtain higher molecular weight. (See Aerojet Report No. 740, p. 22, for earlier preparation). The diisocyanate used assayed 98.9%. The product, JRF-244, had a relative viscosity of 1.17 1% in acetone and $\eta_r^{1\%}$ DMF = 1.46 as compared to $\eta_r^{1\%}$ acetone = 1.16 for the earlier preparation.

(b)   No explanation for the low relative viscosity can be given. The same batch of diol has given high-molecular-weight Polyurethane XIII-H* and the same batch of diisocyanate was used in preparing high-molecular-weight XII-A, above.

(c)   Another preparation of XII-H was made using a different batch of diisocyanate, that assayed 99.0%, and a different batch of diol. (JRF-257) $\eta_r^{1\%}$ acetone = 1.26, $\eta_r^{1\%}$ DMF = 1.67.

(4)   Preparation of Polyurethane I-AN from 3,3-Dinitro-1,5-pentane Diisocyanate and 2,2-Dinitro-1,3-propanediol Plus 1% tris-Hydroxymethyl Nitromethane

(a)   It was of interest to determine the effect of 1% branching agent on the physical properties of Polyurethane I-AN. Twenty-five grams Polyurethane I-A (OB-4) containing 1% nib-glycerol as branching agent ($\eta_r^{1\%}$ acetone = 3.8) was dissolved in 400 ml of 100% nitric acid at room temperature. Excess acid was then removed in vacuo and the residue was dissolved in anhydrous dioxan. The nitrated polymer was precipitated by pouring the dioxan solution into methylene chloride. (JRF-241) $\eta_r^{1\%}$ acetone = 2.19. A control nitration was made in a similar manner on Polyurethane I-A (JKE-174) $\eta_r^{1\%}$ acetone = 1.81. The resulting nitrated product (JRF-240) had a relative viscosity of 1.61, 1% in acetone. Molded strands of each were made. (JRF-241) was superior to (JRF-240).

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*Aerojet Report No. 740, p. 24.

(b.)   Another preparation of Polyurethane I-A, (OB-27-B), containing 1% nib-glycerol as branching agent but differing from (OB-4) in that it was insoluble, was treated with 100% nitric acid for 1 hr at 35°C. A small amount of insoluble material was filtered off, and excess acid was then removed _in vacuo_. The residue was dissolved in anhydrous dioxan, then precipitated in methylene chloride. (JRF-253) $\eta_r^{1\%}$ acetone = 2.02.

2.   Polyureas

a.   New Polyureas

(1)   Preparation of Polyurea XII-f from 3,6-Dinitro-3,6-diaza-1,8-octane Diisocyanate and Water

(a)   Using the new technique of preparing polyureas from diisocyanates and water, a new polyurea was prepared from 3,6-dinitro-3,6-diaza-1,8-octane diisocyanate (see Table III).

(b)   Experimental (JKE-191)

To a 500-ml resin flask containing 1.86 g (103.5 meq) distilled water in 10 ml absolute dimethylformamide was added portionwise 30.67 g (207.0 meq) of diisocyanate (assay, 97.4%) in 40 ml absolute dimethylformamide. Immediate heating and gassing were observed in the reaction solution. A white, solid phase began to separate before all the diisocyanate had been added. After remaining at 65°C for 185 hours, the reaction had set to a solid, white mass, which was ground up with acetone in a blendor. After vacuum drying the following data were obtained: yield, 25.3 g (91%); relative viscosity, 1.32 (1% in formic acid); softening range, 190 to 195°C; impact stability >100 cm/2 kg; X-ray diffraction, polycrystalline; soluble in hot formic acid, insoluble in acetone, dimethylformamide, dioxan.

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TABLE III

NEW POLYUREAS

Polyureas XII-ʃ and XII-ʃ N
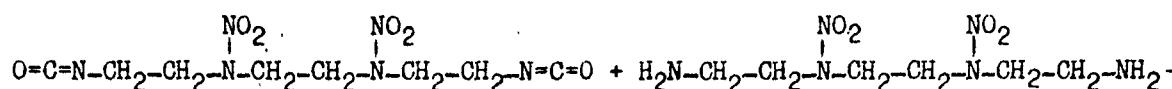
$$O=C=N-CH_2-CH_2-\underset{NO_2}{\overset{|}{N}}-CH_2-CH_2-\underset{NO_2}{\overset{|}{N}}-CH_2-CH_2-N=C=O \; + \; H_2N-CH_2-CH_2-\underset{NO_2}{\overset{|}{N}}-CH_2-CH_2-\underset{NO_2}{\overset{|}{N}}-CH_2-CH_2-NH_2$$

3,6-Dinitro-3,6-diaza-1,8-octane   3,6-Dinitro-3,6-diaza-1,8-
Diisocyanate   octane Diamine

$$C_8H_{12}N_6O_6$$ $$C_6H_{16}N_6O_4$$

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

$$(C_{14}H_{28}N_{12}O_{10})_n$$

Nitration

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

$$(C_{14}H_{26}N_{14}O_{14})_n$$
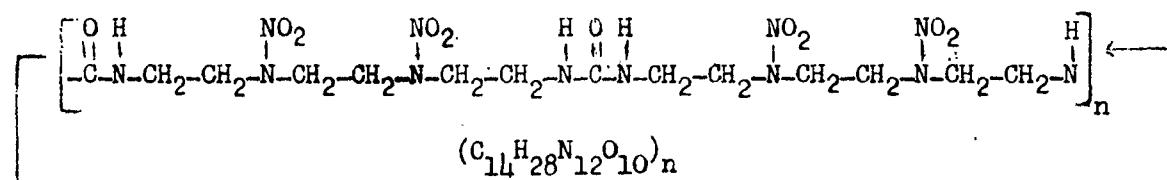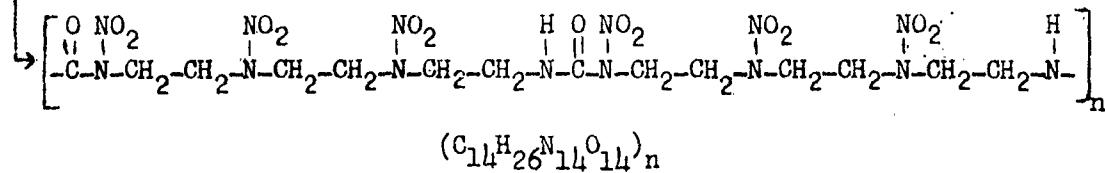
Theoretical I_{sp} = 200 lbf·sec/lbm

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Anal. Calc'd for $(C_{14}H_{28}N_{12}O_{10})_n$: %C, 32.06; %H, 5.38; %N, 32.05

Found: %C, 32.70; %H, 5.53; %N, 32.71

b. Further Work on Previously Described Polyureas

(1) Introduction

The preparation of Polyurea XIII-γ , described in Aerojet Report No. 740, p. 30, gave a high-melting, partially insoluble polymer. Because this polyurea was insoluble in cold nitric acid a temperature of 50°C was maintained for 2 hr during the subsequent nitration. The nitrated product did not give an analysis corresponding to the theoretical, and it was presumed that the high-temperature nitration had caused degradation and oxidation of the polymer. Therefore, the preparation of Polyurea XIII-γ was repeated with certain conditions changed. It was hoped that these changes would lead to a soluble, linear polyurea, which could be easily nitrated at a low temperature. This proved to be the case; when the diisocyanate was added portionwise to water (reversal of the previously described preparation) a high-melting polymer precipitated from dimethylformamide solution as before, but the polymer was now readily soluble in cold formic acid and cold nitric acid. The nitration proceeded according to the standard method, yielding a product whose elemental analysis compared more favorably with the calculated values. Severe degradation, however, was observed during the nitration. Another nitration was attempted wherein the use of dimethylformamide was avoided. Severe degradation was also observed when the nitric acid solution of the polymer was poured directly into water. Further study on the I-α (old III-A) system has also been made.

(2) Preparation of Polyurea XIII-γ (JKE-185) from 3-Nitro-3-aza-1,5-pentane Diisocyanate and Water

To a 500-ml resin flask containing 9.01 g distilled water (0.500 equivalent) in 30 ml absolute dimethylformamide was added dropwise over a period of 30 minutes 100.1 g (1.000 equivalent) of 3-nitro-3-aza-1,5-pentane diisocyanate in 40 ml absolute dimethylformamide. Immediate gassing and heating occurred within the reaction solution. Ice-bath cooling maintained a temperature of 60 to 70°C during the addition. After the addition, the reaction solution was heated to 80 to 90°C for 1 hr, after which no further gassing occurred. Within 1 hr after placing the reaction in a 50°C bath, a solid phase began to separate, and after 24 hr at 50°C, the reaction solution had set up to a hard, white solid. This material was ground with acetone in a blendor, washed free of dimethylformamide, and dried in vacuo. The following physical data were obtained: yield, 85 g (98%); relative viscosity, 2.53 (1% in formic acid); softening range, 165 to 170°C.

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(3)   Preparation of Polyurea XIII-γ N by Nitration of Polyurea XIII-γ , Prepared from 3-Nitro-3-aza-1,5-pentane Diisocyanate and Water

(a)   Experimental (JKE-187)

To 20.0 g Polyurea XIII-γ (JKE-185) in a one-liter flask was added 200 ml 100% nitric acid. Within ten minutes the polymer had completely dissolved. The acid was then stripped off using a vacuum of <1 mm for 2 hr, the pot temperature never rising above $20^{\circ}C$. One hundred ml of absolute dimethylformamide was added to the acid-plasticized residue, which dissolved rapidly. The polymer was precipitated by pouring the DMF solution into methylene chloride. After the polymer was vacuum-dried, the following physical data were obtained: yield, 16.8 g (63%) (Excessive handling losses account for the low yield); relative viscosity, 1.05 (1% DMF); softening range, 80 to $90^{\circ}C$; impact stability, 75 cm/2 kg; storage stability, excessive gassing and ballooning at room temperature within one week.

Anal. Calc'd for $(C_{10}H_{18}N_{10}O_{10})_n$:   %C, 27.40; %H, 4.14; %N, 31.96

Found: %C, 26.46; %H, 4.03; %N, 32.14

Heat of Combustion, Calc'd: 3358 cal/g for half-nitrated polymer.

Found: 3245 cal/g

(b)   Experimental (JKE-196)

To 2.0 g Polyurea XIII-γ (JKE-185) was added 40 ml 100% nitric acid. After the polymer had completely dissolved, the acid solution was poured into ice-water. The precipitated polymer was washed free of excess acid with water, and vacuum dried. Yield, 90%; softening range, 80 to $90^{\circ}C$; relative viscosity, 1.11 (1% in DMF); impact stability, 60 cm/2 kg; solubility, soluble in acetone, dimethylformamide, insoluble in dioxan; storage stability, no apparent decomposition within 4 weeks at room temperature.

Anal. Calc'd for $(C_{10}H_{18}N_{10}O_{10})_n$:   %C, 27.40; %H, 4.14; %N, 31.96

Found: %C, 25.00; %H, 4.04; %N, 31.30

(4)   Preparation of Polyurea I-∝: 3,3-Dinitro-1,5-pentane Diisocyanate and Water

(a)   Discussion

It was of interest to repeat the preparation of Polyurea I-∝ (III-A), using the technique of adding the diisocyanate to water. It was found that a higher-molecular-weight product was obtained, which analyzed well for the desired polyurea.

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                    (b)   Experimental (JKE-188)

                    To 3.367 g distilled water in 30 ml
acetone in a 500-ml resin flask was added portionwise 46.22 g 3,3-dinitro-
1,5-pentane diisocyanate in 30 ml acetone. Neither heating nor decar-
boxylation occurred during the addition of diisocyanate. The solution was
placed in a 50°C bath, and after 10 days the viscosity had noticeably
increased. The polymer solution was diluted with dimethylformamide,
filtered, and precipitated in water in a blendor. After vacuum drying,
the following data were obtained: yield, 39 g (94%); relative viscosity,
2.18 (1% DMF); softening range, 110 to 120°C; impact stability >100
cm/2 kg; X-ray diffraction amorphous; soluble in dimethylformamide,
insoluble in acetone, dioxan.

Anal. Calc'd for $(C_{12}H_{20}N_8O_{10})_n$:   %C, 33.03; %H, 4.62; %N, 25.68
                    Found: %C, 33.04; %H, 4.90; %N, 25.76

                    (5)   Preparation of Polyurea I-αN by Nitration
of Polyurea I-α , prepared from 3,3-Dinitro-1,5-pentane Diisocyanate
Water

                    (a)   Discussion

                    Polyurea nitration studies have shown
that severe degradation usually occurs sometime during the nitration. A
new anhydrous technique of nitrating polyureas has been used and it was
found that degradation also occurred.

                    (b)   Experimental (JKE-198)

                    To 5.00 g Polyurea I-α (III-A,
JRF-220 $\eta_r^{1\%}$ DMF = 1.61) in a 500-ml flask was added 50 ml acetic anhydride.

The polymer dissolved readily. The solution was cooled to 0°C, and 50 ml
of 100% nitric acid was added dropwise with stirring. After most of the
acid had been added, a solid polymer phase began to separate, which then
coalesced into a single, plasticized mass. To this two-phase system was
then added 135 ml more acetic anhydride, and after stirring 30 minutes
at room temperature complete dissolution had occurred. The solution was
filtered and precipitated in methylene chloride, followed by two washes
in methylene chloride. After vacuum drying the following data were
obtained: yield, 4.7 g (78%); softening range, 60 to 70°C; relative
viscosity, 1.17 (1% in acetone).

Heat of Combustion, Calc'd: 3071 cal/g (half-postnitrated)
                    Found : 2954 cal/g

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3.   Polyamides

a.   Introduction

The synthesis of nitro polyamides via the nitro ω-aminocarboxylic acids was considered in an effort to overcome the difficulties of preparing polyamides by the usual nylon methods. The synthesis of ε-4,4-dinitrocaprolactam was described in Aerojet Report No. 638, p. 95. Efforts to polymerize this lactam have failed.

b.   Discussion

Hanford and Joyce have described the polymerization of ς-caprolactam.* One method consists of first hydrolyzing the lactam, followed by polymerization at elevated temperature in vacuo. In the other, a small amount of an alkali metal salt of ω-aminocaproic acid is used as catalyst. These and other methods have failed to give polymeric material from ε-4,4-dinitrocaprolactam. Either the starting material has been recovered or decomposition has taken place. No further work is planned at this time.

c.   Experimental

(1)   To 2 g ε-4,4-dinitrocaprolactam in 10 ml dioxan was added 0.10 g ferric acetylacetonate. The slurry was kept at 100°C for 24 hours. The dinitrolactam was recovered unchanged.

(2)   To 2 g ε-4,4-dinitrocaprolactam in 20 ml diphenyl ether was added one drop of water. The mixture was warmed slowly to 150°C for 4 hours; it slowly darkened and evolved oxidizing gases. Upon cooling, most of the dinitrolactam was recovered.

(3)   To 2 g ε-4,4-dinitrocaprolactam in 25 ml diphenyl ether was added 0.10 g sodium methylate. The mixture was warmed slowly to 150°C. Oxidizing gases were evolved and only a small amount of dinitrocaprolactam was recovered.

(4)   To 0.225 ε-4,4-dinitrocaprolactam was added 10 ml 0.10 N sodium hydroxide. The mixture was warmed on the steam bath for half an hour, then evaporated to dryness. Two g ε-4,4-dinitrocaprolactam was added, and the flask was swept out with nitrogen. It was then placed in an oil bath at 190°C, 5°C above the melting point of the dinitrolactam. A mild fume-off occurred after 5 min in the bath.

(5)   Procedure (4) was repeated, 5 ml purified dimethylformamide was added, and the mixture kept at 150°C. The solution darkened and oxidizing gases were evolved after 10 min at 150°C.

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*J. Polymer Sci., 3, 167 (1948).

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III. TECHNICAL PROGRESS: FORMULATION STUDIES (Contract N7-onr-46201)

A.   INTRODUCTION

In order to find utility as solid rocket propellants, the linear nitropolymers require some modification in structure so as to yield desirable physical and mechanical properties. Furthermore, the structural characteristics of the polymer determine the methods which may be used for the preparation of a propellant grain. During the past quarter an intensive study has been made of the methods for increasing molecular weight by the introduction of small quantities of branching and/or cross-linking agents. It was found that approximately 1% branching of the polymer gives improved physical and mechanical properties (see Section V). Furthermore, plasticization of such branched nitropolyurethanes gives products with rubbery characteristics. Consideration is given to the problem of producing propellant grains with these branched polyurethanes.

B.   EFFECT OF CROSS-LINKING ON POLYURETHANE I-A

1.   Preliminary results have been reported on the problem of modifying Polyurethane I-A by cross-linking with nib glycerol.* Three more preparations of Polyurethane I-A (from 3,3-dinitro-1,5-pentane diisocyanate and 2,2-dinitro-1,3-propanediol) containing various amounts of nib glycerol as a cross-linking agent were undertaken, using 50 wt % dioxan as the solvent. Experimental results are given in Table IV.

TABLE IV

EFFECT OF CROSS-LINKING ON POLYURETHANE I-A

Run No.	Time, at 50°C, hr	Eq. Nib-G., %	Excess Diiso, %	$\eta_r^{1\%}$
OB-21	140	1.0	1.0[a]	1.64
OB-27	40	1.0	0.52[b]	2.75[c]
OB-28	16	1.5	0	2.18[c]

[a] The excess of diisocyanate was added at the beginning of the reaction.
[b] Added after 21 hr.
[c] These preparations set to insoluble gels when allowed to stand for 48 hr at room temperature. Relative-viscosity values were obtained on small portions removed after the specified period of reaction at 50°C.

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*Aerojet Report No. 740, p. 54

2.   A relatively low-molecular-weight polymer was obtained in Run No. OB-21, where 1% excess of diisocyanate was added at the beginning of the reaction. A very high-molecular-weight polymer was formed in Run No. OB-27, where monomer equivalence was obtained by later adjustment with 0.52% diisocyanate. These results indicate that only about 0.5% of the 3,3-dinitro-1,5-pentane diisocyanate is lost through side reactions under these conditions and that high molecular weights cannot be attained when the diisocyanate is present in slight excess. However, high-molecular-weight product was formed in Run No. OB-28, containing 1.5% nib-glycerol, even without monomer adjustment.

3.   In Runs OB-27 and OB-28, the preparations were removed from the 50°C bath when they were too viscous to stir. Both preparations set to tough dioxan-plasticized gels on standing for an additional 48 hr at room temperature. In each case, the gel was refluxed with a large volume of acetone and then worked in the Waring Blendor. The resultant slurry could be precipitated with water in the Morehouse mill to give a fine, fibrous product which was insoluble in acetone.

C.   EFFECT OF CROSS-LINKING ON POLYURETHANE XIII-A

1.   The availability of 3-nitraza-1,5-pentane diisocyanate (XIII) in abundant quantity and high purity (assay = 99.1%) indicated the desirability of extending the cross-linking studies to systems utilizing this monomer. Some results observed in several preparations of cross-linked Polyurethane XIII-A are discussed below.

