

Acetylenic Propellant Binders

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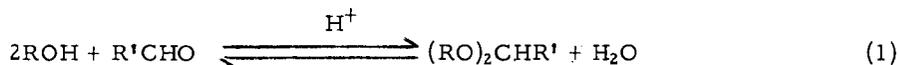
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INTRODUCTION

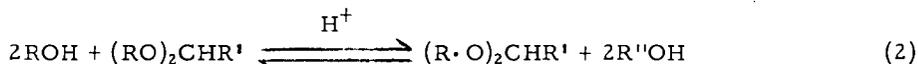
One approach to improving the performance of composite solid propellants containing organic fuel binders is to introduce endothermic groups into the binder structure. Since the acetylenic bond is one of the most energetic organofunctional groups, a program was undertaken to synthesize polymers containing carbon-carbon triple bonds and to evaluate these polymers as binders in castable propellant systems. The studies reported here include the synthesis of prepolymers, curing of the prepolymers to elastomeric binders with diisocyanates, laboratory propellant evaluation, and small rocket motor tests.

PREPOLYMER PREPARATION

The formation of acetals by the reaction of aldehydes with alcohols (equation 1)

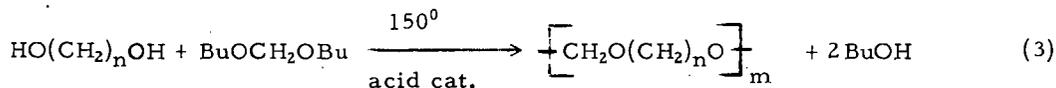


is a well-known and useful preparative method in organic chemistry.¹ As indicated in equation 1, it is an equilibrium reaction, which is catalyzed by strong acids and favored by the removal of water. A modification of this method is the acetal exchange reaction (equation 2). The success of this method depends on the ability to remove



$\text{R}''\text{OH}$ preferentially and thereby shift the equilibrium in equation 2 to the right. This is generally accomplished by distillation, and the conversion therefore requires that $\text{R}''\text{OH}$ be significantly more volatile than ROH . The acetal exchange reaction has found application in the preparation of acetals where direct reaction of an alcohol and aldehyde is difficult or inconvenient, or where the acetal of a low-boiling alcohol is more readily available. Both reactions have been used frequently to protect carbonyl groups during other synthetic operations, since regeneration of the free aldehyde or ketone can usually be accomplished readily.

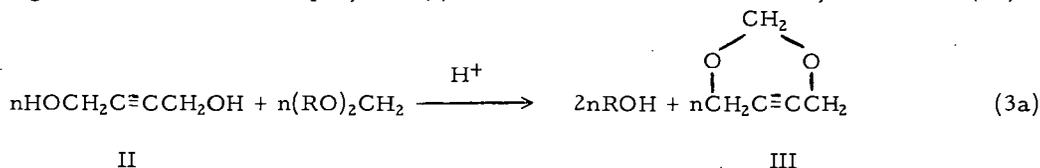
Hill and Carothers² investigated the acetal exchange reaction as a method of preparing polymers (equation 3). When n was 3 or 4, cyclic formals were the



principal products. Pentamethylene glycol ($n=5$) afforded a syrupy liquid polymer. The reaction with decamethylene glycol, where cyclic structures are not favored, was studied most extensively. Initially a waxy polymer (m.p. 56.5-57°) of

molecular weight 2190, was formed. On heating this product in vacuo at 230-250°, polymers of 10-20,000 molecular weight, capable of being drawn into fibers, were obtained.

