

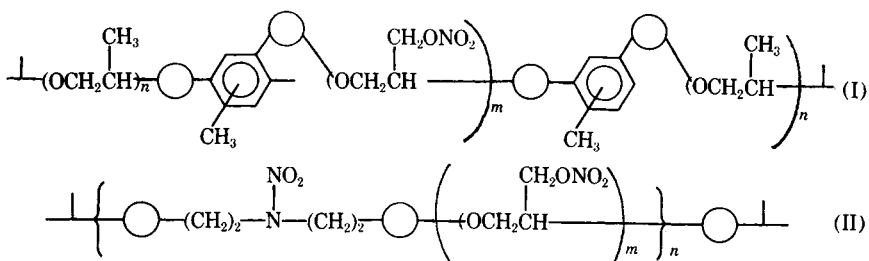
### Physical Properties of Nitropolyurethane Elastomers

Good physical and ballistic properties are required for composite solid propellants. Propellant chemists have been making many attempts to improve these properties. Since the properties of the propellant are much dependent upon the properties of the fuel binder, a major improvement in the former requires a major change in the latter.

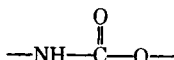
Polyurethane is one of the excellent binders that fulfill the requirements and is one of the most commonly used commercial binders. Because nitropolymers have both a fuel and an oxidizer component in their molecule, the propellants prepared from this polymer will show excellent ballistic performance.

We prepared nitropolyurethanes containing the greatest number of nitro groups ( $-\text{ONO}_2$  and  $>\text{N}-\text{NO}_2$ ) possible. We examined whether introducing a nitro group into the molecule has a negative effect on the physical properties of the polymers.

Nitropolyurethanes with the following structural units were chosen as model compounds:



where  $\bigcirc$  is a urethane linkage,



The ratio  $R$  in equivalents of isocyanate to hydroxyl groups in the starting mixture the fraction  $\rho_t$  in equivalents of OH from triol in the starting mixture, the mechanical properties, the density, and the heat of combustion of the resulting elastomers are given in Table I.

TABLE I  
Composition and Properties of Nitropolyurethanes

Compn.		Properties					
$R$	$\rho_t$	Elong. at break pt., %	100% modul., kg./cm. <sup>2</sup>	300% modul., kg./cm. <sup>2</sup>	Ult.	Heat combust., cal./g.	
					tens. streng., kg./cm. <sup>2</sup>		Dens. at 20°C., g./ml.
Structure (I):							
1.043	0.252	470	11.5	15	22	1.139	—
1.132	0.184	430	8	21	30	1.201	—
1.116	0.246	450	7	15	22	1.149	4404
1.045	0.245	400	8.5	19	22	1.150	—
Structure (II):							
1.123	0.249	350	19	26	34	1.453	—
1.06	0.249	350	10	14	20	1.491	2939
1.231	0.276	300	40	—	50	1.387	—
1.014	0.294	350	06	9	12	1.399	2926

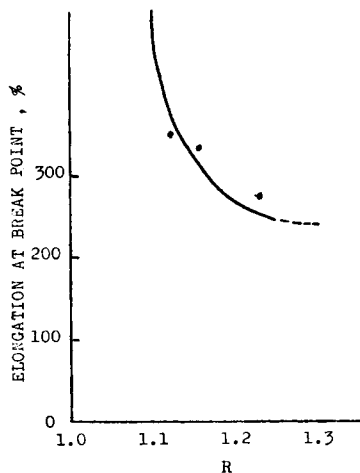


Fig. 1. Plot of elongation at break point versus  $R$ ;  $t = 0.249$ .

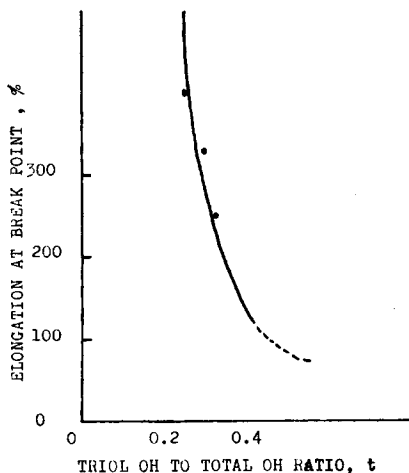


Fig. 2. Sensitivity of elongation at break point versus crosslinker concentration;  $R = 1.1$ .

Considering elongation and tensile strength, we thought that (II) could be applied practically as a solid-propellant binder; however, its elongation was slightly less than that of (I). The higher degree of crosslinking in the (II) elastomers and the incorporation of many urethane linkages may be the cause of the lesser elongation of (I). In this polymer, elongation depends upon the degree of crosslinking and the number of rigid urethane linkages in the main chain rather than upon the number of nitro groups. The relationship between elongation and the parameters  $\rho_t$  and  $R$  for polyurethane elastomers are known.<sup>1</sup> The relationship for nitropolyurethane elastomers (II) is shown in Figures 1 and 2. The figures indicate that elongation varies with  $R$  when  $\rho_t$  is held constant and with  $\rho_t$  at constant  $R$ , as is the case of polyurethane elastomers. The elongation of nitropolyurethane is not as sensitive to stoichiometry as is that of polyurethane.

The density of nitropolyurethanes increases with the number of nitro groups. It is similar to that of nitroalkyl acrylate and methacrylate polymers.<sup>2</sup>

## EXPERIMENTAL

### Raw Materials

Polynitratoglycol (Nippon Oil & Fats Co., Ltd.; average molecular weight 800 and 1,000) and polyoxypropylene triol (Sanyo Chemical Ind., Ltd.; average molecular weight 3,000) were used after water was evaporated *in vacuo* at 120–130°C.

3-Nitrazapentane diisocyanate (Aerojet General Corp.) was used after recrystallization from dichloroethane. Tolylenediisocyanate (an 80:20 mixture of the 2,4- and 2,6 isomers) was supplied by Hodogaya Chem. Co., and trimethylolpropane was obtained commercially. A ferric acetyl acetonate was used as a curing catalyst.

### Preparation and Measurement of Elastomers

Nitropolyurethane was prepared by a one-shot method. Polynitratoglycol, triol, diisocyanate, and a curing catalyst were mixed together. The mixture was heated to 40°C. in an oil bath, stirred at 40–50°C. for 15–50 min., degassed, and then poured into a glass cell.<sup>3</sup> The glass cell was kept for 7 days at 50°C. in an oven.

The tensile properties of the elastomers were measured on the basis of a testing procedure given in the literature.<sup>2</sup> The heat of combustion was measured with a Nenken type of bomb calorimeter.

We are greatly indebted to Nippon Oil & Fats Co., Ltd., for generously donating polynitratoglycol and to Teikoku Kakohin Mfg. Co., Ltd., for generously donating 3-nitrazapentanediiisocyanate, triol and ferric acetyl acetonate and wish to thank M. Ito for assistance with the experimental work.

### References

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