2.   Preparation OB-29 utilized the calculated equivalents of 3-nitraza-1,5-pentane diisocyanate with 99% 2,2-dinitro-1,3-propanediol and 1% nib-glycerol, and yielded an acetone-insoluble gel within 18 hr at 50°C. The product was worked up with acetone and precipitated in the Morehouse mill to give a fine, fibrous material. In Run No. OB-31, which was an exact duplication of OB-29, it was established that the gel time in this system is about 10 hr at 50°C. Preparation OB-30 utilized the same amounts of reactants, but the addition of the 1% nib-glycerol was delayed for 5 hr, until a linear pre-polymer having a solution viscosity of 30 seconds (50% dioxan, 8 mm pipette) had been formed. On standing overnight (16 hr) at 50°C, this preparation also set up to an insoluble gel. Work-up in the usual manner gave a fine fibrous product. Preparation OB-34 utilized a 5% excess of diisocyanate with 98% diol and 2% nib-glycerol. After 24 hr at 50°C, the solution viscosity was only 2 seconds. To this thin syrup the calculated amount of diol required to restore equivalence was added, and the reaction continued. The solution viscosity increased to 55 seconds and leveled off. That too much diol had been added was seen when the addition of a small quantity lowered the solution viscosity to 51 seconds. To this branched polymer, having hydroxyl end-groups, there was added an amount of diisocyanate estimated to be in 0.3% excess. Gelation occurred within 15 minutes at 50°C. The product was worked up with acetone as before.

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        3.   It is expected that the variations in the order of addition
of the diisocyanate, diol, and triol investigated in the above preparations
will affect the distribution of branch units (triol) in the final polymer.
The several polymers obtained in fibrous condition will be compression-molded
into strands for stress-relaxation determinations. It is desired to establish
whether or not the differences in distribution of branch units cause sig-
nificant changes in the physical properties of the cross-linked polyurethanes.

    D.   CROSS-LINKING IN THE PRESENCE OF PLASTICIZERS

        1.   An important problem in formulating nitropolymers is to
find a suitable process for manufacturing propellant grains. A casting
process would be a convenient method, provided that the polymerization could
be conducted in the plasticizer. The effect of plasticizers on the I-A
system has been reported.* This report deals with work done on both the
I-A and the XIII-A systems.

        2.   Preparation OB-33 utilized a 5% excess of 3-nitraza-1,5-
pentane diisocyanate with 98% 2,2-dinitro-1,3-propanediol and 2% nib
glycerol in an equal weight-volume of 5,5-dinitro-2-hexanone. After 2 hr
at $50^{\circ}C$, the solution viscosity had reached 45 seconds. However, efforts
to convert this pre-polymer to a gel by the addition of the calculated
equivalents of either diethylene glycol or 1,5-pentanediol were unsuc-
cessful. Considerable darkening occurred in this preparation, as the
result of decomposition reactions involving the 5,5-dinitro-2-hexanone.

        3.   Previous attempts to develop a casting process have met
with serious difficulties due to bubble formation.** It has now been found
that the intermittent application of the vacuum of an aspirator to an uncured
casting of Polyurethane I-A (with 2% nib-glycerol) in 30 wt% 5,5,5-trinitro-
2-pentanone served to "work out" most of the bubbles. However, the cured
material, a rubbery solid obtained after 64 hr at $50^{\circ}C$, still contained a
number of relatively large bubbles. It is believed that the thermal decom-
position of 5,5,5-trinitro-2-pentanone (see below) was at least partially
responsible for this result. An attempt to prepare a casting of Polyurethane
I-A with only 20 wt % 5,5,5-trinitro-2-pentanone showed that it is very
difficult to operate at this low plasticizer level, because of the limited
solubility and high viscosity of the reaction mixture. After 30 hr at
$50^{\circ}C$ the cured material was hard at room temperature, but contained many
bubbles.

    E.   PLASTICIZATION OF BRANCHED AND CROSS-LINKED POLYURETHANE I-A

        The use of high-energy plasticizers as solvents for polyurethane
formation has, in certain instances, prevented the formation of high-
molecular-weight polymers. It was therefore of interest to investigate

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*Aerojet Report No. 740, p. 55.
**Aerojet Report No. 740, p. 56.

methods for the incorporation of these plasticizers into the high-molecular-weight, branched and cross-linked polymers isolated from dioxan solution. The following method was found to be satisfactory: The fibrous polyurethane was suspended in water and the plasticizer added slowly while stirring in a Waring Blendor. The resultant spongy mass was collected on a sintered-glass filter. The excess water was removed by passing the material through an unheated roller mill. The material was then worked on the roller mill at 150 to 170°F to obtain a homogenous mass of rubbery consistency. The samples were cut up while still warm into small granules suitable for compression molding or extrusion.

F.   COMPRESSION-MOLDING OF PLASTICIZED POLYURETHANE I-A

1.   A number of 5-in. strands were obtained by compression-molding of the plasticized samples on the Carver press at 180°F, and 6000 lb/sq in. pressure. The plasticizers studied include methyl 4,4-dinitro-valerate (MDNV), 5,5-dinitro-2-hexanone (DNH) and 5,5,5-trinitro-2-pentanone (TNP). The results are summarized in Table V.

TABLE V

PLASTICIZATION OF POLYURETHANE I-A

Polymer	Plasticizer	Appearance of Strand at R.T.
Slightly branched (OB-2)	5% MDNV	Slightly flexible, brittle
Slightly branched (OB-2)	10% DNH	Flexible, brittle
Slightly branched (OB-2)	15% MDNV	Flexible
Slightly branched (OB-2)	17% TNP	Flexible, dark yellow
Slightly branched (OB-2)	20% MDNV	Plastic to rubbery, tough
Highly branched (OB-4)	5% MDNV	Slightly flexible, brittle
Highly branched (OB-4)	15% MDNV	Rubbery, tough
Cross-linked (OB-27)	5% MDNV	Brittle
Cross-linked (OB-27)	15% MDNV	Rubbery, tough
Cross-linked (OB-27)	20% MDNV	Rubbery, extremely tough

2.   All of the molded strands were transparent, but the marked discoloration of the sample containing 5,5,5-trinitro-2-pentanone suggests that thermal decomposition of this compound occurs at the temperatures required for milling. Those strands described as being flexible and brittle were flexible when stressed slowly, but brittle when stressed rapidly. The

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rubbery samples had excellent recovery from 100% elongation. All of the more highly plasticized strands had rather poor dimensional stability and were observed to warp and develop surface "warts" on standing at room temperature. This behavior is probably associated with the "elastic memory" of the molding granules. Those strands which appeared suitable for physical property studies have been forwarded for that purpose.

G.   CONCLUSIONS

1.   It has been established that tough, rubbery materials may be obtained by plasticization of cross-linked nitropolyurethanes. The more detailed rheological studies will determine how well these materials meet the physical and mechanical requirements of a rocket propellant. There remains the pressing problem of devising a practical process for the preparation of propellant grains from these materials. The solution to this problem must also satisfy the need for sufficient specific impulse in the final product. Some approaches to this problem will now be considered.

2.   The possibility of utilizing a plasticized post-nitrated polyurethane as a "monopropellant" is made more attractive by the availability of very high-molecular-weight, yet predominantly soluble, branched polymer of the type of sample OB-4.* However, the accumulated experience of the past quarter has shown that it is rather difficult to obtain such material consistently. As the polymerizations are pushed to completion, there is great danger of exceeding the gel point, beyond which the reaction mixture is rapidly converted to more and more intractable material. Furthermore, the economics of a process involving isolation of the branched polymer from dioxan solution, drying, post-nitration, isolation from nitric acid solution, and finally plasticization, do not appear favorable. On the other hand, this method of obtaining pure nitropolymers of high specific impulse may be justified if it can be shown that they confer certain unique properties, perhaps as minor constituents of the propellant formulation.

3.   In Preparation OB-30 it was demonstrated that a linear pre-polymer formed in the presence of excess diisocyanate can be converted to an insoluble, three-dimensional polymer by the addition of the tri-functional monomer nib-glycerol. It should be possible to replace the solvent dioxan with a nitro-plasticizer and thus prepare a linear polymer-plasticizer matrix. To this matrix can be added the proper amounts of inorganic oxidizer, burning-rate catalyst, etc., and finally, the calculated amount of nib-glycerol. The mixture may then be extruded cold and the resultant strands cured in an oven at 50°C in order to complete cross-linking. Casting of the mixture and curing would also result in a tri-functional grain.

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*Aerojet Report No. 740, p. 55).

4.   The viscosity of the linear polymer-plasticizer matrix may be controlled by altering the amount of plasticizer and also by fixing the degree of polymerization of the pre-polymer according to the equation:[*]

$$DP_{\eta} = \frac{1 + r}{2r(1-p) + 1-r} \qquad (1)$$

where p is the extent of reaction and r is the monomer mole ratio.

5.   Preparation OB-34 demonstrates the possibility of utilizing another type of pre-polymer. In this case, the trifunctional branching agent is incorporated in the original reaction mixture, but gelation is prevented by using an excess of one or the other difunctional monomer. The situation is described by the equation:[**]

$$\propto = \frac{rpA^2 P}{1-rpA^2(1-P)} \qquad (2)$$

where $\propto = 1/2$ represents the critical condition for gel formation; pA, the extent of reaction of hydroxyl groups (when nib-glycerol is the branching agent); r, the ratio of hydroxyl groups to isocyanate groups initially present; and P, the ratio of hydroxyl groups (reacted and unreacted) belonging to nib-glycerol to the total number of hydroxyl groups in the mixture. For a given concentration of nib-glycerol, there is theoretically a minimum amount of excess diioscyanate required to prevent gelation. The actual amount will always be somewhat less than this because of the disregard of intramolecular reaction in the theory.

H.   EXPERIMENTAL

1.   Preparations No. OB-21, 27, 28, 29, 30, 31, 33, and 34 were 100-g batches prepared in a 500-ml resin flask equipped with dropping funnel, thermometer, viscosity pipette, and low-speed, high-torque stirrer. Specially purified, anhydrous dioxan (50 wt %) was used as the solvent (except for OB-33). Ferric acetylacetonate was used as the catalyst, 1×10^{-4} mole/equiv for XIII-A. The diisocyanate, disolved in a minimum quantity of dioxan, was always added slowly to a solution of the other reactants, with intermittent ice-bath cooling to maintain a reaction temperature of 45 to 50°C. Further reaction was conducted in a constant temperature bath at 50 $\pm$ 1°C.

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[*]P. J. Flory, Chem Rev. 39, 137 (1946).
[**]Ibid.

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2.   When insoluble gels were obtained, these were removed from the resin flask, broken up into small pieces, and refluxed with acetone (ca. 2 liters) for several hours. The resultant slurry was diluted further with acetone while being ground in the Waring Blendor. The total volume of the acetone slurry was usually about 3.5 liters. This was precipitated by running it slowly into a large volume of water in the Morehouse mill. The precipitated polymer was reground many times with decreasing separation of the stones. The resultant fine, fibrous material was squeezed free of excess water and air-dried overnight. Final drying was done in a vacuum desiccator over P_2O_5 and a pressure of <1 mm.

IV.   TECHNICAL PROGRESS: PHYSICAL STUDIES (Contract N7onr-46201).

A.   HEATS OF COMBUSTION

1.   Introduction

The importance of the determination of the heat of combustion has always been strongly emphasized on this program.[*] In particular, this method gives the best evaluation of the completeness of post-nitration. However, several months ago irregularities in the determination were observed. This was caused by corrosion of the Parr bomb, which yielded unreliable results. This phenomenon, called "corrosive burning," has been under investigation during the past quarter, and the problems associated with it have been solved.

2.   Corrosive Burning

The difficulties encountered in verifying the structure of certain postnitrated polyurethanes by the heat of combustion determination have been described previously.[**] The occurrence of corrosion of the Parr bomb was observed particularly when polyurethanes containing the nitramino group were burned. Further investigations of these polymers have shown that the problem is not as serious as was first supposed. In the first place, not all of the polyurethanes containing the nitramino group have resulted in corrosive burning, as shown in Table VI. Second, a method of computing the experimental heat of combustion has been devised which gives satisfactory checks with the predicted values even though corrosion is encountered. Finally, a device for avoiding the corrosion altogether has been developed.

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[*]Aerojet Report No. 740, p. 33.
[**]Ibid.

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TABLE VI

NORMAL AND CORROSIVE BURNING

Corrosive Burning	Normal Burning
XIII-AN	XIII-A
XIII-JN	XIII-J
XIII-MN	XIII-M
XIII-NN	XIII-N
XIII-ON	XIII-O
XII-AN (amorphous)	XII-A
	XII-AN (crystalline; two preparations)
	XIII-H, XIII-HN
	XII-J, XII-JN
	XII-N, XII-NN
	XII-MN
	XII-ON
	XII- γ, XIII-γ N

Legend:
    <u>Diisocyanates</u>

XIII	3-Nitraza-1,5-pentanediisocyanate
XII	3,6-Dinitraza-1,5-octanediisocyanate

    <u>Diols</u>

A	2,2-Dinitro-1,3-propanediol
J	2-Methyl-2-nitro-1,3-propanediol
M	N,N'-bis (2-Hydroxyethyl) oxamide
N	Ethylene glycol
O	5,5-Dinitro-12,-hexanediol

    <u>Diamine</u>

3-Nitraza-1,5-pentane diamine

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3.   Arbitrary Correction Terms for Corrosive Burning

Corrosive burning makes it impractical to try to measure the acid correction and the unburned-sample correction, as described in Report No. 740. These corrections normally vary over a comparatively small range. A nominal value for the acid correction is about 15 cal, and the nominal amount of unburned sample is about 10 milligrams when the sample weight is approximately 1.5 grams. These correction values were arbitrarily assumed in computing the experimental heats of combustion shown in Table VII. The end point of the temperature rise due to combustion in the bomb was distinguished from the temperature rise due to reaction of acids with the walls of the bomb by measuring the time of temperature rise on samples which did not show corrosive burning. The agreement of the experimental heats of combustion in Table VII with the predicted values is considered sufficient to verify the composition of the polymer.

4.   The Glass Liner for the Parr Bomb

a.   A means of avoiding corrosive burning has been found, which consists of protecting the walls of the bomb with a Pyrex glass liner. The liner is designed to shield all of the metal in the bomb from spattering solid particles or acids, with the exception of the electrodes which extend downward from the cover. These electrodes are apparently corrosion-resistant, so that no protection is necessary. The heat capacity of the bomb is corrected by adding the water equivalent of the total weight of glass used.

b.   The bomb with the glass liner was tested by burning a preparation of nitrated Polyurethane XII-AN, JRF-239-A. This preparation gave very corrosive burning, when run in the bomb without using the glass liner. When the glass liner was used there was no corrosion observed, and nominal values were obtained for both the correction for acid formed in the combustion and for unburned sample residue. The experimental value obtained for the heat of combustion was 2595 cal g^{-1}, which checks well with the predicted value of 2584 cal g^{-1}.

c.   A further test of the validity of the glass liner technique was made by burning a non-corrosive compound in the bomb, with and without the glass liner. The preparation was XII-AN, JRF-239-B, a crystalline precipitation of the same polymer preparation tested previously. The crystalline preparation gave non-corrosive burning in the bomb without the glass liner, and a heat of combustion of 2670 cal g^{-1}. With the use of the glass liner, the value was 2668 cal g^{-1}. The close agreement between these runs shows that no appreciable error is introduced by the use of the glass liner. The reason for the high experimental value for the crystalline preparation is given elsewhere in this report.

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TABLE VII

POST-NITRATED XIII POLYURETHANES

		Heat of Combustion, cal g^{-1}	
Polymer	Preparation	Obtained	Predicted
XIII-AN	JKE-179-2	2377	2379
XIII-JN	JRF-231-B	2994	2964
XIII-NN	JKE-180-2	2832	2843
XIII-ON	JKE-181-2	3067	3054

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   d. Drawbacks to the use of the glass liner are that its heat transfer is slow, so that the time required for attainment of temperature equilibrium is prolonged, and it is awkward to manipulate and subject to breakage.

   e. Another run was made on preparation JRF-239-A, without the use of the glass liner, but with the addition of 30% of cupric oxide. No corrosion was observed in this run, but the bomb washings contained soluble copper salts, which interfered with the analysis for acid correction and unburned-sample correction in the same manner as the soluble nickel salts obtained in corrosive burning. Assuming nominal correction values, the experimental heat-of-combustion value was 2496 cal g^{-1}, compared with a predicted value of 2584 cal g^{-1}. It is suggested that the cupric oxide reacts with oxides of nitrogen to give gaseous nitrogen, as in the Dumas method for nitrogen analysis. From this standpoint, the cupric oxide technique is a satisfactory means of avoiding corrosive burning. However, there is no readily applicable method of correcting for the thermal contribution of the cupric oxide, so that the method has no practical value. The low result obtained on the cupric oxide run indicates that the endothermic contribution of the cupric oxide is large.

5. Effect of Molecular Structure on Corrosive Burning

   The summary of polymers which did and did not give corrosive burning, shown in Table VI, gives very few definite correlations between structure and incidence of corrosive burning. All postnitrated polyurethanes of the XIII series except one (XIII-H) have given corrosive burning. Only postnitrated polyurethanes containing the nitraza group in the hydrocarbon chain give corrosive burning, but not all of them. The nitraza group does not necessarily give corrosive burning, as has been shown by the clean burning of many monomers and high explosives containing this group. The only postnitrated polyurethane of the XII series which has given corrosive burning is XII-AN; XIII-AN gave the greatest amount of corrosion in the XIII series. Only the amorphous preparation of XII-AN (preparation JRF-239-A) gave corrosive burning; two crystalline preparations (JRF-239-B, 2669 cal g^{-1}, and JRF-234-A, 2736 cal g^{-1}) gave normal burning. It is suggested that the presence of acetone in the crystalline precipitations could account for the high experimental heat of combustion in the crystalline preparations, and could also modify the speed of combustion so that corrosive burning would not occur. On the basis of heat-of-combustion computations, with 7346 cal g^{-1} and 2584 cal g^{-1} as the respective values for acetone and pure XII-AN, 1.6% is obtained as the acetone content of JRF-239-B and 3.1% as the acetone content of JRF-234-A. However crystallinity is not necessarily associated with corrosive burning, as not all the preparations in the left-hand column of Table VI are highly crystalline.

B.   MOLECULAR WEIGHT STUDIES OF A FRACTIONATED POLYURETHANE

1.   Introduction

One of the principal purposes of the fractionation of the large batch of Polyurethane I-J[*] was to obtain samples suitable for correlation of the methods used in this laboratory for molecular weight estimation. Although extensive descriptions of the osmometric molecular-weight determination, the isopiestic molecular-weight determination, and the relative-viscosity determination have been given in previous reports, no attempt has been made to interrelate values obtained by the respective methods, because the wide distribution of molecular weights within the samples studied has not permitted a rigorous basis for comparison. However, with the separation of the wide distribution into relatively homogeneous fractions, shown in Table VIII, it is possible to obtain significant values by the viscosity method, and by one or the other of the methods for number average molecular weight. These values partly reported previously have been completed and they permit calculation of the constants for the Staudinger equation, so that relative-viscosity values may be converted to molecular weights.