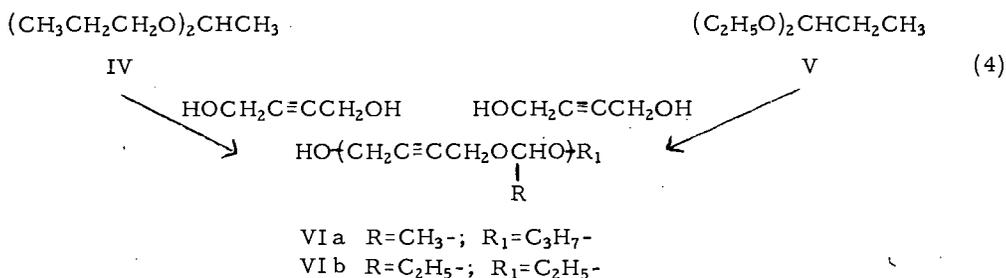
The present study had as its objective the preparation of low molecular weight hydroxy-terminated polymers containing acetylenic bonds and their evaluation as binders for castable solid propellant formulations. Since 2-butyne-1,4-diol (II) was commercially available, the formation of polyacetals from this glycol seemed to be an attractive route to the desired polymers. It was believed that the rigid triple bond would inhibit the cyclic acetal formation observed by Hill and Carothers with the lower members of the saturated glycol series. Thus, in an acetal exchange reaction the linear polymer (I) should be favored over the cyclic acetal (III):



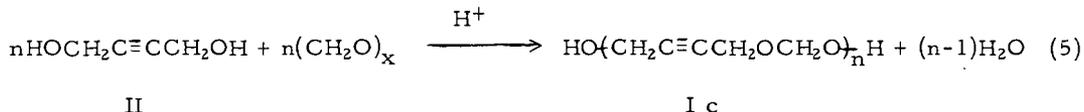
- I a R = n-propyl
 I b R = n-butyl

Initial studies with butynediol (II) employed the reaction with di-n-butyl formal and di-n-propyl formal. The reaction of the former with II required relatively high temperatures (ca. 190°) in order to remove the by-product n-butyl alcohol (b. p. 117.7°), and this apparently caused some polymer degradation. As a result, only a semi-solid polymer (Ib) of molecular weight 475 was obtained. The reaction with di-n-propyl formal, however, gave polymers with molecular weights of 680 and 1020 in two experiments. The higher molecular weight material was obtained by heating an equimolar mixture of the reactants at 130-180° for nine hours in the presence of polyphosphoric acid and continuously removing the n-propyl alcohol by distillation into a Dean-Stark trap. The product was a waxy material, m. p. 55°, which was shown by chemical and infrared analysis showed to have the structure Ia where R = n-propyl.

Similar acetal exchange reactions were carried out between II and di-n-propyl acetal (IV) and II and diethyl propional (V), to give low molecular weight, liquid polyacetals (VI a and VI b):



Despite the success achieved in preparing low molecular weight acetylenic ether polymers by the acetal exchange reaction, an improved method was desired, since it was difficult to obtain molecular weights above 1,000, and the reactions were slow. It was found at this point that direct reaction of II with paraformaldehyde (equation 5) proceeded rapidly in refluxing benzene or toluene to yield polymers



having molecular weights in the 1500-2500 range. These were hard, brownish-colored waxes, quite similar, except for their molecular weights, to the products obtained in the acetal exchange reactions. The reaction proceeded approximately twice as fast in toluene as in benzene due to the higher temperature attainable. The generality of the method was shown by the fact that it could also be successfully employed with 2,4-hexadiyne-1,6-diol and paraformaldehyde, and with II and 2-ethylbutyraldehyde, although in these cases only low molecular weight (600-800) products were obtained.

The polyacetals obtained in these reactions were characterized by wet chemical and infrared analyses, and by cryoscopic molecular weight determinations. For the latter, the preferred method was the freezing point depression of an ethylene bromide solution.

Infrared and functional group analyses showed the presence of two hydroxyl end-groups in the products obtained from formaldehyde (Ic). In addition, the results of chain extension and cross-linking reactions with diisocyanate (vide infra) confirmed the presence of two terminal hydroxyl groups.

CURING STUDIES

Curing of the acetylenic polyacetals to rubbery polyurethanes could be achieved with any of a number of commercially available diisocyanates, including 2,4-toluene-diisocyanate (TDI), hexamethylenediisocyanate (HDI), dianisidine diisocyanate (DADI), and 4,4'-diisocyanatodiphenylmethane (MDI). The first two diisocyanates were studied most extensively. The reactions were carried out in solution in benzene, toluene, or ethylene bromide, or in bulk. The bulk reaction in general gave products with superior properties and, of course, it is the only suitable method for use in a practical propellant process.