2.   Discussion of Individual Fractions

a.   The choice between the osmometric and the isopiestic method for the respective fractions was governed by the amount of leakage by diffusion encountered in attempting to run the fraction by the osmometric method. Of the fractions reported as osmometric determinations in Table VIII, none showed diffusion except R-2 and T-3. Molecular weight for these two fractions is reported for the portion which did not diffuse, according to the method described previously.[**] An attempt to run fraction S-3 by the osmometric method showed diffusion in excess of 25%, so that no significance was attached to the determination. It would be desirable to have values by the isopiestic method for fraction Q-2 and some of the higher fractions, but the attempt was not deemed advisable because significant results by the isopiestic method require a concentration of 0.1 molar or higher.

b.   Curvature of the π/c vs c plot was definitely found in all of the osmometric determinations except R-2, T-3, and Q-2. There was no indication of curvature in the Q-2 plot. There was some indication of curvature in the R-2 and T-3 plots, although the issue was somewhat confused as the result of inaccuracies caused by the slight leakage by diffusion.

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[*] Aerojet Report No. 712, pp. 20-24; No. 740, pp. 34-41.
[**] Aerojet Report No. 686, 3 April 1953, pp. 30-31.

TABLE VIII

MOLECULAR WEIGHT STUDIES, POLYURETHANE I-J (JRF-195)

Fraction	$\eta_r^{1\%}$ (1)	$[\eta]$ (2)	Experimental Method	M_n by Extrapolation (3)	M_n by Equation (4)	μ by Extrapolation	p by Equation
P-1	3.41	1.050	Osmometric	241,000	285,000	0.47	0.44
T-1	2.96	0.800	Osmometric	177,000	184,000	0.48	0.48
T-2	2.23	0.800	Osmometric	159,000	177,000	0.47	0.44
S-2	1.97	0.735	Osmometric	149,000	146,000	0.43	0.45
R-2	1.63	0.532	Osmometric(5)	81,300	112,000	0.45	0.45
T-3	1.49	0.424	Osmometric(6)	57,200	108,000	0.45	0.47
Q-2	1.42	0.300	Osmometric	43,800	—	0.42	—
S-3	1.37	—	Isopiestic	3,630	—	0.28	—
R-3	1.23	—	Isopiestic	1,330	—	0.17	—
Q-3	1.15	—	Isopiestic	1,420	—	0.01	—
O-3	1.08	—	Not determined	—	—	—	—
L-4	1.07	—	Isopiestic	820	—	0.01 to 0.41	—

(1) Relative viscosity of 1 gram of polymer in 100 ml of acetone solution
(2) Intrinsic viscosity, defined in Aerojet Report 540, 19 Sept. 1951, p. 13
(3) Number average molecular weight obtained by direct extrapolation of the π/c vs c plot
(4) Number average molecular weight obtained by use of Flory's equation.
(5) <1% leakage by diffusion was obtained on this fraction
(6) 6.1% leakage by diffusion was obtained on this fraction

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It may be noted in columns 5 and 6 of Table VIII that the molecular weight calculated by Flory's equation[*] agrees reasonably well with the molecular weight obtained by direct extrapolation, for fractions R-2 and T-3, which were the two fractions showing leakage by diffusion. This could be expected in view of the recent publication of Cleverdon and co-workers,[**] in which it is implied that curvature of the π/c vs c plot is necessarily attended by leakage through the membrane.

      c.   The values of the interaction parameter, μ, show a significant trend only with the fractions of lowest molecular weight. This is in accord with the observation that the rate of dissolution of the lower fractions in acetone was much greater than that observed for the higher fractions. The accuracy of the μ values is not considered sufficient for quantitative estimates of solubility, however, principally because the μ value is only slightly dependent on the slope of the π/c vs c curve when the osmometric method is used, but is strongly dependent on the slope of the curve of c vs the reciprocal of the apparent molecular weight when the isopiestic method is used. This strong dependence accounts for the wide variation in possible values for μ in fraction L-4. The precision in this determination was poor, due to the presence of a large amount of residual catalyst and impurities. This poor precision resulted in a large possible variation in slope, compared with the variation in the intercept, from which the molecular weight was calculated.

      d.   The molecular weight of fraction O-3 was not determined, because the sample was small and the relative viscosity did not differ appreciably from that of L-4.

3.   Calculation of Staudinger Equation Constants

      a.   Intrinsic viscosities were calculated from relative viscosities at several concentrations in accordance with the method described previously.[***] The log of these viscosities was plotted against the log of the molecular-weight values obtained on the two bases shown in Columns 5 and 6 of Table VIII. The resulting graphs are shown in Figures 1 and 2. The intercepts and slopes of the best straight lines for these graphs gave values of the constants K and a in the modified Staudinger equation

$$\left[\eta\right] = K \, M^a \tag{1}$$

[*] Aerojet Report 712 (10 July 1953) pp. 31-33
[**] D. Cleverdon, D. Laker, and P. G. Smith, J. Polymer Sci., XI, 3, 225 (1953)
[***] Aerojet Report No. 540 (19 Sept. 1951) pp. 12-20

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Polyurethane I-J Fractions; Molecular Weight by Extrapolation

Figure 1

Polyurethane I-J Fractions; Molecular Weight by Equation
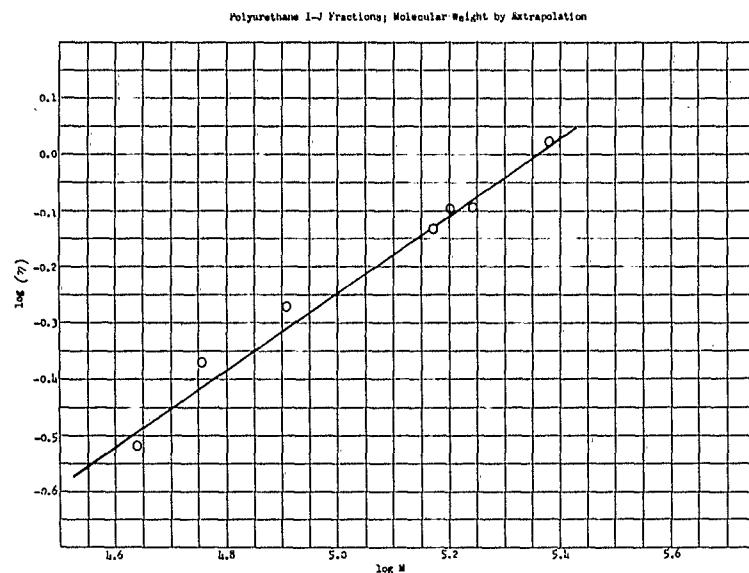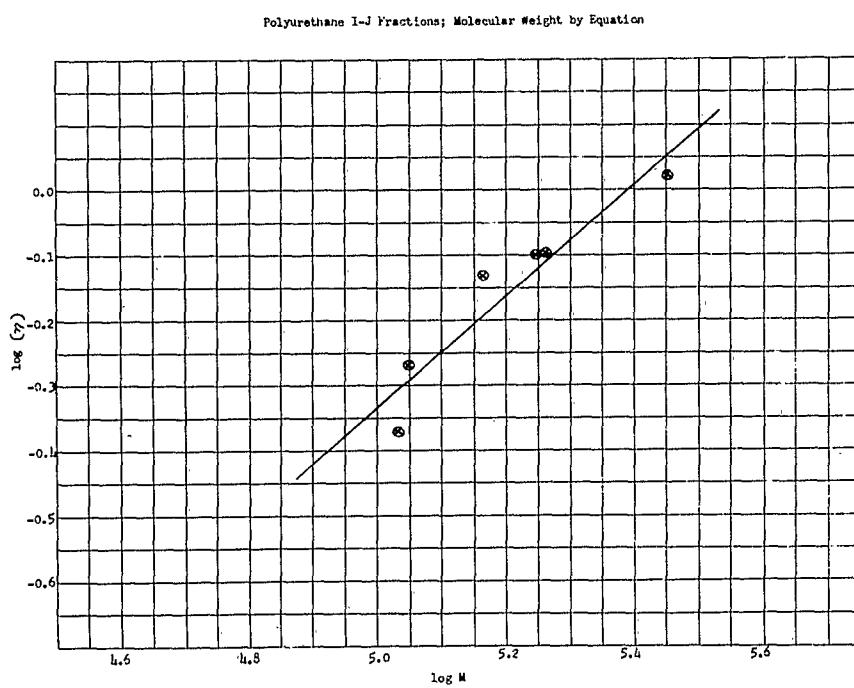
Figure 2

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where $[\eta]$ is the intrinsic viscosity and M is the molecular weight. The constants are given below:

Staudinger Equation Constants, Polyurethane I-J

	K	a
M_n by extrapolation	2.155×10^{-4}	0.684
M_n by equation	2.820×10^{-5}	0.844

Comparison of Figure 1 with Figure 2 shows that the points obtained by direct extrapolation to obtain M_n show the least deviation from the straight line. Accordingly, the values 2.155×10^{-4} and 0.684 are preferred for K and a, respectively, and will be used in future calculations for Polyurethane I-J. A reference curve, in which values of molecular weight and intrinsic viscosity are plotted directly on a log-log graph, is presented in Figure 3.

       b.   The quantity M in Equation (1) denotes viscosity-average molecular weight, which is more often designated M_v. The values obtained by the osmometric and isopiestic methods, on the other hand, are number-average molecular weights, usually designated M_n. Formulas for the two methods of expressing molecular weight are:

$$M_n = \left(\frac{n_1 M_1 + n_2 M_2 + - - -}{n_1 + n_3 + - - - -} \right) \quad (2)$$

$$M_v = \left(\frac{m_1 M_1^a + m_2 M_2^a + - - -}{m_1 + m_2 + - - -} \right)^{1/a} \quad (3)$$

where M_i is the molecular weight of a single homogeneous fraction, m_i is the mass of the i-th fraction, n_i is the number of moles of the i-th fraction, a is the constant from Equation (1), and the series is continued as far as necessary to account for all fractions present. It is readily seen that when a single, homogeneous fraction is involved, $M_i \equiv M_n \equiv M_v$. The use of Equation (1) in working with the M_n values of Table VIII presumes that single, homogeneous fractions were obtained in the fractional precipitation. An examination of Table VIII reveals an abrupt change in magnitude of M_n in

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Polyurethane I-J

Intrinsic Viscosity vs Molecular Weight

10^{-5} M

Figure 3
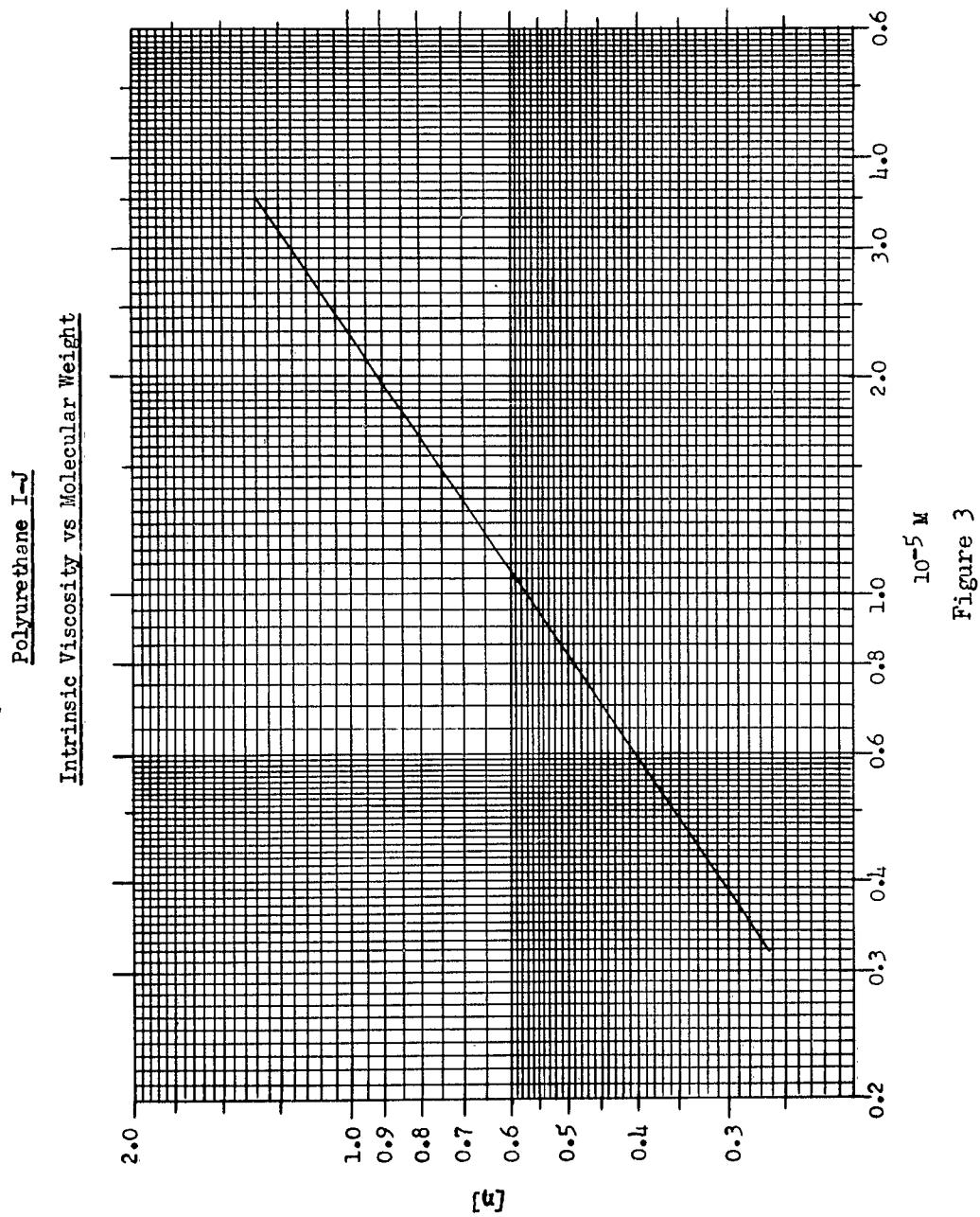
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progressing from Q-2 to S-3, and a very slight change thereafter, in progressing to L-4. The progression in values of relative viscosity is quite regular, however. All fractions designated 3 and 4 were precipitations of the last substance to come down from a second or third refractionation, and all (including T-3) contained appreciable amounts of substance which could permeate the osmometer membrane. For these reasons it is presumed that fractions P-1 through Q-2, with the exception of R-2 and T-3, are all homogeneous, high-molecular-weight polymer fractions; that R-2 and T-3 are also homogeneous, high-molecular-weight fractions except for a slight amount of low-molecular-weight material, most of which was removed by dialysis during the osmometric determination; and that S-3 through L-4 are all predominantly low-molecular-weight materials, contaminated to a great or lesser degree by portions of fractions P-1 through Q-2. According to this reasoning, it would not be permissible to place values of M_n for fractions S-3 through L-4 of Table VIII into Equation (1), because the fractions are not homogeneous. The inhomogeneity necessitates values of M_v, instead of M_n.

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

   A.   INTRODUCTION

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

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

      3.   Three techniques appear to be useful for examining the nature and magnitude of the inter-chain forces and thereby characterizing the nitropolymers with respect to suitability for propellant fabrication and formulation. Measurement of thermal expansivity has been used to define a second-order or "glass" transition temperature below which the polymer is brittle. The cohesive energy density of a polymer can be determined from measurements of the amount of swelling of the polymer by a "poor" solvent. This quantity in turn can serve as a guide in the choice of good solvents or good plasticizers for the polymer and can be useful in formulating propellants for fabrication by a plastisol casting process or by an extrusion process. Lastly, measurement of the relaxation of stress as a function of

time and temperature is used to determine a graphical equation of state (master curve) which associates a value of Young's modulus with a given temperature and given rate of strain. This master curve, which is a plot of the logarithm of the modulus versus the logarithm of reduced time, gives a concise summary of many mechanical properties, e.g., those involved in temperature cycling and embrittlement at low temperature.

Investigations during the current report period have been concerned with the measurement and interpretation of stress-relaxation data on various nitropolymers. The first section contains a mathematical analysis of stress-relaxation data, concluded by a non-mathematical summary of the significance of the analysis. The second section is concerned with the experimental data.

B.   STRESS RELAXATION STUDIES: THEORETICAL

1.   It has been shown that the master curve of the stress-relaxation data obtained on Nitropolymer I-J, (Preparation 195, Fraction P-1) is well represented by the formula*

$$\frac{E_G - E \,(\log t/K)}{E_G - E_F} = F_N\left(\frac{\log t/K}{\sigma}\right) \tag{1}$$

where

E_G, the "glassy" modulus, equals 10^{10} dynes cm^{-2}

E_F, the "fibrous" modulus, equals 3×10^8 dynes cm^{-2}

σ, the standard deviation of log reduced time, equals 0.85

Further,

$$F_N\,(Z) = \int_{-\infty}^{Z} \frac{e^{-u^2/2}\,du}{\sqrt{2\pi}}$$

where

$$Z = \frac{\log p}{\sigma} \text{ and } p = \frac{t}{K}$$

The characteristic relaxation time K is a function of the absolute temperature, determined empirically in such a way as to conjoin the

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*Aerojet Report No. 740 (15 September 1953), p. 46.

relaxation curves obtained at different temperatures, and proportioned to a value which adjusts the inflection point of the master curve to unit reduced time (t/K). Equation (1) may be rewritten succinctly:

$$E = E_G \left(\frac{E_F}{E_G}\right)^{F_N(Z)} \tag{2}$$

Formula (2) represents the S-shaped part of the master curve out to the "fibrous" plateau, but does not represent the behavior associated with the second dispersion region. For this reason, Equation (2) must be associated with a mechanical model which includes both a single fibrous spring and a distribution of Maxwell elements. The equation for such a model is

$$E = E_F + \Sigma E_i \, e^{-t/\mathcal{T}_i} \tag{3}$$

2.   The basic approach of a rheological program is implied in relation (3). For if an expression for the instantaneous modulus E as a function of time and temperature is known, then in principle it is possible to find a sequence of weighted exponentials $E_i e^{-t/\mathcal{T}_i}$, such that their sum will reproduce the time dependence of E at any temperature. The physical significance of any one of these weighted exponentials is that it locates the relaxation process on the absolute time scale through the value assigned to $\mathcal{T}_i$ and that it measures the contribution to the overall modulus by the value assigned to E_i. It is possible then to choose the most important terms of this sum and construct a mechanical model which simply approximates the behavior of the model. From this model it is then possible both to calculate and predict the behavior of a propellant grain made of this material under the influence of any arbitrary time-dependent stress or strain. For example, the amount of deformation resulting from creep under a constant load at a given temperature may be calculated. Or for example, the instantaneous modulus associated with a given high rate of loading at any temperature is readily calculated. In fact, the tensile curve at high rates of loading can be calculated. Further data would be necessary to determine the point of rupture.

3.   Besides allowing for the calculation of the response of the material to any time-dependent stress or strain, Equation (3) contains, through the temperature dependence of the $\mathcal{T}_i$ values, the basis for simply stating qualitatively whether failure because of brittleness is a problem or not. For example, if the most important relaxation processes at -75°F take place in less than 10^{-4} sec, the propellant will almost certainly fire successfully at this temperature, almost regardless of its strength, for it is becoming evident that failure takes place in the first 1 or 2 millisec after firing. On the other hand, if the relaxation processes take place between 100 millisec and 100 sec, as with linear nitropolymers (not branched), then the propellant must rely upon its toughness or strength (defined as the

work required to rupture) in order to withstand a high rate of stress loading at relatively low temperatures.

      4.   In order to facilitate the analysis of the relation between the instantaneous modulus, E, and the distribution function, E_i, it is convenient to replace the sum by an integral. Further, since $E \equiv E\ (p)$ is a function of reduced time ($p = t/K$), consistency is maintained by factoring the scale and temperature dependencies of T_i into α_i and K, where α_i is the new temperature-independent dimensionless relaxation time of the i-th element in the characteristic relaxation time. Thus

$$E(p) = E_F + \Sigma E_i\ e^{-p/\alpha_i} \qquad (4)$$

By taking the temperature dependence from the dummy variable, the difficulty of associating a distribution function with a temperature is avoided. This will be discussed in the next section. Equation (4) may now be converted into integral form by grouping the weighted exponentials $E_i e^{-p/\alpha_i}$ according to their density along the reduced relaxation time scale, α_i. Thus, if $dn(\ )$ is the differential number of relaxation processes characterized by relaxation times between α and $\alpha + d\alpha$, then

$$E(p) = E_F + \int_0^\infty E(\alpha)e^{-p/\alpha}\ dn(\alpha) \qquad (5)$$

where

$$\int_0^\infty dn(\alpha) = 1$$

It is operationally meaningless to separate $E(\alpha)$ and $n(\alpha)$, and a density distribution function may therefore be defined by the relation $E(\alpha)\ dn(\alpha) = D(\alpha)\ d\alpha$. Equation (5) then becomes:

$$E(p) = E_F + \int_0^\infty D(\alpha)e^{-p/\alpha}d\alpha \qquad (6)$$

The distribution function $D(\alpha)\ d\alpha$ indicates the contribution to the part of the modulus which is in excess of the fibrous modulus from relaxation processes taking place in the interval α to $\alpha + d\alpha$. In dealing with stress-relaxation data on linear amorphous polymers, other investigators[*] have written

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[*] B. Catsiff and A. V. Tobolsky, ONR Tech. Rpt. RLT-8, Princeton University.

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$$E(t) = \int_0^\infty D'(\tau) e^{-t/\tau}\, d\tau \tag{6a}$$

This relation involves an inconsistency in that, if $E(t)$ is represented by an analytical function which levels off at a finite value ("rubbery" modulus, for example) at infinite time, then the distribution function $D'(\tau)$ must become infinite as τ approaches ∞ in order to overcome the damping effect of the exponential factor $e^{-t/\tau}$. Another difficulty with Equation (6a) is that it is not suited to representing the reduced time data, for the integral on the right-hand side of (6a) is a function of time only, τ serving merely as a dummy variable. Therefore, it is necessary to factor the temperature dependence out of τ. Equation (6) can be rewritten as:

$$E(p) = E_F \int_0^\infty \frac{(1/\alpha)}{\alpha^2} e^{-p/\alpha}\, d\alpha + \int_0^\infty D(\alpha) e^{-p/\alpha}\, d\alpha \tag{6b}$$

or

$$E(p) = \int_0^\infty D'(\alpha) e^{-p/\alpha}\, d\alpha \tag{6c}$$

where

$$\alpha D'(\alpha) = \alpha D(\alpha) + \frac{E_F}{\alpha}\, \delta(1/\alpha)$$

Since the Dirac delta function $\delta(1/\alpha)$ is non-zero only when α approaches infinity, it follows that $D'(\alpha)$ equals $D(\alpha)$. Thus, investigators who have used Equation (6a) have obtained the correct distribution function, even though Equation (6a) may not be used in conjunction with an analytic function which approaches a finite value at infinite time.

5.   If one were able to provide an analytical expression which would represent not only the S-shaped part of the master curve, but also the second dispersion region, in which the modulus drops off to zero for a linear amorphous polymer, then it would be correct to use

$$E(p) = \int_0^\infty D(\alpha) e^{-p/\alpha}\, d\alpha \tag{6d}$$

Further, a physical significance may be attached to the area under the relaxation curve obtained at any one temperature on linear coordinates:

$$\int_0^\infty E(p)dt = \int_0^\infty E(p)Kdp = K \int_0^\infty \alpha D(\alpha)d = K\Sigma \alpha_i E_i \qquad (7)$$

$$= \Sigma T_i E_i = \Sigma \eta_i = \bar{\eta}$$

In other words, the bulk viscosity $\bar{\eta}$ is directly related to the distribution function $D(\alpha)$ by the relation:

$$\log \bar{\eta} = \log K + \log \int_0^\infty \alpha D(\alpha) \cdot d\alpha \qquad (8)$$

This is to be compared with the relation used by Tobolsky[a]

$$\log \bar{\eta} = \log \int_0^\infty T D(T) \, dT \qquad (8a)$$

Since T is merely a dummy variable, one is confronted with the concept of a temperature-dependent distribution function in order to obtain the temperature dependence of the viscosity. But the distribution function per se is a topological invariant of the polymer network and therefore should not be considered as temperature-dependent. For this reason, it is preferable to make extensive use of the quantity K (characteristic relaxation time) to express temperature dependence, log K being an empirically known function of the temperature.

6.   In a similar manner, the expressions for the real (E_1) and imaginary (E_2) parts of the complex dynamic modulus $(E^* = E_1 - iE_2)$ may be expressed in terms of p, K, and α. In order to preserve symmetry the definition $p = \frac{1}{K\omega}$ is used. This allows for a dimensional equivalence between the dynamic "p" and the static "p". Thus,

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[a] A. V. Tobolsky, ONR Technical Report RLT-2, Princeton University.

$$E_1 = E_F + \Sigma \frac{E_i \omega^2 \gamma_i^2}{1 + \omega^2 \gamma_i^2} = E_F + \int_0^\infty \frac{\alpha^2 D(\alpha)\, d\alpha}{p^2 + \alpha^2} \tag{9}$$

$$E_2 = \Sigma \frac{E_i \omega \gamma_i}{1 + \omega^2 \gamma_i^2} = \int_0^\infty \frac{p\alpha D(\alpha)\, d\alpha}{p^2 + \alpha^2} \tag{10}$$

$$\eta_{dyn} = \frac{E_2}{\omega} = K \int_0^\infty \frac{p^2 \alpha D(\alpha)\, d\alpha}{p^2 + \alpha^2} \tag{11}$$

Note that as $\omega \longrightarrow \infty$, $p \longrightarrow 0$, $\eta_{dyn} \longrightarrow 0$, no viscous loss;

and as $\omega \longrightarrow 0$, $p \longrightarrow \infty$, $\eta_{dyn} \longrightarrow \bar{\eta}$

Similarly as $\omega \longrightarrow$, $p \longrightarrow 0$, $E_1 \longrightarrow E_G = E_F + \int_0^\infty D(\alpha)\, d\alpha$, cf. Eq. 6; (12)

and as $\omega \longrightarrow 0$, $p \longrightarrow \infty$, $E_1 \longrightarrow E_F$, cf. Eq. 6 \hfill (13)

Now consider Eq. (6) again. As $t \longrightarrow 0$, $p \longrightarrow 0$,

$$E(p) \longrightarrow E_G = E_F + \int_0^\infty D(\alpha)\, d\alpha = E_F + 2.303 \int_0^\infty \alpha D(\alpha)\, d\log \alpha \tag{14}$$

Since α extends over many cycles of log reduced time, it is convenient to introduce the new variable $\log \alpha$ into (14). The density distribution function $D(\alpha)$ then is replaced by the function $\alpha D(\alpha)$, which has the physical significance of the modulus of an element whose reduced relaxation time is exactly α. In other words,

$$E_G - E_F = \int_0^\infty D(\alpha)\, d\alpha = 2.303 \int_0^\infty \alpha D(\alpha)\, d\log \alpha \tag{15}$$

This means that the area under the distribution function is equal to the difference between two areas, one equal to the "glassy" modulus and the other equal to the "fibrous" modulus. No other decomposition is possible because the Laplace transform is a contact transformation which preserves sign and reverses parity.* For example, t^n becomes p^{-n-1}. Thus, it follows that $\alpha D(\alpha)$ must become negative somewhere along the reduced relaxation-time scale.

7.   The following analysis was used for obtaining $\alpha D(\alpha)$ from the experimental data. If $F(p)$ is a real positive function with no branch points along the real axes and is given by

$$F(p) = \int_0^\infty f(t)\, e^{-pt}\, dt \qquad (16)$$

then

$$f(t) = \lim_{n\to\infty} \frac{(-1)^n}{n!} \left(\frac{n}{t}\right)^{n+1} \left[F^{(n)}\right]_{p=\frac{n}{t}} \qquad (17)$$

where $F^{(n)}$ indicates the nth derivative with respect to p. Similarly, if

$$E(p) - E_F = \int_0^\infty D(\alpha) e^{-p/\alpha}\, d\alpha \qquad (18)$$

then

$$\alpha D(\alpha) = \lim_{n\to\infty} \frac{(-1)^n}{(n-1)!} \left[p^n E(p)^{(n)}\right]_{p=n\alpha} \qquad (19)$$

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*Widder, <u>Laplace Transform</u>, Princeton University Press.

Successive approximations to $\propto D(\propto)$ are tabulated below:

$$(1) = -p \frac{dE}{dp} = - \frac{1}{\sigma_n} \frac{dE}{dZ} \tag{20}$$

$$(2) = p^2 \frac{d^2E}{dp^2} = \frac{-1}{\sigma_n} \frac{dE}{dZ} + \frac{1}{\sigma_n^2} \frac{d^2E}{dZ^2} \tag{21}$$

$$(3) = -\frac{p^3}{2} \frac{d^3E}{dp^3} = \frac{-1}{\sigma_n} \frac{dE}{dZ} + \frac{3}{2\sigma_n^2} \frac{d^2E}{dZ^2} - \frac{1}{2\sigma_n^2} \frac{d^3E}{dZ^3} \tag{22}$$

Here Z is equal to $\frac{\log p}{\sigma} = \frac{\ln p}{\sigma_n}$, where $\sigma_n = 2.303$

The successive derivatives of E with respect to Z are related by a recursion polynomial whose coefficients are derived from a generalized Pascal triangle. This makes it possible to set this computation up as an iterative problem. Because the power series in σ_n (which is of the order of 2) converges fairly rapidly, it has not been necessary to do this. A plot of the first four approximations to $\propto D(\propto)$ versus $\log \propto$ is shown in Figure 4, which reveals that the general shape of the distribution function is already well determined by the second approximation. The first approximation becomes better the larger the value of σ_n, which in turn means a broader dispersion region in the master curve.

       8.   Attempts are now under way to approximate $\propto D(\propto)$ by two delta functions. The negative area introduces a new type of behavior which necessitates the use of a new mechanical element in the model.

       9.   The location of the positive peak on the reduced relaxation time scale reveals that most of the relaxation processes take place at a value of $\Upsilon = \frac{K}{6}$ and distribute themselves on the characteristic time scale roughly from $10^{-2}K$ to 10^2K. Thus, at the distinctive temperature of L-J, which is $116°F$, the value of the characteristic relaxation time is roughly 160 sec,[*] and so the relaxation times at this temperature range from 2 sec to 16,000 sec with a maximum density at 27 sec. This may be interpreted physically by stating that, if a given stress be applied to a high-molecular-weight, amorphous Nitropolymer L-J at its distinctive temperature within 16,000 sec, then the tensile strength of the polymer

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Aerojet Report No. 740 (15 September 1953), pp. 42, 46
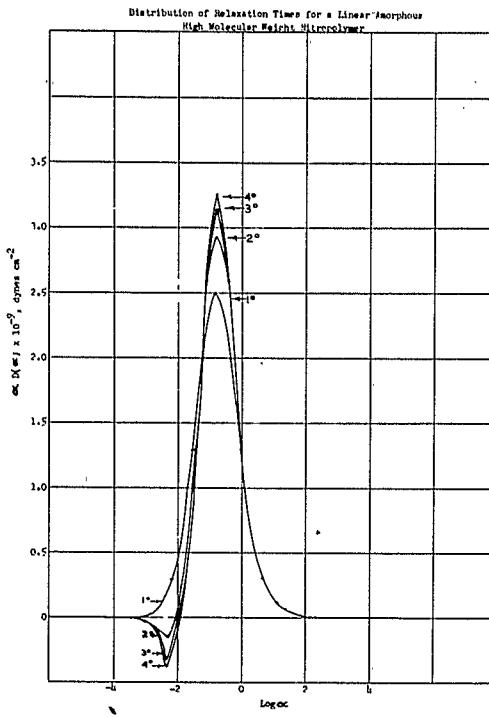
Figure 4

must exceed the given stress in order to avoid rupture. Another way of interpreting the physical value of T = 27 sec is by the (retardation) time it takes the nitropolymer to deform (creep) a maximum amount, determined by the given stress imparted at the distinctive temperature. Remembering that the activation energy which retards flow in linear, amorphous nitropolymers is approximately 60 kcal/mole, the retardation times at ambient temperature can become astronomically large.

C.   STRESS RELAXATION AND OTHER STUDIES: EXPERIMENTAL

1.   Polycrystalline Materials

a.   Stress-relaxation data were obtained on Nitropolymer XIII-γ (insoluble gel, polyurea of 3-nitraza-1,5-pentanediamine and 3-nitraza-1,5-pentane diisocyanate) at 136°F (Figure 5). Although this material has an X-ray diffraction pattern characteristic of strongly crystalline materials, it relaxes rapidly and seems to be characterized by a very broad distribution of relaxation times.

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Stress Relaxation of XIII-γ at 136°F
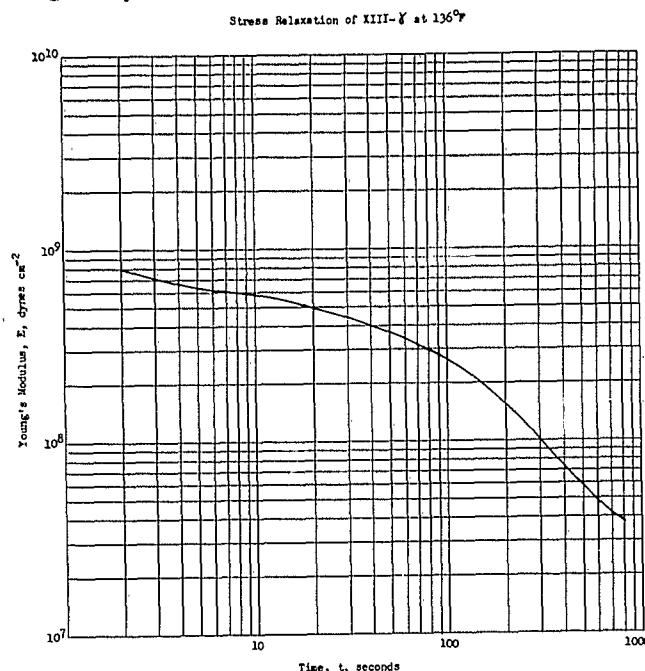
Figure 5

      b.   The results of stress-relaxation studies on XIII-γ and XII-A* (polyurethane of 2,2-dinitro-1,3-propanediol and 3,6-dinitraza-1,8-octane diisocyanate) indicate that, although these nitropolymers reveal diffraction patterns characteristic of strongly crystalline materials, the amount of crosslinking due to the presence of crystallites is not enough to prevent the long-time modulus from declining to zero. This decrease of the modulus below the "rubbery" or "fibrous" modulus is known as a "second dispersion effect", as distinguished from the "first dispersion" or glass transition", sometimes also called "second-order transition". Not only is the amount of crosslinking by crystallites insufficient to bring about a rubbery behavior, but also the presence of the crystallites seems to lower the tensile strength of the nitropolymer. This is evidenced

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*Aerojet Report No. 740 (15 September 1953), p. 47.

by the fact that the amount of crystallization which takes place in XII-A is roughly proportional to its digestion time in acetone, after which period of digestion the now-crystalline material has become quite brittle and friable. Finally, no strongly crystalline nitropolymers of high molecular weight have been prepared with softening points above 90°C. For these reasons the search for a promising crystalline nitropolymer was postponed temporarily in order to investigate the recently developed highly branched gel structures, comprised of a linear nitropolymer to which has been added 1 to 5% of a trifunctional alcohol, nitroisobutylglycerol, (nib glycerol).

2.   Branched Materials

a.   Strands fabricated from Nitropolymer I-A, (Preparation OB4, polyurethane plus 1% NBG) became insoluble in acetone after compression-molding, although the raw powder was completely soluble. This is a significant development, for it indicates the possibility of making a propellant grain by curing in a gel structure during compression molding. Since gel structures swell rather than dissolve in a solvent, these new branched, rubbery, gel structures will be useful for swelling studies and further rheological studies.

b.   Since the addition of 1% nib-glycerol appears to be barely sufficient to bring about gelation, two fractions of IA containing 1% nib-glycerol have been prepared, one soluble in acetone, the other insoluble. Stress relaxation data obtained upon the former, denoted by IA-OB4, are shown in Figure 6. Data obtained upon the latter, denoted by IA-OB27A, are shown in Figure 7. The master curve for IA-OB4 comprises data obtained over a range of temperature from 86°F to 130°F. Below 86°F the relaxation is too slow to produce any significant addition to the master curve. Over this limited range of temperature the log K vs T plot (Figure 8) shows no inflection point, and thus at present a distinctive temperature for IA-OB4 cannot be defined by the procedure outlined previously[*].

c.   From the initial results obtained on IA-OB27A at 90 and 120°F, it begins to appear doubtful that the "fibrous" modulus of 3×10^8 dynes cm^{-2} has a real significance. Although the master curve for OB27A reveals a slight plateau at approximately 2×10^8 dynes cm^{-2}, this can be explained by hysteresis in the Schaevitz dynamometer in the region where the stress reading is being determined by the difference between two large quantities. A final conclusion on this point must wait until data is obtained on larger cross-sectioned samples above 120°F. In either case, both OB4 and OB27A are characterized by very broad distributions of relaxation times. This is what one would expect from a highly branched structure as opposed to a regularly crosslinked structure.