In addition to the diisocyanate, cross-linking agents, catalysts and plasticizers were used to accelerate the cure reaction and to improve the physical properties of the ultimate binder composition. The cross-linking agents consisted of tri-functional alcohols (castor oil and trimethylolpropane), aminoalcohols and aliphatic or aromatic diamines. Best results were obtained with castor oil and trimethylolpropane. Castor oil was preferred because of its lower rate of reaction with the isocyanate, which resulted in a longer pot life for the propellant mix. Catalysts for the polyurethane formation reaction included tertiary amines and ferric acetylacetonate. A variety of typical ester-type plasticizers were investigated to give improved physical properties. The best of these was butyl cyclohexyl phthalate. Finally, a study of reaction stoichiometry vs. physical properties showed that a molar ratio of polyformal:diisocyanate:cross-linking agent of 1:1.5:0.2 gave

Table I
Physical Properties of Selected Acetylenic Polyurethane Binders

Sample No.	Prepolymer Mol. Wt.	Diisocyanate	Cross-linking Agent	Plasticizer	Catalyst	Ult.		Shore A-2 Hardness	
						Strength (psi)	Elongation (%)		
1	1915	TDI	TMP	-----	-----	913	73	31	97
2	1915	HDI	TMP	-----	-----	773	63	37	--
3	1180	HDI	TMP	-----	-----	681	64	28	96
4	1180	HDI	TMP	BCPH	14	FeAA, DPPD	412	184	64
5	1915	HDI	CO	BCPH	14	FeAA, DPPD	506	215	--

Abbreviations:

- TDI = 2, 4-Tolylene diisocyanate
- HDI = Hexamethylenediisocyanate
- TMP = Trimethylolpropane
- CO = Castor Oil
- BCPH = Butyl cyclohexylphthalate
- FeAA = Ferric acetylacetonate
- DPPD = Diphenyl-p-phenylenediamine

the best results. Cure was essentially complete in 20 hours at 80°C.

In Table I are listed the physical properties of some typical binder compositions, both with and without plasticizer. These all used the stoichiometry and cure conditions given above, except for sample 5 for which a 44 hour cure time was used.

LABORATORY PROPELLANT FORMULATION AND EVALUATION

Propellant compositions containing the acetylenic fuel binder and ammonium perchlorate oxidizer were prepared and cured and their physical and ballistic properties determined. Formulations containing up to 83% by weight of ammonium perchlorate oxidizer have been prepared. This represents the optimum level of oxidizer for this fuel binder. Processing characteristics and propellant physical properties were good. A description of the preparation of a typical propellant batch is given in the Experimental Section, and Table II summarizes the principal physical properties of a characteristic batch of cured propellant. The tensile properties were measured on dumbbell specimens, 4 to 6 inches long with a 1-inch guage length 3/32 inch thick and ends of 1/4 inch thickness.

Table II

Physical Properties of Acetylenic Polyurethane Propellants

Formulation No.	Tensile Strength (psi)	Elongation (%)	Density (lbs./in. ³)	Impact Sensitivity (in.)	Autoignition Temp. (°F)
57	90	16	0.0625	9-10	670
66	108	14	0.061	8	660
73	110	25	0.061	9-10	685

Notes:

1. Formulations 57 and 73 used HDI; 66 used TDI.
2. All three formulations contained about 5% (by wt. of propellant) of BCPH and used castor oil as cross-linking agent.
3. Oxidizer loadings for formulations 66 and 73 were 75%, for 57, 77.8%.

Among the most interesting features of the acetylenic polyurethane propellants were their ballistic properties. Burning rates of propellant strands were determined in a Crawford bomb apparatus. The burning rates measured at 1,000 psia were normal for ammonium perchlorate type composite propellants, ranging from 0.5 to 1.25 in./sec. What was unusual was the occurrence of a plateau in the burning rate vs. pressure curves in the 700-2000 psia region. The exact position and extent of the plateau region varied somewhat from batch to batch, but it was a constant feature of all the compositions containing the acetylenic polyurethane binder. The value of such a region of relative lack of pressure dependence of burning rate in providing controlled burning despite pressure fluctuations is obvious. It was

possible through the use of a catalyst to increase the propellant burning rate up to 2.2 in./sec. Curves of burning rate vs. pressure for catalyzed and uncatalyzed propellant compositions are shown in Figure 1.