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[*]Aerojet Report No. 740 (15 September 1953), p. 46.

Master Curve for IA-OB4

T, °F	K, sec.
130	1
124	3.1
120	4.3
116	9.6
112	13.
106	94.
100	250.

Reduced time, t/K, dimensionless

Figure 6

Master Curve for IA-OB27A

T, °F	K, sec
120	1
90	1700

Reduced time, t/K, dimensionless
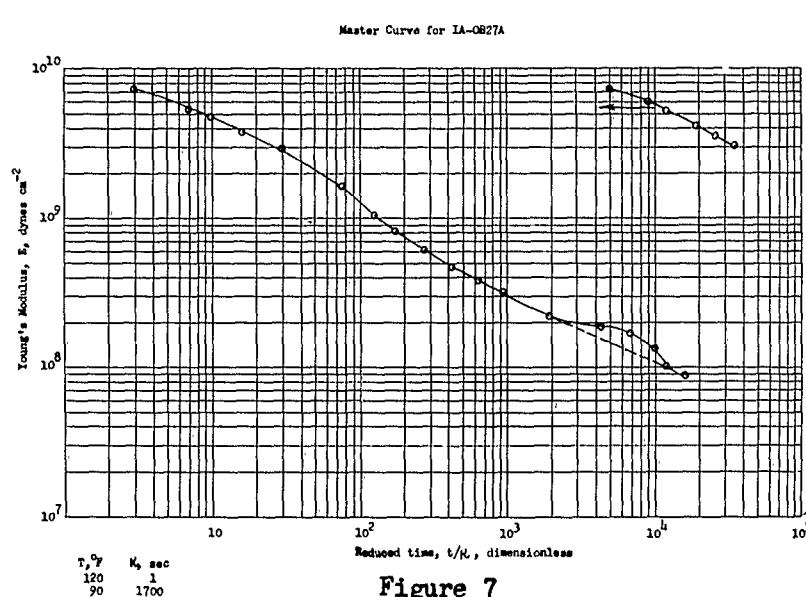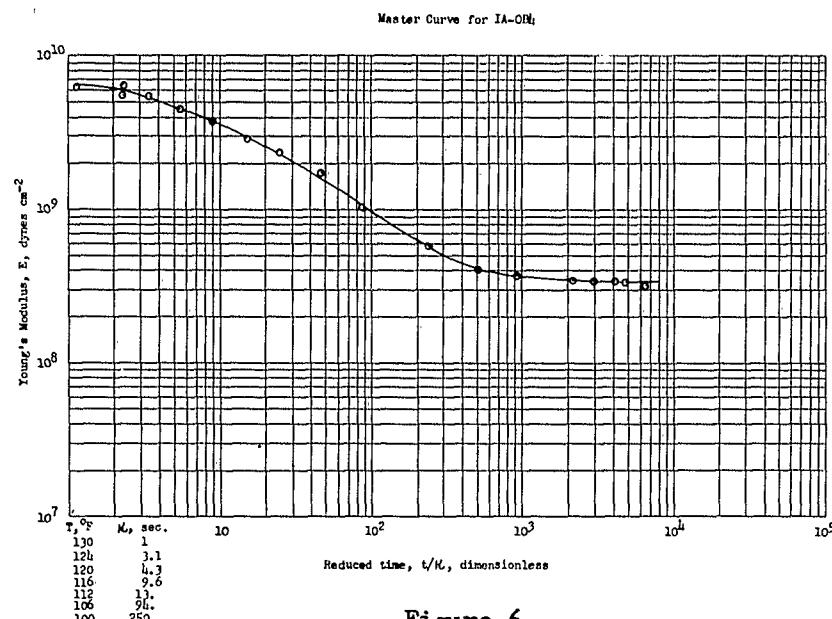
Figure 7

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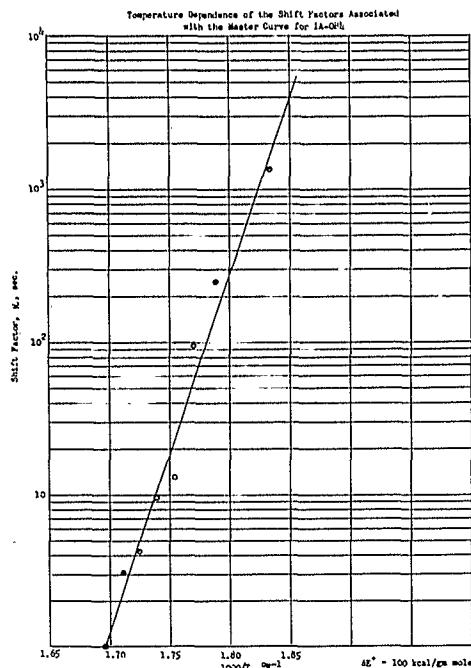
Figure 8

        d.   Evidence for the existence of a real "rubbery" modulus
in highly branched nitropolymers is afforded by the relaxation data obtained
at 120°F on OB4 in which 5% methyl dinitrovalerate has been incorporated
(Figure 9). This material has a high extensibility (approx. 100%) and recovers
rapidly and completely. At 120°F, the modulus imparted by a 1% deformation
relaxes to a value of 4×10^7 dynes cm^{-2} in 100 sec, and remains constant
thereafter, indicating that IA-OB4 is a true gel structure, which evinces
rubbery behavior upon plasticization. A comparison of the mechanical
behavior of the branched I-A samples and the plasticized branched IA is
shown in Figure 10.

        e.   Another nitropolymer which has been used for
fabrication studies is XIII-A, a polyurethane of 3-nitraza-1,5-pentane
diisocyanate and 2,2-dinitro-1,3-propanediol. In order to study the effect
of the competition between the -triol (nib glycerol) and the -diol (A)
for the isocyanate groups, two fractions were prepared, one to which the
1% nib-glycerol was added at the start of polymerization, the other to
which it was added at the end. A comparison of the mechanical behavior
of these two materials at 120°F is shown in Figure 11. At this tempera-
ture at least there is no apparent difference. The two curves lie within
the limits of experimental accuracy.

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Stress Relaxation of IA-OB4 Plasticized with 5% Methyl Dinitrovalerate at 120°F
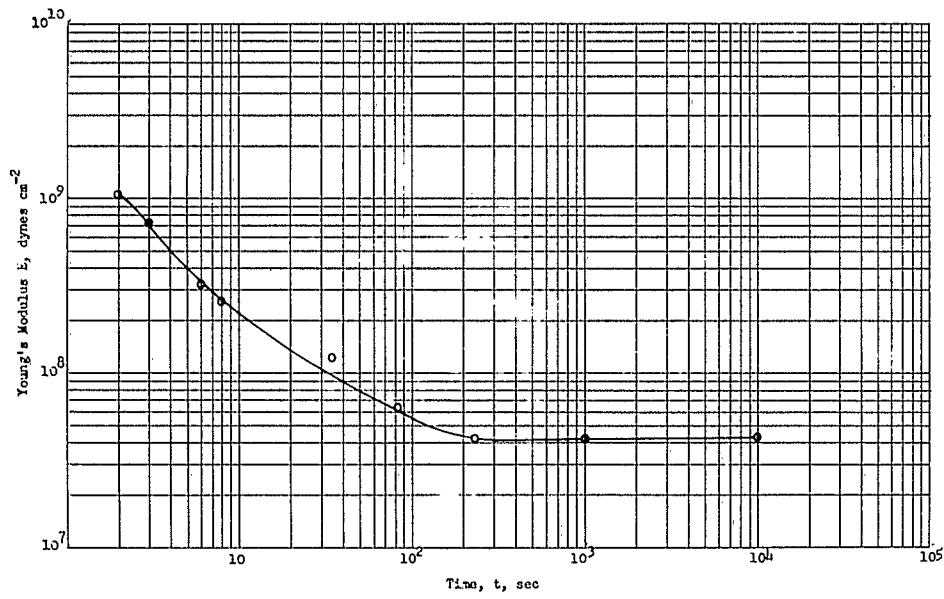
Figure 9

Comparison of Relaxation Behavior of IA-OB4, IA-O827A, and IA-OB4 + 5% MDNV at 120°F
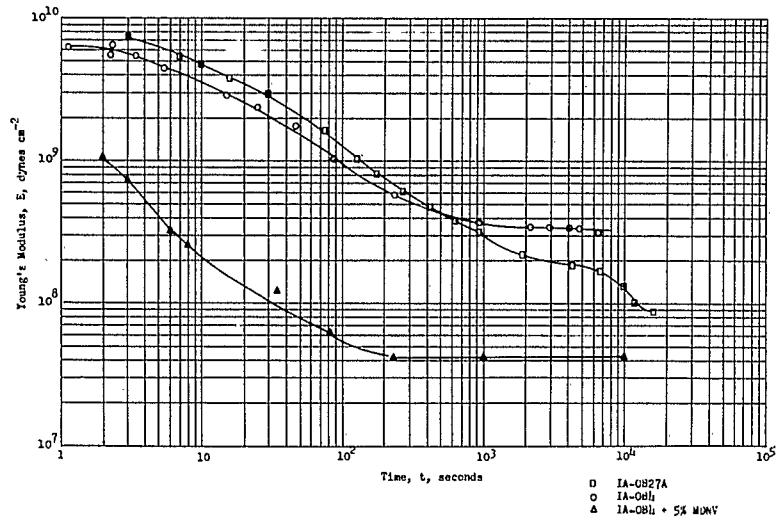
Figure 10

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Stress Relaxation of XIII-A Containing 1% NBG at 120°F·Comparison of

Initial and Final Additions of Branching Agent to Polymerization
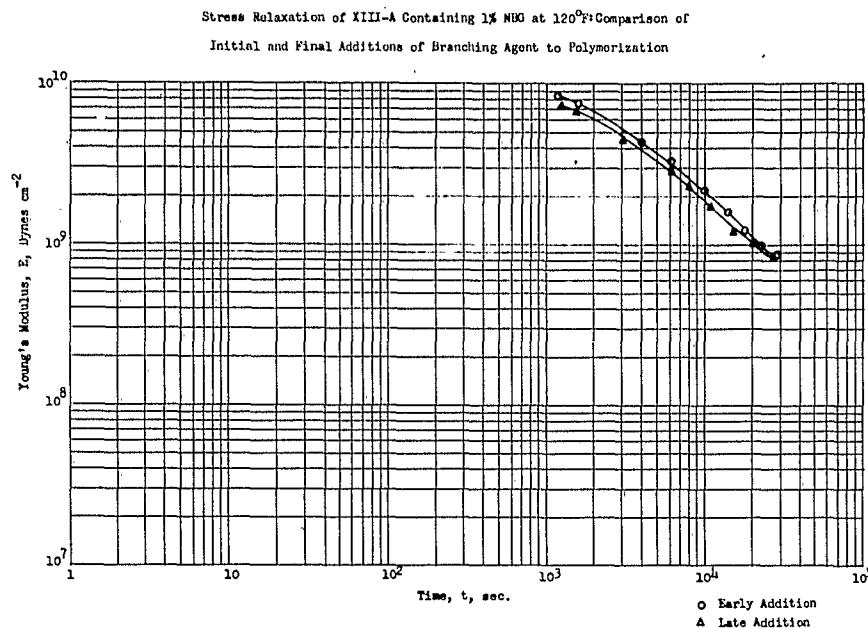
Figure 11

3.   Linear Amorphous Materials

Although the material is extremely brittle, it was
possible to follow the stress relaxation in 3,3-dinitrobutylacrylate at
60°F (Figure 12). It appears that the "glassy" modulus of this material
lies somewhat below the usual value of 3×10^{10} dyne cm^{-2}, i.e. at 5×10^9 dyne cm^{-2}. This may correlate with the extremely low tensile strength.
The sharp drop in the value of the modulus after 10,000 sec indicates
that the short polymer chains (low-molecular-weight material) have
become disentangled and that the material will proceed to behave mechani-
cally as a liquid. A liquid, by definition, cannot sustain a tensile
or shear stress.

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

A.   INTRODUCTION

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

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Stress Relaxation of 3,3-Dinitrobutyl Acrylate at 60°F
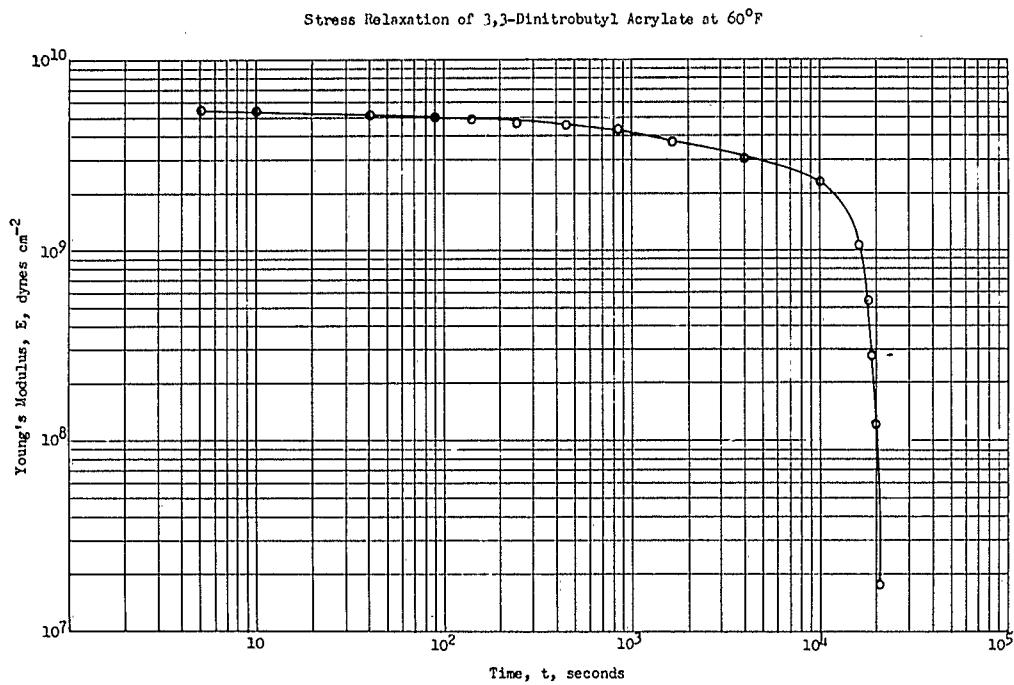
Figure 12

B.   BALLISTIC PROPERTIES

        1.   Measurements made on a 90/10 mixture of Polyurethane
I-AN and the sodium salt of dinitroacetonitrile (DNAN), containing two
parts of lead salicylate, reveal a burning rate of 0.80 in./sec at 1000
psia and a pressure exponent, n, of 1.1.[*] A comparison between the burning
rate vs pressure curves determined for the 90/10 mixture with and without
the addition of the lead salt is shown in Figure 13.

        2.   Burning rates were determined as a function of pressure
at 60°F for several of the recently developed nitropolymers. Figure 14
reveals that the pressure exponent for three of these has the value of
0.94. The values of the burning rates at 1000 psia and the chemical
composition of these nitropolymers are listed in Table IX. Nitropolymer
I-A is included for the sake of comparison. The strongly crystalline
Polyurea XIII-γ did not ignite.

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[*]Aerojet Report No. 740 (15 September 1953), p. 53.

VI Technical Progress, B (cont.)   Report No. 772

Burning Rate-Pressure Curves for I-AN/DNAN With and Without Lead Salicylate
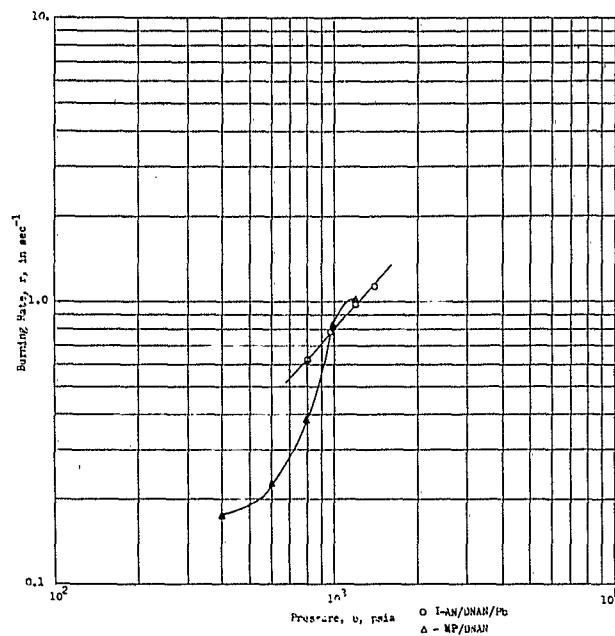
Figure 13

Burning Rate-Pressure Curves for I-⋘, XIII-A, XII-A
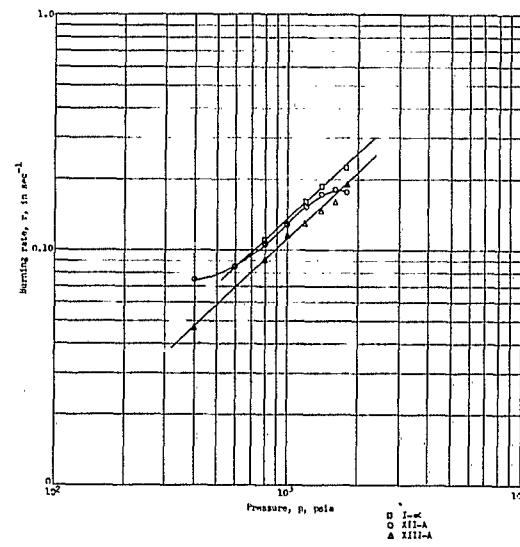
Figure 14

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3.   The striking effect of the incorporation of 10 wt % of the sodium salt of dinitroacetonitrile upon the burning rates of branched nitropolymers is shown in Figures 15 and 16. The burning rate of OB28 (contains 1.5% nib glycerol) is increased from 0.13 to 0.30 at 1000 psia and 60°F. The burning rate of OB4 (contains 1% nib glycerol) is increased from 0.10 to 0.14 at 1000 psia and 60°F. In all four cases the slopes of the burning rate vs pressure curves are much greater than 1. A 50/50 mixture of OB3 (contains 0.75% nib glycerol) and NH_4NO_3 has a burning rate of 0.1 at 1000 psia and 60°F (Figure 15). This is not different from that of ordinary I-A. The addition of 10 wt % of solid boron hydrides (B_{10} and higher) to nitropolymer I-H yields a material (IH-BH) with a burning rate of 0.28 in. sec^{-1} at 1200 psia and 60°F. Although this is an interesting example of a good burning-rate catalyst, the toxicity and instability of the boron hydrides restricts their use in solid propellants to laboratory investigation.

TABLE IX

BURNING RATES OF SOME NITROPOLYMERS

Symbol	Derivation	Burning Rate at 1000 psia, in. sec^{-1}
I-α	Polyurea of 3,3-dinitro-1,5 pentane-diisocyanate and 3,3-dinitro-1,5-pentanediamine	0.135
XIII-A	Polyurethane of 3-nitraza-1,5-pentanediisocyanate and 2,2-dinitro-1,3-propanediol	0.128
XII-A	Polyurethane of 3,6-dinitrazo-1,8-octane diisocyanate and 2,2-dinitro-1,3-propanediol	0.11
XIII-γ	Polyurea of XIII-diisocyanate and α-diamine	—
I-A		0.10
OB4	IA + 1% nib-glycerol	0.10
OB28	IA + 1.5% nib-glycerol	0.125

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Burning Rate-Pressure Curves for OB-28, 90/10 OB28/DNAN, and 50/50 OB3/NH₄NO₃
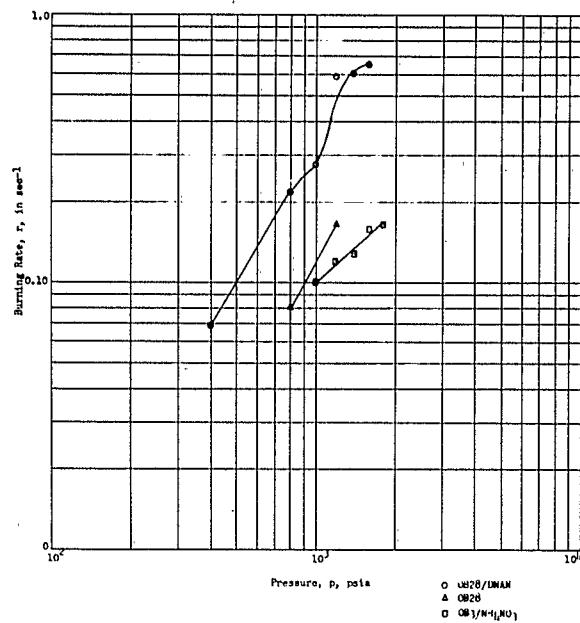
Figure 15

Burning Rate-Pressure Curves for OB4, 90/10 OB4/DNAN, and 90/10 IH/BH


Figure 16

Page 66
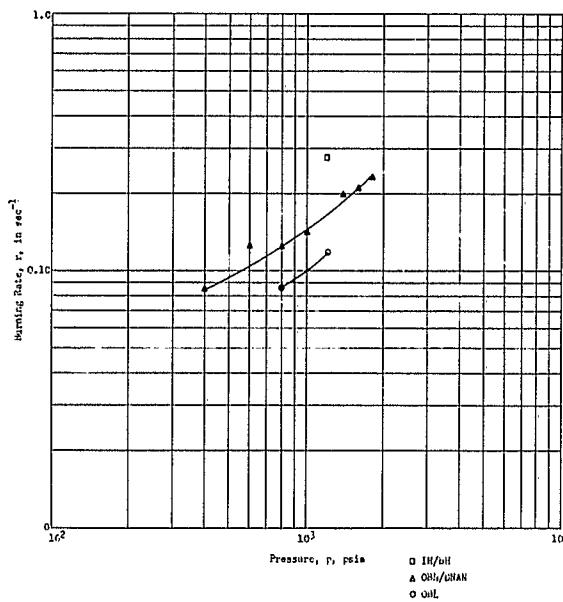
VII. TECHNICAL PROGRESS: ORGANIC SYNTHESIS (Contract N7-onr-46201)

A. INTRODUCTION

The synthesis of monomers and intermediates deals with the intro-
duction of certain functional groups into a structure containing nitro groups
For example, the establishment of a suitable double bond will lead to a vinyl
monomer, and the introduction of hydroxy or isocyanate groupings will lead
to monomers for condensation and addition-type polymers. The other alternative
for the production of nitromonomers is to start with compounds containing the
functional groups and introduce the energy-donating nitro groups. During
the last quarter attempts have been made to prepare polymerizable vinyl
monomers with a low chain-transfer constant. 2-Nitraza-1,4-butyl diisocyanate,
a new monomer containing the nitramino group, has been prepared for condensatio
polymerization. Furthermore, a program has been started to prepare a series
of diols containing the nitramino group.

B. NITROOLEFINS

1. The Attempted Preparation of Nitraminoethyl Acrylate

Nitraminoethyl acrylate appears to be a desirable vinyl
monomer because of its low chain-transfer constant, even though the estimated
specific impulse is rather low. On the other hand it is expected that the
acid sensitivity[*] of nitramino alcohol will cause difficulties in the prepa-
ration of the acrylate ester. Esterification of this alcohol with acrylic
acid was attempted by several methods. Refluxing a solution of the alcohol
and acid in benzene containing a small amount of p-toluene-sulfonic acid was
found to give no esterification, and the same reaction attempted in concentrated
sulfuric acid caused decomposition and polymerization. The alcohol with
acrylyl chloride in a calcium carbonate slurry gave mostly a thick oil, along
with a small amount of the ester. Satisfactory esterification, however, was
obtained by the use of an acrylic acid—trifluoroacetic anhydride mixture
with the alcohol. The product was a liquid boiling at about 35°C at 3 μ,
insoluble in water but soluble in aqueous bicarbonate solution with gas
evolution. However, the results of two elementary analyses were quite un-
satisfactory. From these results it can be concluded that a severe degradation
has taken place during the esterification reaction, causing loss of most of
the nitramino group. This is in agreement with a similar result obtained by
the Rohm and Haas Co., in an attempt to prepare the methacrylate of nitra-
minoethanol.[**]

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[*] Franchimont and Lubin, Rec trav. chim. 21, 45 (1902).
[**] Rohm and Haas Progress Report No. P-53-2, March, 1953.

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2.   Attempted Preparation of N-Nitro-N-methyl Acrylamide

a.   Discussion

(1)   The result of the chain-transfer studies on vinyl polymerization was a shift in interest to the use of postnitrated acrylamides as monomers. As recorded previously, many attempts have been made to prepare various nitro-substituted acrylamides.* However, post-nitration of the monomers or polymers did not yield satisfactory products. In order to learn more about the nitration of this type of compound, N-methyl acrylamide was chosen. After successful nitration on the amide nitrogen this would yield a compound with an estimated specific impulse, I_{sp}, of 144 lbf sec/lbm.

(2)   The nitration of N-methyl acrylamide has been carried out using an acetic anhydride—anhydrous nitric acid mixture to give a crystalline product, mp 120 to 121°C. The elemental analysis of this substance did not agree with that of the desired N-nitro-N-methyl acrylamide, but corresponded most closely with the empirical formula $C_4H_6N_4O_7$. The material failed to give a Liebermann nitroso reaction, and no N-H band appears in its infrared spectrum. The data available at present are insufficient to assign a structure for this new compound.

(3)   Nitration of N-methyl acrylamide with anhydrous nitric acid at room temperature, 0, -20, and -30°C, gave only water-soluble products. The compound, mp 120 to 121°C, could not be formed under these conditions.

(4)   In order to protect the double bond in the nitration, hydrogen chloride was added across the double bond to yield β-chloropropionamide as a white solid. Nitration of this compound with anhydrous nitric acid or with a nitric acid—acetic anhydride mixture gave a yellow oil which could not be crystallized. Attempts to dehydrohalogenate this with pyridine or sodium carbonate gave only dark-brown oils which could not be crystallized and decomposed during attempts at distillation.

b.   Experimental – Nitration of N-Methyl Acrylamide*

To 5 ml of 100% nitric acid, cooled to -30°C, was slowly added 1.5 g of N-methyl acrylamide dissolved in 5 ml of acetic anhydride. The mixture was permitted to warm to room temperature over 1 hr, and was then poured, with stirring, onto crushed ice. The resulting gum solidified after about 10 minutes, and was filtered and washed with ice water. The 1.65 g of white product, mp 114 to 116°C, was recrystallized twice from methylene chloride. The resulting colorless crystals melted at 120 to 121°C dec.

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*Aerojet Reports No. 740, p. 57; 686, p. 55-60; 663, p. 70, and 638, p. 73.
**Mourreu, Ann. chim. et phys. [7] 2, 178 (1894)

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Anal. Calc'd for $C_4H_6N_2O_3$: %C, 36.93; %H, 4.57; %N, 21.54

$C_4H_6N_4O_7$: %C, 21.63; %H, 2.72; %N, 25.23

Found: %C, 20.59; %H, 2.52; %N, 25.00

3. Attempted Preparation of N-Nitro-N-(3,3-dinitro-butyl) Acrylamide

The acetic anhydride--nitric acid method of nitration was found to give a solid product with methyl acrylamide, and the same procedure was attempted with dinitrobutyl acrylamide in the hope of obtaining the corresponding nitramide. In each of several nitrations using the nitric acid--acetic anhydride mixture a thick white gum, which could not be solidified, was obtained. On standing, and during attempts to crystallize, the material yellowed and bubbled. Distillation at 4 μ was not successful. Nitration in anhydrous nitric acid and in a nitric acid--sulfuric acid mixture gave no water-insoluble product.

C. PREPARATION OF NITRO ALCOHOLS

1. Attempted Preparation of 3-Nitramino-1,2-propanediol

The synthesis of 3-nitramino-1,2-propanediol has been attempted, using in part the same series of steps as in the Franchimont synthesis of nitraminoethanol.[*] This involves the nitration of 2-oxazolidone and then hydrolysis with loss of carbon dioxide. In the present case, the known 5-chloromethyl-2-oxazolidone[**] was chosen as an intermediate so as to present only one reactive center for nitration. It was hoped that the nitrated compound could be then converted to the 5-acetoxymethyl derivative and transesterified to the 5-hydroxymethyl-3-nitro-2-oxazolidone. Hydrolysis of this compound would then yield the desired nitramino diol The procedure is outlined as follows (I to V):

[*]A.P.N. Franchimont and A. Lubin, Rec. trav. chim. 21, 45 (1902)
[**]A. L. Thomsen, Ber. 11, 2136 (1878). E. Paterno and M. Cingolami, Gazz. chim. ital. 38, I, 243 (1908).

$$\text{ClCH}_2\text{-CH}\underset{\underset{\text{C}}{\underset{\|}{\text{O}}}}{\overset{}{\text{---}}}\overset{}{\underset{\text{NH}}{\text{CH}_2}} \longrightarrow \text{ClCH}_2\text{-CH}\underset{\underset{\text{C}}{\underset{\|}{\text{O}}}}{\overset{}{\text{---}}}\overset{}{\underset{\text{N-NO}_2}{\text{CH}_2}} \longrightarrow \text{CH}_3\text{COOCH}_2\text{-CH}\underset{\underset{\text{C}}{\underset{\|}{\text{O}}}}{\overset{}{\text{---}}}\overset{}{\underset{\text{N-NO}_2}{\text{CH}_2}}$$

$$\qquad\qquad\text{I} \qquad\qquad\qquad\qquad \text{II} \qquad\qquad\qquad\qquad \text{III}$$

$$\longrightarrow \quad \text{HOCH}_2\text{-CH}\underset{\underset{\text{C}}{\underset{\|}{\text{O}}}}{\overset{}{\text{---}}}\overset{}{\underset{\text{N-NO}_2}{\text{CH}_2}} \qquad\qquad \text{ClCH}_2\text{-CHOH-CH}_2\text{NHNO}_2$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{VI}$$

$$\qquad\qquad\qquad \text{IV}$$

$$\qquad\qquad\qquad \text{HOCH}_2\text{-CHOH-CH}_2\text{NHNO}_2$$

$$\qquad\qquad\qquad\qquad \text{V}$$
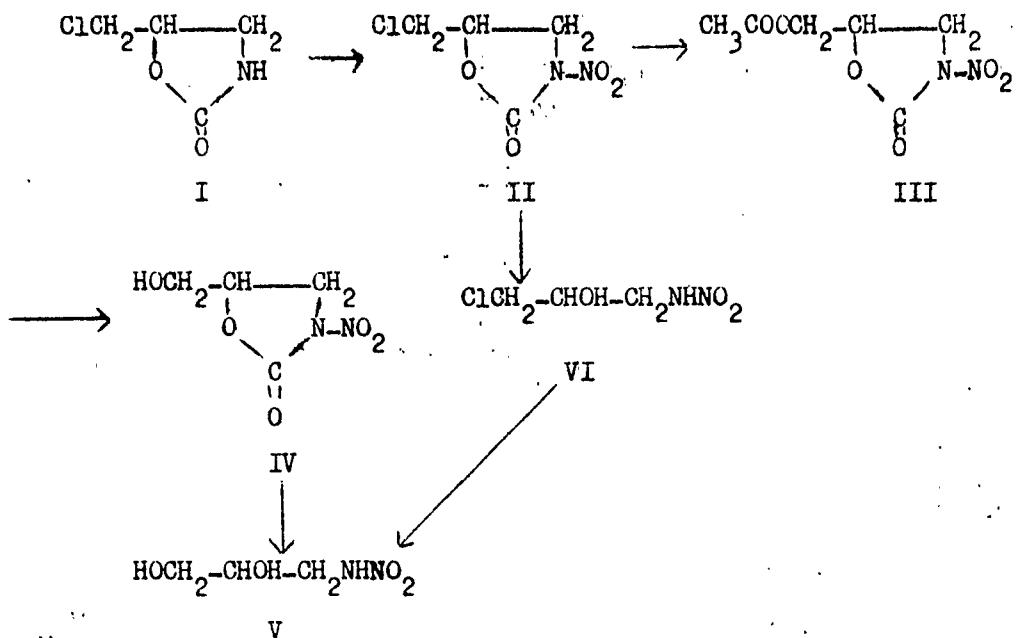
An alternate procedure would consist of decarboxylation of II to give VI, which would then be converted to yield the desired product V. However, all efforts to bring this series of reactions to a successful end failed. The chloromethyl oxazolidone was prepared by refluxing epichlorohydrin and potassium cyanate in aqueous solution (15% yield) and was nitrated with 100% nitric acid (75% yield). Replacement of the chlorine atom has not been achieved under a variety of conditions. Refluxing the 5-chloromethyl-3-nitro-2-oxazolidone with silver acetate in glacial acetic acid or acetonitrile, or with potassium acetate in glacial acetic acid gave, in every case, little or no chloride salt. Only starting material could be isolated as an organic product. No reaction could be detected after refluxing the compound with $CaCO_3$ in aqueous acetone for one hour. Refluxing in water for three hours gave a colorless liquid, bp $105^\circ/2\mu$, containing chlorine and soluble in water. In the aqueous reaction mixture halide ion could be detected, corresponding to 2% hydrolysis of the organic halide during the boiling. This liquid is believed to be 1-chloro-3-nitramino-2-propanol.

Because of the well-known ease of dehydrohalogenation of chlorohydrins with alkali, the reaction of the 1-chloro-3-nitramino-2-propanol with base was studied. The chlorohydrin was found to decompose under treatment with hot sodium hydroxide solution, but to eliminate hydrogen chloride with only slight yellowing at room temperature with sodium hydroxide or sodium bicarbonate. However, neutralization of the reaction product, the sodium salt of the nitramine, was found to be accompanied by vigorous bubbling whether carried out with dilute sulfuric or acetic acid, or with hydroxylamine hydrochloride.[*] No non-volatile organic product could be isolated from the resulting solutions.

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[*]N. Kornblum and G. E. Graham, J. Am. Chem. Soc. 73, 4041 (1951).

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2. Preparation of 3-Nitraza-1,5-pentanediol

a. Discussion

(1) Two procedures have been used to prepare 3-nitraza-1,5-pentanediol. The first path utilizes the F-1 process[*] to prepare the dinitrate of the nitramino diol (DINA), which is then hydrolyzed in boiling water.

$$(HOCH_2CH_2)_2NH \xrightarrow{HNO_3} (O_2NOCH_2CH_2)_2NH \cdot HNO_3 \xrightarrow[Ac_2O]{AcCl}$$

$$(O_2NOCH_2CH_2)_2N-NO_2 \xrightarrow{H_2O} (HOCH_2CH_2)_2N-NO_2$$
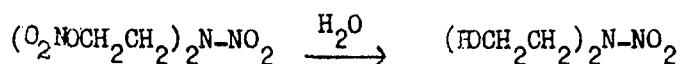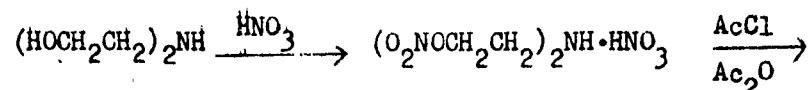
This method is capable of giving high yields of the crude diol, but a convenient procedure for preparing the pure material has not been worked out as yet.

(2) The second path to the 3-nitraza-1,5-pentanediol (III) is via the oxidation of 3-aza-3-nitroso-1,5-pentanediol (II) with pertrifluoroacetic acid[**] according to the equation:
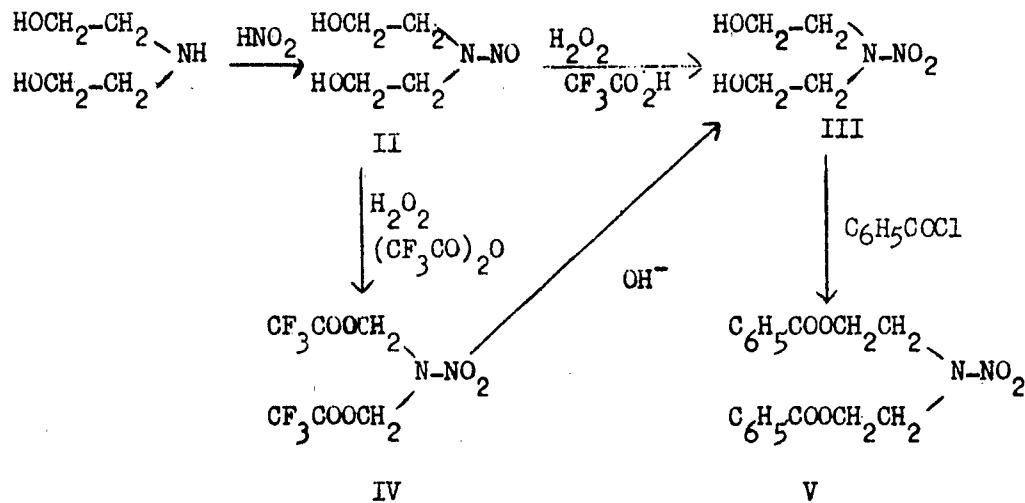
This reaction gave a mixture of water-soluble and water-insoluble products, both of which could be converted to 3-nitraza-1,5-pentanediol dibenzoate (V) by the Schotten-Baumann procedure. Since the water-insoluble fraction gave the pure dibenzoate (V) only after preliminary treatment with base, this fraction is believed to be the bis-trifluoroacetate (IV), which would be expected to be easily saponified. This fraction (corresponding to a 19%

[*]M. Carmack, OSRD Report 5157, June 19, 1945.
[**]W. D. Emmons and A. F. Ferris, J. Am. Chem. Soc. 75, 4623 (1953).

yield) was also colorless, in contrast with the violet product obtained from the water-soluble fraction (47%) containing III. More work will be done in order to obtain this valuable diol in a form suitable for polymerization.

b.   Experimental

(1)   Preparation via 3-Nitraza-1,5-pentanediol

Dinitrate

Following the procedure reported by Carmack,[*] 26 g (0.25 mole) of diethanolamine was slowly added to 50 g (0.8 mole) of anhydrous nitric acid while the solution was stirred and maintained at -10 to -20°C. The resulting mixture was permitted to warm to room temperature and was then added dropwise to a stirred solution of 80 ml (0.85 mole) of acetic anhydride and 0.4 g (0.0051 mole) of acetyl chloride. The temperature was maintained at 35 to 40°C during the addition (0.5 hr) and for 15 minutes thereafter. The product was precipitated by pouring the reaction mixture into 600 ml of ice water, filtered, and washed with water. Stabilization was effected by refluxing with 25 ml of methanol and 10 ml of water for 0.5 hr, cooling, and precipitating in 120 ml of water. This 3-nitraza-1,5-propanediol dinitrate (DINA) amounted to 43.2 g (72%), mp 45 to 49°C. The hydrolysis of 35 g of this material by refluxing in 2 liters of water for 11 hr has been carried out, but the isolation of the product has not been completed. The crude yield of DINA is reported to vary from 85 to 95%, and for the hydrolysis step a 90% yield is reported. Melting points of the pure material are reported to be 52.5 to 53.5°C and 22.5 to 23.5°C, respectively, for DINA and DINA glycol.[**]

(2)   Preparation via 3-Aza-3-nitroso-1,5-

pentanediol

(a)   The 3-nitroso-3-aza-1,5-pentane-diol[***] was prepared by adding a solution of 17 g (0.25 mole) of sodium nitrite in 50 ml of water to a mixture of diethanolamine (26 g, 0.25 mole), 21 ml of conc. hydrochloric acid, and 25 ml of water. Removal of the solvent in vacuo and filtration left 20 g (60%) of a yellow oil which was characterized as the known crystalline dibenzoate.