Safety tests were carried out in order to determine the handling characteristics of the propellant system. The impact sensitivity of the propellant was found to be approximately the same as that of pure ammonium perchlorate (9-12 inches) when tested with a 2 kg weight in the Picatinny Arsenal impact dropweight tester.³ Detonation tests made with a number eight blasting cap and 20 grams of tetryl indicated that the propellant is not sensitive to detonation. The autoignition temperature of these propellants is in the range of 220 to 240°C as measured by the Picatinny Arsenal test method.³ Propellant samples have been stored at 80°C (175°F) for periods up to 30 days without any signs of degradation or change in their physical properties.

SMALL MOTOR FIRINGS

Although the program was primarily concerned with the synthesis and laboratory evaluation of these new propellant compositions, some practical confirmation of their theoretical performance was also desired. Consequently, a limited number of small motor firings were carried out.

Theoretical performance calculations were first made on propellant compositions containing the acetylenic polyurethane binder and ammonium perchlorate as the oxidant. These calculations assumed a shifting equilibrium in the rocket exhaust. Specific impulse values of 251-252 lbf-sec./lbm. were calculated at 1000 psia chamber pressure for optimum oxidizer loadings. For the actual compositions tested, the theoretical values were somewhat lower. In all, 18 acetylenic polyurethane propellant grains were test fired in small motors. These ranged in weight from 0.40 to 6 lb. and included both 3-inch and 6-inch diameter end-burning grains. Two compositions were used, one containing 75% oxidizer, which had a theoretical Isp of 243 seconds at 1000 psia chamber pressure, and one containing 77.8% oxidizer, having a calculated Isp of 249 seconds. Experimental Isp values for these motors ranged from 214 to 222 seconds for the 75% oxidizer compositions, indicating efficiencies of 88.1 to 91.2%. For the 77.8% oxidizer grains, the experimental values were from 225 to 229 seconds, with the corresponding efficiencies being 90.4 to 92.0%. Chamber pressures in these tests ranged from 300 to 1000 psi and thrust levels were in the range of 25 to 100 lbs.

EXPERIMENTAL

Poly(2-butyne-1, 4-dioxymethylene)

A. From Di-n-propylformal (1) - A three-necked, round-bottom flask, fitted with a gas inlet tube, a mechanical stirrer and a graduated Dean-Stark moisture trap with a condenser attached, was charged with 66 g. of di-n-propyl formal, 45 g. of 2-butyne-1, 4-diol and 0.5 g. of p-toluenesulfonic acid. A slow stream of nitrogen was passed through the system via the gas inlet tube to aid in entrainment of the by-produced n-propanol, and the mixture was heated in an oil bath. When it became sufficiently fluid, the mixture was stirred mechanically and was heated for two to three hours at 125° to 150°. During this time 60-70 ml. of n-propanol was distilled into the Dean-Stark trap. The mixture then was heated for another three hours under reduced pressure (1 to 3 mm.). Traps cooled with Dry Ice-acetone were placed in the system to collect any additional alcohol formed in the reaction. An additional 5 to 15 ml. of n-propanol was isolated during this heating cycle. The reaction mixture then was allowed to cool. The product, a waxy solid, weighing 46 g., melted at 60°, and represented a 90% yield. Its molecular weight, based on the freezing-point depression in ethylene bromide, was 680.

Anal. Calcd. for C₅H₆O₂: C, 61.26; H, 6.75.

Found : C, 60.76; H, 6.75.

An experiment, in which the same reactants and substantially the same procedure were used as in A, except that polyphosphoric acid was the catalyst and a longer reaction time (9 hours) and higher temperature (130-180°) were employed, resulted in a quantitative yield of a polymer in the form of a dark brown, waxy solid, m.p. 55° with a molecular weight of 1020 (determined cryoscopically).

Anal. Found: C, 60.44; H, 6.58.

B. From Di-n-butyl Formal - When 2-butyne-1, 4-diol and di-n-butyl formal were allowed to react in a similar manner at temperatures up to 190° in the presence of a catalytic amount of p-toluenesulfonic acid, nearly two equivalents of n-butanol distilled off. The product was a mushy, light brown solid, of molecular weight 475, as determined cryoscopically in a benzene solution.