(b)   A 6.7-g quantity (0.05 mole) of 3-nitroso-3-aza-1,5-pentanediol was added dropwise to a solution of 7.2 g (0.212 mole) of 90% hydrogen peroxide in 25 ml of trifluoroacetic acid, with cooling to keep the temperature below 30°C. After two days of standing at room temperature the reaction mixture was poured on ice, and the liquid which separated was taken up in methylene chloride. Evaporation of the methylene chloride left 3.3 g (19%) of a colorless liquid. This liquid, consisting mostly of the bis-trifluoro acetate of 3-nitraza-1,5-pentanediol, turned black when attempts were made to distill at 2 μ and up to 85°C. A sample of this

[*]M. Carmack, OSRD Report 5157, June 19, 1945.
[**]Ibid.
[***]Ibid.

mixture, when shaken with benzoyl chloride and aqueous sodium hydroxide, yielded a solid which could not be purified to a uniform material. However, when shaken with aqueous sodium hydroxide until completely dissolved and then treated with benzoyl chloride, a product was obtained in an 82% yield. After purification from ethanol the melting point was 125.5 to 127°C (literature 124.5 to 125°C). The water solution containing the 3-nitraza-1,5-pentanediol was evaporated and yielded 8 g (47%) of a violet liquid, partially soluble in water. This could be converted to the dibenzoate in a 75% yield. A mixed melting point of this dibenzoate with those prepared above was not depressed.

D.   PREPARATION OF 3-NITRAZA-1,6-HEXANEDIOIC ACID

1.   Discussion

a.   The preparation of 3-nitraza-5-cyanopentanoic acid (N-nitro-N-(β-cyanoethyl)-glycine), an intermediate for the proposed preparation of 2-nitraza-1,4-butane diisocyanate, was described previously.[*] As some difficulty was encountered in the attempted purification of 3-nitraza-5-cyanopentanoic acid, it was decided to prepare the corresponding methyl ester, methyl 3-nitraza-5-cyanopentanoate (III), in the hope of obtaining a more readily purified product. Hydrolysis of either of these compounds should yield the desired 3-nitraza-1,6-hexanedioic acid (IV). The preparation of methyl 3-nitraza-5-cyanopentanoate was carried out, paralleling the preparation of 3-nitraza-5-cyanopentanoic acid by replacing glycine with methyl aminoacetate as in the first step in the synthesis.

$$CH_2=CHCN+ClH \cdot H_2NCH_2CO_2CH_3 \xrightarrow{+ NaOH} NCCH_2CH_2NHCH_2CO_2CH_3 \xrightarrow{HNO_3}$$

I

$$NCCH_2CH_2\overset{HNO_3}{N}HCH_2CO_2CH_3 \xrightarrow{Ac_2O} NCCH_2CH_2\overset{NO_2}{N}CH_2CO_2CH_3 \xrightarrow{H+} HO_2CCH_2CH_2\overset{NO_2}{N}CH_2CO_2H$$

II   III   IV
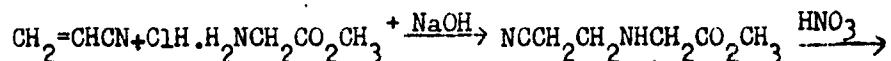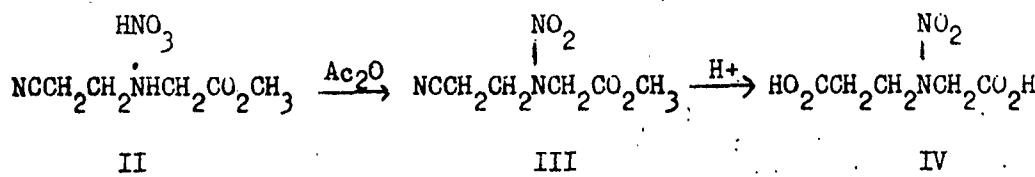
b.   The attempted hydrolysis of methyl 3-nitraza-5-cyanopentanoate in concentrated hydrochloric acid gave a mixture which was presumed to be the desired 3-nitraza-1,6-hexanedioic acid contaminated with ammonium chloride. As this mixture was not readily separated, the actual presence of the 3-nitraza-1,6-hexanedioic acid was in doubt, particularly since it is known that improper hydrolysis conditions can cause extensive degradation. (For example, methyl N-nitro-N-trinitroethylglycine in hydrochloric acid at too high a temperature results in complete conversion of

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[*]Aerojet Report No. 740, p. 75.

the amino-nitrogen to ammonium chloride.) To eliminate ammonium chloride
as one of the hydrolysis products, methyl 3-nitraza-5-cyanopentanoate was
converted to dimethyl 3-nitraza-1,6-hexanedioate, and the latter was hydrolyzed
to 3-nitraza-1,6-hexanedioic acid.

$$CH_3O_2CCH_2\overset{\overset{NO_2}{|}}{N}CH_2CH_2CN + CH_3OH + HCl \longrightarrow + H_2O \longrightarrow$$

III

$$CH_3O_2CCH_2\overset{\overset{NO_2}{|}}{N}CH_2CH_2CO_2CH_3 \xrightarrow{37\% \ HCl} HO_2CCH_2\overset{\overset{NO_2}{|}}{N}CH_2CH_2CO_2H$$

V   IV
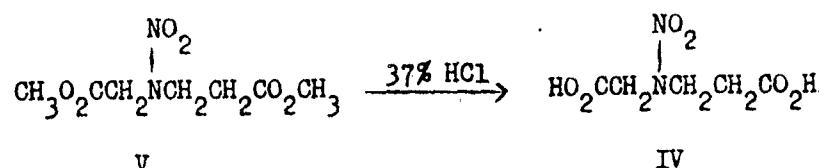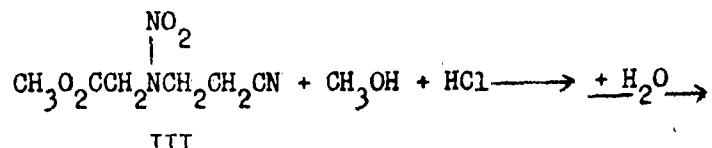
Dimethyl 3-nitraza-1,6-hexanedioate (V) was obtained as an oil (bp, 110°
C/3 microns) which yielded the crystalline acid (mp, 156.5 to 158°C) on
hydrolysis.

2.   Experimental

a.   Preparation of Methyl 3-Aza-5-cyanopentanoate

To a solution of 371 g (9 moles) 97% sodium hydroxide
in 900 ml water was added 1130 g (9 moles) methyl aminoacetate hydrochloride
while the temperature was held below 20°C. To the resulting solution of
methyl aminoacetate (with some sodium chloride in suspension) was added 477 g
(9 moles) acrylonitrile while the temperature was held at 40°C. The mixture
was stirred for 2 hr at 40°C and then stored at room temperature for several
days. Sufficient water was added to the mixture to dissolve the sodium
chloride, and the resulting two-phase mixture was treated once with one
liter of methylene chloride and three times with 500-ml portions of methylene
chloride. After the methylene chloride solution had been dried over anhydrous
calcium sulfate, the solvent was removed by distillation in vacuo to give a
dark-colored, viscous residue (ca 500 g) which did not crystallize upon
prolonged storage at room temperature. The residue was subjected to vacuum
distillation to yield 178.5 g methyl 3-aza-5-cyanopentanoate (bp, 109 to
111°C/2mm). Distillation was stopped at this point, since the rate of
distillation had diminished appreciably and the distillation was accompanied
by an increasing amount of decomposition. The higher-boiling residue
(180 g) formed a semi-crystalline mass on cooling to room temperature. A
sample of this material was recrystallized once from water, air-dried, and
recrystallized twice from absolute ether. Analysis of the colorless crystals
(mp, 58.5 to 59.5°C) indicated the material to be the 2:1 acrylonitrile--
methyl glycine adduct, N-(carbomethoxymethyl)-4-aza-1,7-heptane dinitrile.

Anal. Calc'd for $C_9H_{13}O_2N_3$:   %C, 55.37; %H, 6.71; %N, 21.53;

%OCH$_3$, 15.90

Found: %C, 55.45: %H, 6.73; %N, 22.25;

%OCH$_3$, 15.51

      b.   Preparation of the Nitric Acid Salt of Methyl 3-Aza-5-cyanopentanoate

To a solution of 146.5 g (1.05 moles) methyl 3-aza-5-cyanopentanoate in 1000 ml absolute ethanol was added 70 ml (1.1 mole) 70% nitric acid with vigorous stirring at 15 to 20°C. The reaction mixture was chilled to 5°C, and the white crystalline product was collected by filtration, washed with absolute ether, and dried in a vacuum desiccator over potassium hydroxide. The product weighed 190 g, corresponding to a 90% yield. A sample was purified for analysis by recrystallization once from a methanol-ether mixture and twice from absolute ethanol. The salt melted at 103 to 104°C.

Anäl. Calc'd for $C_6H_{11}O_5N_3$:   %C, 35.12; %H, 5.41; %N, 20.48

Found: %C, 35.56; %H, 5.84; %N, 20.62

      c.   Preparation of Methyl 3-Nitraza-5-cyanopentanoate

A nitrating solution was prepared by the addition of 0.28 ml (0.0033 mole) 37% hydrochloric acid and 0.83 ml (0.02 mole) anhydrous nitric acid to 16.8 ml (0.178 mole) acetic anhydride at 20°C. To this solution, 20.5 g (0.1 mole) of the nitric acid salt of methyl 3-aza-5-cyanopentanoate was added portionwise with stirring while the temperature was maintained at 15 to 20°C. The addition was carried out in a 10-min period with the complete solution of the nitric acid salt. The solution was stirred for 30 min at 21 to 23°C (no cooling necessary during this period), chilled to 5°C, and diluted with 40 ml ice water. A two-phase liquid mixture resulted, which was separated, and the aqueous phase was extracted with methylene chloride. The latter extracts and the original product phase were combined, washed successively with sodium bicarbonate solution and water, and dried over anhydrous calcium sulfate. The solvent was removed by distillation in vacuo, leaving 15 g pale-yellow residual oil (80% of theory). A sample of the product was distilled from a bulb-tube (bp, 125 to 135°C/2 microns). The distillate was crystallized, mp 48 to 49°C. In subsequent preparations, the product was obtained as a solid in a state of high purity without distillation.

Anal. Calc'd for $C_6H_9O_4N_3$:   %C, 38.50; %H, 4.85; %N, 22.45
                                    %OCH$_3$, 16.58

                 Found: %C, 38.57; %H, 4.95; %N, 22.81
                           %OCH$_3$, 16.29

      d.   Preparation of Dimethyl 3-Nitraza-1,6-hexanedioate

      Anhydrous hydrogen chloride was passed into a solution of 18.7 g (0.1 mole) methyl 3-nitraza-5-cyanopentanoate in 50 ml methanol at 10°C until the solution was saturated. The reaction solution was stored in the deep-freeze overnight and then distilled to dryness in vacuo. The crystalline residue was dissolved in 50 ml cold water, and the solution was neutralized with sodium carbonate yielding a two-phase mixture. The lower, oily phase was collected, and the aqueous phase was extracted three times with methylene chloride, (ca 175 ml, total). The product phase and the methylene chloride extracts were combined, dried, and distilled in vacuo to give a faint yellow, oily residue weighing 17.3 g (78.6%). A sample of this product was twice-distilled from a bulb-tube (bp, 110°C/3 microns) prior to analysis.

Anal. Calc'd for $C_7H_{12}O_6N_2$:   %C, 38.18; %H, 5.50; %N, 12.73;
                                       %OCH$_3$, 28.19

                 Found: %C, 38.09; %H, 5.47; %N, 13.14;
                           %OCH$_3$, 27.69

      e.   Preparation of 3-Nitraza-1,6-hexanedioic Acid

      A solution of 13.8 g (0.0628 mole) dimethyl 1,6-hexanedioate in 65 ml 37% hydrochloric acid was heated on the steam bath at 85 to 90°C for 6.5 hr. The solution was chilled at 0°C, and the product crystallized with scratching. The 3-nitraza-1,6-hexanedioic acid was collected on a sintered-glass Buchner funnel and pressed as dry as possible. The material was thoroughly dried in a vacuum desiccator over potassium hydroxide to yield 9.6 g, corresponding to 80% of the theoretical. A sample of the product was purified for analysis by recrystallizing twice from absolute ether. The acid melted at 156.5 to 158°C and had an impact stability ≥100 cm/2 kg.

Anal. Calc'd for $C_5H_8O_6N_2$:   %C, 31.25; %H, 4.20 %N, 14.58
                 Found: %C, 31.64; %H, 4.12; %N, 15.11

   E.   PREPARATION OF 2-NITRAZA-1,4-BUTANE DIISOCYANATE

     1.   Discussion

      An initial preparation of 2-nitraza-1,4-butane diisocyanate (IV) has been made on a small (0.1 mole) scale. This diisocyanate was

obtained via the 3-nitraza-1,6-hexanedioyl azide (III), the latter having been prepared by the action of sodium azide on 3-nitraza-1,6-hexanedioyl chloride (II) in a heterogeneous reaction medium of chloroform and water. The acid chloride resulted from treatment of 3-nitraza-1,6-hexanedioic acid (I) with thionyl chloride.

$$\underset{\text{I}}{HO_2CCH_2\overset{\overset{\displaystyle NO_2}{|}}{N}CH_2CH_2CO_2H} \quad \xrightarrow{SOCl_2} \quad \underset{\text{II}}{ClOCCH_2\overset{\overset{\displaystyle NO_2}{|}}{N}CH_2CH_2COCl}$$

$$\text{II} \quad \xrightarrow{NaN_3} \quad \underset{\text{III}}{N_3OCCH_2\overset{\overset{\displaystyle NO_2}{|}}{N}CH_2CH_2CON_3} \quad \xrightarrow{\Delta}$$

$$\underset{\text{IV}}{OCNCH_2\overset{\overset{\displaystyle NO_2}{|}}{N}CH_2CH_2NCO}$$
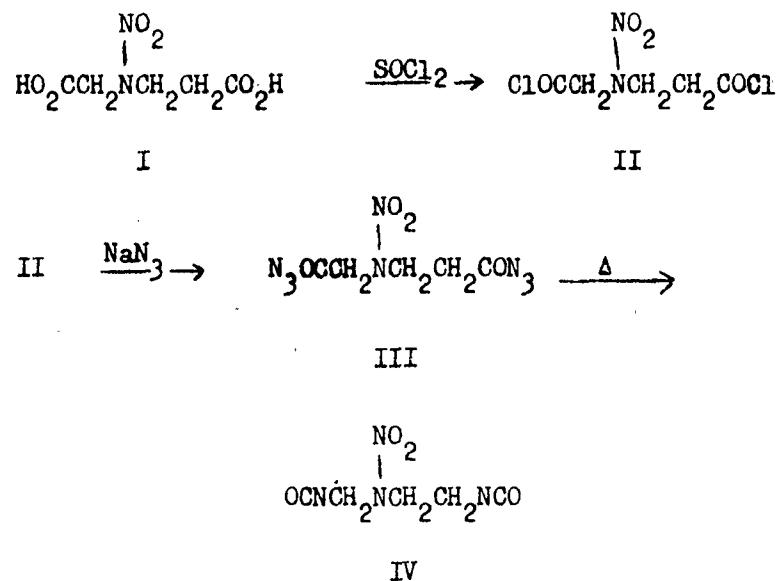
2-Nitraza-1,4-butane diisocyanate is apparently a liquid at ambient temperatures although analysis for isocyanate function indicates a purity of only 93 to 94%. The material appears to be fairly sensitive to heat, decomposing slowly at room temperature. The 2-nitraza-1,4-butane diisocyanate was characterized by analysis and by conversion to the dimethyl urethane, dimethyl 4-nitro-2,4,7-triaza-1,8-octanedioate.

2. Experimental

a. Preparation of 3-Nitraza-1,6-Hexanedioyl Chloride

A mixture of 63 g (0.328 mole) 3-nitraza-1,6-hexanedioic acid and 100 ml thionyl chloride was heated on the steam bath for 45 min. The resulting solution was filtered to remove a minute quantity of undissolved solid and the reaction flask and filter were washed with a small quantity of thionyl chloride. The product crystallized from the filtrate on chilling to 0°C. The mixture was further chilled and filtered, and the solid was washed with a small amount of chilled absolute ether. The product was recrystallized twice from 125 ml absolute ether to yield 40.2 g (59.6%) 3-nitraza-1,6-hexanedioyl chloride, melting at 46 to 47°C.

Anal. Calc'd for $C_5H_6O_4N_2Cl_2$:　%C, 26.22; %H, 2.64; %N, 12.23;
%Cl, 30.96

Found:　%C, 26.66; %H, 2.66; %N, 11.67;
%Cl, 29.98

The acid chloride apparently decomposes slowly at room temperature with an accompanying color change from colorless to orange-red.

　　　　　b.　　Preparation of 2-Nitraza-1,4-Butane Diisocyanate

　　　　　A solution of 22.9 g (0.1 mole) 3-nitraza-1,6-hexanedioyl chloride in 100 ml dry, alcohol-free chloroform was added dropwise with vigorous stirring to a solution of 19.8 g (0.3 mole) sodium azide in 50 ml water. The addition was carried out during a 20-min period at 5°C. Stirring was continued for 2 hr at 0 to 5°C. The chloroform layer was removed and the aqueous phase was extracted twice with 75 ml chloroform. The combined chloroform solution was washed with 100 ml ice water and dried over Drierite. A portion of the solvent was distilled in vacuo to insure complete removal of moisture, and the azide was rearranged on warming the chloroform solution on the steam bath at atmospheric pressure. When decomposition was complete, the solvent was distilled, leaving a residue of crude 2-nitraza-1,4-butane diisocyanate weighing 18.1 g (94.4%). An attempt was made to distill a sample of the yellow-orange liquid from a bulb-tube using a high vacuum. This attempted distillation was unsuccessful, since the material evolved a considerable amount of gas on warming to 40 to 45°C, with an accompanying increase in pressure. On recooling the material, the original pressure was obtained, but increasing the temperature again caused decomposition. The main fraction of product was purified by treatment with absolute ether and filtering. A small amount of highly colored viscous oil was removed in this manner. The solvent was distilled from the filtrate in vacuo to yield the diisocyanate as a faint yellow, fluid liquid. The material is apparently somewhat unstable at room temperature, as evidenced by a slow evolution of gas. The material was analyzed for isocyanate function by treatment with an excess of n-butylamine and back-titration with standard acid. Duplicate analyses showed 93 and 94% purity.

Anal. Calc'd for $C_5H_6O_4N_4$:　%C, 32.26; %H, 3.25; %N, 30.10
Found:　%C, 31.95; %H, 3.30; %N, 31.02

The dimethyl urethane, dimethyl 4-nitro-2,4,7-triaza-1,8-octanedioate, was prepared by treatment of a sample of the crude diisocyanate with methanol. The crystalline product was purified by recrystallization from methanol. The material melted at 133 to 134°C.

Anal. Calc'd for $C_7H_{14}O_6N_4$:　%C, 33.60; %H, 5.64; %N, 22.39
Found:　%C, 33.83; %H, 5.82; %N, 22.30

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VII Technical Progress, (cont.)   Report No. 772

F.   INTERMEDIATES

1.   Preparation of N-Methyl Acrylamide

a.   Discussion

N-Methyl acrylamide is a polymerizable intermediate for the preparation of poly N-methyl-N-nitro acrylamide. The synthesis of this compound from acrylyl chloride and methylamine is reported. An alternate procedure to prepare this compound from β-propiolactone and methylamine yielded N-methyl-β-hydroxy propionamide.

b.   Experimental

(1)   Preparation of N-Methyl Acrylamide

Methylamine was generated from 500 ml of its 40% aqueous solution by the portionwise addition of sodium hydroxide flakes. The gas was dried by passing over potassium hydroxide and then bubbled into a solution of 230 g (2.55 mole) of acrylyl chloride in 1 liter of dry benzene. When there was no longer any acid chloride odor the benzene was removed in vacuo leaving 193 g (89 %) of a very heavy red liquid. This was distilled at 3 mm pressure to give 126 g (58%) of the amide boiling between 77.5 and 83°C. A boiling point of 84°C at 3.0 mm is reported.*

(2)   Preparation of N-methyl-β-hydroxy propionamide

An attempt was made to prepare this amide by the reaction of β-propiolactone with methylamine,** but the product was found to distill at a much higher temperature than reported for the methyl acrylamide and not to analyze correctly for the hydracrylamide. To 500 ml of a stirred and cooled 40% solution of methylamine was added dropwise 432 g (6 moles) of β-propiolactone at such a rate as to maintain the temperature between 10 and 20°C. The addition took 8 hr, and after the solution had stood overnight at room temperature the water was removed under reduced pressure. The oily residue was distilled at 95 to 105°C/20μ to give a white solid melting at about 40°C. Neither two recrystallizations from methylene chloride (A) nor three more distillations at 83°C/3μ (B) served to raise this melting point.

Anal. Calc'd for $C_4H_9NO_2$:   %C, 46.59; %H, 8.80; %N, 13.59
                              Found: (A)   %C, 44.53; %H, 9.02; %N, 12.52
                                       (B)   %C, 44.55; %H, 8.87; %N, 9.83

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*B. F. Goodrich Co., Brit. Patent 648,886, Jan. 17, 1951.
**Chem. Abst., 45, 8032 (1951)

VII Technical Progress, F (cont.)   Report No. 772

2.   Preparation of 2-Nitraminoethanol

a.   Discussion

The synthesis of 2-nitraminoethanol for esterification with acrylic acid has been carried out following the procedure of Franchimont and Lubin.[*]
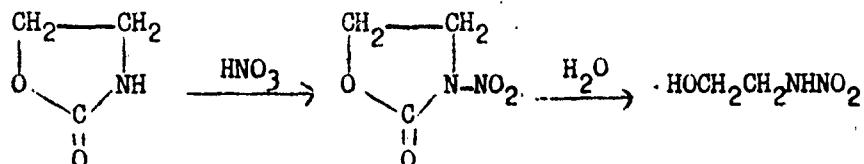
The nitration of the 2-oxazolidone, prepared from diethyl carbonate and ethanolamine,[**] gave yields of 76 and 82% of the 3-nitro compound, which in turn could be hydrolyzed to the desired alcohol in a 94% crude yield. After recrystallization from methyl ethyl ketone the nitraminoethanol was found to be a very hygroscopic solid, melting at about 35°C.

b.   Experimental

(1)   Preparation of 2-Oxazolidone

Three liters (26 moles) of redistilled diethyl carbonate and 1200 ml (20 moles) of redistilled ethanolamine were stirred and heated in the presence of sodium methoxide prepared from 50 ml of anhydrous methanol and 4 g of sodium metal. The ethanol formed in the reaction was fractionated off as formed, until 2420 ml had been collected. The solution was then cooled, and the product was collected and recrystallized from 1.8 liters of chloroform to give 1066 g (61%) of the 2-oxazolidone, melting at 83 to 86°C. The reported melting points range from 87 to 91°C. When this reaction was carried out with one-third the quantities used above, it was found that ethanol could be distilled off before any sodium methoxide had been added. Distillation was continued until the product began to crystallize from the reaction mixture. The yield in this case was 69% of material melting at 84 to 87°C before recrystallization. After three recrystallizations from benzene the melting point was raised to 87 to 88°C.

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[*]A. P. N. Franchimont and A. Lubin, Rec. trav. chim 21 45, (1902)
[**]A. H. Homeyer, U.S. Patent 2,399,118, April 23, 1946.

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VII Technical Progress, F (cont.)   Report No. 772

(2)   Preparation of 3-Nitro-2-oxazolidone

2-Oxazolidone (605 g, 7 moles) was added slowly to 1200 ml of anhydrous nitric acid and after the addition was complete, the mixture was heated for 1 hr on a steam bath. Removal of the acid in vacuo and recrystallization of the product from methanol gave 756 g (82%) of white needles, mp 109 to 110°C.

(3)   Preparation of 2-Nitraminoethanol

A mixture of 524 g (4 moles) of 3-nitro-2-oxazolidone and 600 ml of water was maintained at an active boil for 3 hr. The water was then removed in vacuo while heating on a steam bath. Further drying under a high vacuum yielded 393 g (94%) of a white solid. Recrystallization was carried out by dissolving in an equal volume of methyl ethyl ketone at room temperature and cooling to -10°C. The material liquefied when exposed to air and could be resolidified by pumping off the moisture in vacuo.

APPENDIX A

BEKEN MIXER

A Beken dispersion blade mixer has been installed. This mixer will permit polymerization mixtures to be studied under conditions comparable to those encountered during actual manufacturing operations. Two photographs of the machine are shown.
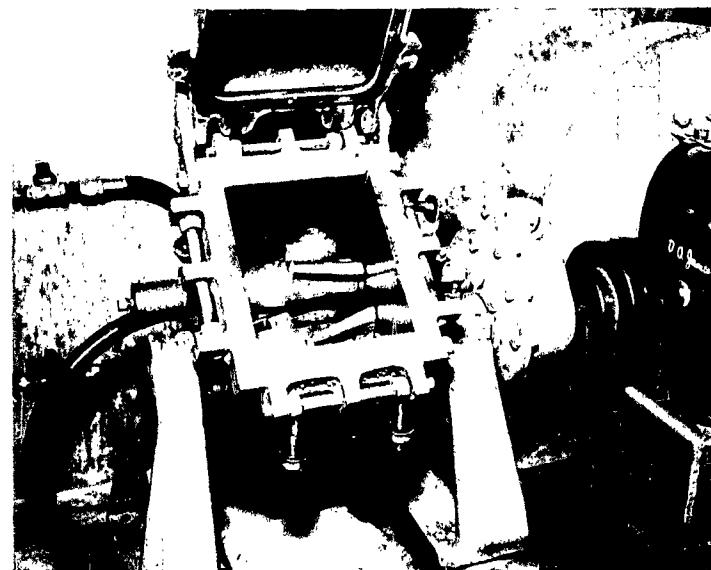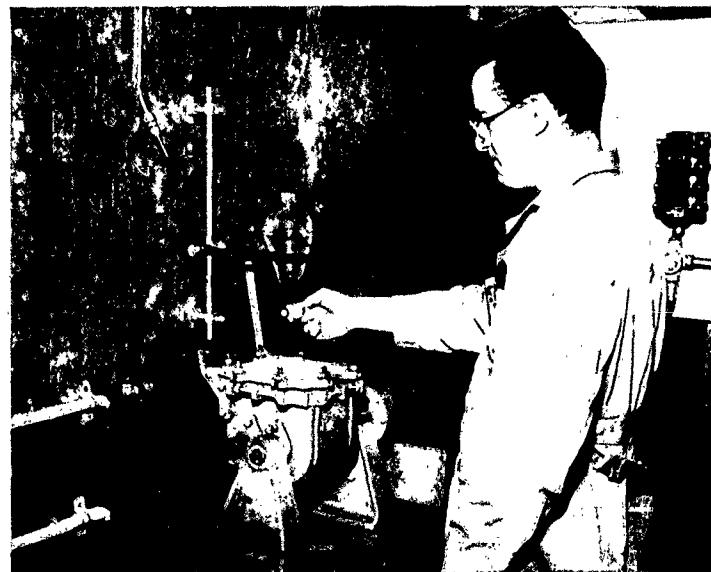
APPENDIX B

NEW SYSTEM OF NOMENCLATURE FOR CONDENSATION POLYMERS

With the increasing number of new nitropolymers, it has become necessary to revise the system of nomenclature which has been in general use for the past several years. To eliminate some ambiguities which have existed, it has been decided to assign to each monomer a single character (letter or number). The presence of this monomer in any polymer system is indicated by the use of this character. The following general assignments have been made:

Diols are characterized by capital letters (A, B. . .)
Diisocyanates are characterized by Roman numbers (I, II . . .)
Diamines are characterized by Greek lower case letters (α, β . . .)
Diacids (acid chlorides, esters) are characterized by Arabic
   numbers (1, 2 . . .)

Thus, a polyurethane made from the I diisocyanate, 3,3-dinitro-1,5-pentane diisocyanate, and the A diol, 2,2-dinitro-1,3-propanediol, is designated as Polyurethane I-A (as previously): the polyurea made from the I diisocyanate and the α diamine, 3,3-dinitro-1,5-pentane diamine, is designated as Polyurea I-α (III-A in the old system). The new designations for the monomers have been selected to give a minimum amount of change from the old system. The class of polyurethanes suffers no change at all in nomenclature. The following table shows the various monomers and their corresponding code characters.

TABLE I

NOMENCLATURE OF NITROMONOMERS

Diols

Code	Monomer
A	2,2-Dinitro-1,3-propanediol
B	1,3-Propanediol
D	5,7,9-Trinitraza-3,11-dioxa-1,13-tridecanediol
F	2,2,4,4-Tetranitro-1,5-pentanediol
G	5,7,9,11-Tetranitraza-3,13-dioxa-1,15-pentadecanediol
H	5,5,5-Trinitro-1,2-pentanediol
J	2-Nitro-2-methyl-1,3-propanediol
K	4,4,6,8,8-Pentanitro-1,11-undecanediol
L	4,4,6,6,8,8-Hexanitro-1,11-undecanediol
M	N,N'-bis(2-hydroxyethyl) Oxamide
N	Ethylene Glycol

Diisocyanates

Code	Monomer
I	3,3-Dinitro-1,5-pentane Diisocyanate
VI	Methylene Diisocyanate
XI	3,3,5,7,7-Pentanitro-1,9-nonane Diisocyanate
XII	3,6-Dinitraza-1,8-octane Diisocyanate
XIII	3-Nitraza-1,5-pentane Diisocyanate
XIV	3,3,5,7,7-Pentanitro-5-aza-1,9-nonane Diisocyanate

Diamine

Code	Monomer
α	3,3-Dinitro-1,5-pentane Diamine
β	Ethylene Diamine
γ	3-Nitraza-1,5-pentane Diamine
δ	3,6-Dinitraza-1,8-octane Diamine

Diacid Chlorides and Diesters

Code	Monomer
1	4,4-Dinitro-1,7-heptanedioyl Chloride
2	4,4,6,8,8-Pentanitro-1,11-undecanedioyl Chloride
3	N-Nitro-N-trinitroethyl Aspartyl Chloride
4	N-Nitro-N-trinitroethyl Glutamyl Chloride
5	Diethyl Oxalate

Table I
Appendix B

APPENDIX C

SPECIFIC IMPULSE OF CONDENSATION POLYMERS

The following tables show calculated specific-impulse values for the four classes of condensation polymers -- polyurethanes, polyesters, polyureas, and polyamides. All values are in units of lbf sec/lbm.

TABLE I

SPECIFIC IMPULSE OF CONDENSATION POLYMERS - POLYURETHANES

Code Diisocyanates	I 3,3-Dinitro-1,5-pentane Diisocyanate		VI Methylene Diisocyanate		XI 3,3,5,7,7-Pentanitro-1,9-nonane Diisocyanate	
Code / Diols	Un-nitrated	Post-nitrated	Un-nitrated	Post-nitrated	Un-nitrated	Post-nitrated
A 2,2-Dinitro-1,3-propanediol	174	233	165	233	203	231
B 1,3-Propanediol						
D 5,7,9-Trinitraza-3,11-dioxa-1,13-tridecanediol		211			194	218
F 2,2,4,4-Tetranitro-1,5-pentanediol	203	234	166	212	214	236
G 5,7,9,11-Tetranitraza-3,13-dioxa-1,15-pentadecanediol	188	217			202	223
H 5,5-Trinitro-1,2-pentanediol	188	226	180	232	205	230
J 2-Nitro-2-methyl-1,3-propanediol	125	202			179	214
K 4,4,6,8,8-Pentanitro-1,11-undecanediol	175	209	165	210	193	
L 4,4,6,6,8,8-Hexanitro-1,11-undecanediol	191	219			204	224
M N,N'-bis(2-hydroxyethyl)oxamide	94	210			140	218
N Ethylene glycol		202			175	217
O 5,5-Dinitro-1,2-hexanediol		203				

Table I
Sheet 1 of 2
Appendix C

TABLE I (cont.)

Code	Diols	XII 3,6-Dinitraza-1,8-octane Diisocyanate		XIII 3-Nitraza-1,5-pentane Diisocyanate		XIV 3,3,5,7,7-Pentanitro-5-aza-1,9-nonane Diisocyanate	
		Un-nitrated	Post-nitrated	Un-nitrated	Post nitrated	Un-nitrated	Post-nitrated
A	2,2-Dinitro-1,3-propanediol	178	221	167	222	212	237
B	1,3-Propanediol					179	218
D	5,7,9-Trinitraza-3,11-dioxa-1,13-tridecanediol	175				202	
F	2,2,4,4-Tetranitro-1,5-pentanediol	199	229			221	242
G	5,7,9,11-Tetranitraza-3,13-dioxa-1,15-pentadecanediol	186				208	
H	5,5,5-Trinitro-1,2-pentanediol	185	222	178	211	213	236
J	2-Nitro-2-methyl-1,3-propanediol	135	198		189	189	222
K	4,4,6,8,8-Pentanitro-1,11-undecanediol						
L	4,4,6,6,8,8-Hexanitro-1,11-undecanediol						
M	N,N'-bis(2-hydroxyethyl)oxamide				205		
N	Ethylene glycol	117	197	142	192	188	225
O	5,5-Dinitro-1,2-hexanediol	148	200		196		

Table I
Sheet 2 of 2
Appendix C

TABLE II

SPECIFIC IMPULSE OF CONDENSATION POLYMERS – POLYESTERS

Code	Diacid chlorides	1 4,4-Dinitro-1,7-heptanedioyl Chloride	2 4,4,6,8,8-Penta nitro-1,11-un-decanedioyl chloride	3 N-Nitro-N-tri-nitroethyl aspartyl chloride	4 N-Nitro-N-trinitro-ethyl glutamyl chloride
Diols					
A	2,2-Dinitro-1,3-propanediol	185	207	237	228
B	1,3-Propanediol	—	—	204	193
H	5,5,5-Trinitro-1,2-pentanediol	192	209	235	228
J	2-Nitro-2-methyl-1,3-propanediol	130	181	212	203
N	Ethylene Glycol	—	182	215	204

Table II
Appendix C

TABLE III

SPECIFIC IMPULSE OF CONDENSATION POLYMERS - POLYUREAS

| | | Code | | | |
| | | I | VI | XII | XIII |
Code	Diamines	Diisocyanates	3,3-Dinitro-1,5-pentane Diisocyanate	Methylene Diisocyanate	3,6-Dinitraza-1,8-octane Diisocyanate	3-Nitraza-1,5-pentane Diisocyanate
α	3,3-Dinitro-1,5-pentane Diamine		PN/2 * 207	PN/2 208		
β	Ethylene Diamine		PN/2 197	PN/2 184		
γ	3-Nitraza-1,5-pentane Diamine					PN/2 193
δ	3,6-Dinitraza-1,8-octane Diamine				PN/2 200	

$$\text{half-post-nitration:} \quad \begin{array}{ccc} H & O & NO_2 \\ | & \| & | \\ -N & -C & -N- \end{array}$$

* PN/2 indicates half-post-nitration

* PN/2 * indicates half-post-nitration

Table III
Appendix C

TABLE IV

SPECIFIC IMPULSE OF CONDENSATION POLYMERS - POLYAMIDES

		Code	Diacid Chlorides diesters	
			1	5
			4,4-Dinitro-1,7-heptanedioyl chloride	Diethyl Oxalate
Code	Diamines			
α	3,3-Dinitro-1,5-pentane Diamine		PN * 213	PN 208

* PN indicates post-nitration on amide nitrogens.

Table IV
Appendix C