C. From Paraformaldehyde - A three-necked, 300 ml. flask was equipped with a thermometer, mechanical stirrer and Dean-Stark trap with a condenser attached. The flask was charged with 130 g. of toluene and 43 g. of 2-butyne-1, 4-diol. Paraformaldehyde (15 g.) and 0.5 g. of p-toluenesulfonic acid were added portionwise to the mixture, over a 3.5-hour period. After addition of the first portion of paraformaldehyde and catalyst the mixture was heated to reflux temperature (100°-110°). During the reaction nearly 9 ml. of water were collected in the Dean-Stark trap. The reaction mixture was allowed to cool, and the toluene was decanted from the solid polymer, which had separated from the solution. The polymer then was heated for 4 hours, under a vacuum of 1 to 2 mm., at 80°-115°. A yield of 46 g. (94%) of a hard, waxy polymer, of molecular weight 2300, was obtained.

Poly(2, 4-Hexadiyne-1, 6-dioxymethylene) - A three-necked flask, equipped as in Example A, was charged with 130 g. of benzene, 22 g. of 2, 4-hexadiyne-1, 6-diol, and 6.1 g. of paraformaldehyde. p-Toluenesulfonic acid (0.2 g.) was added, and the

mixture was heated at reflux temperature for 3 hours. Approximately 3.0 ml. of water was distilled into the Dean-Stark trap during this time. The mixture was allowed to cool, and the benzene was decanted from the solid polymer. The polymer then was heated for 3 hours at 90°-100° under a vacuum (2 to 3 mm). The product was a dark-colored, waxy solid, melting at 70°-75°, and having a molecular weight of 810.

Poly(2-butyne-1, 4-dioxyethylidene)- A 250 ml., three-necked flask equipped as in Example I, was charged with 43 g. of 2-butyne-1, 4-diol, 73 g. of di-*n*-propyl acetal, and 0.5 g. of *p*-toluenesulfonic acid. The mixture was heated at 125° to 150° for three hours at atmospheric pressure, under a slow stream of nitrogen to aid in the entrainment of the by-produced alcohol during which time 65 ml. of *n*-propanol were collected. The reaction mixture then was heated for an additional four hours at 1 to 3 mm. pressure; and an added 10 ml. of *n*-propanol were isolated. The product, obtained in quantitative yield, was a viscous, dark-brown liquid. Its molecular weight was 920 when determined cryoscopically in ethylene bromide.

Poly(2-butyne-1, 4-dioxy-2'-ethylbutylidene)- A 500 ml., three-necked, round bottom flask, equipped as in Example A above, was charged with 43.0 g. of crude 2-butyne-1, 4-diol, 0.5 g. of *p*-toluenesulfonic acid, and 250 ml. of benzene. The mixture was heated to 60°, and 50.1 g. of 2-ethylbutyraldehyde was added. The theoretical amount of water was collected by azeotropic distillation during an 8-hour heating period at 75°-82°. To remove the acid catalyst a mildly basic ion exchange resin, Amberlite IR-45 (10 g.), was added, and the mixture was stirred at room temperature for 2 to 3 hours. The resin and impurities then were filtered off, and benzene and volatiles were distilled from the remaining product during a 5-hour heating period at 80°-90°/2-15 mm. A dark, viscous liquid was obtained. Its molecular weight, measured by the cryoscopic method, was 620.

Polyurethanes from Poly(2-Butyne-1, 4-dioxymethylene)

A. Reaction with 2, 4-Toluene Diisocyanate - A sample of polyformal of molecular weight 1915 (95.7 g., 0.05 mole) was melted in a 500 ml. beaker, and 1.34 g. (0.01 mole) of trimethylolpropane (TMP) was added. The mixture was heated to 80°, agitated thoroughly, and then degassed at 80°/5mm. in a vacuum oven. After cooling to 50°, 13.05 g. (0.075 mole) of 2, 4-toluenediisocyanate (TDI) was added and the mixture was again heated to 80° and thoroughly mixed. It was then cast into a Teflon-coated mold, degassed at 80°/5mm again for one hour, and cured at 80° for 20 hours. The physical properties of the resulting polyurethane are given in Table I (Sample 1).

B. Reaction with Hexamethylene Diisocyanate - 1. The above procedure was repeated using 12.60 (0.075 mole) of hexamethylenediisocyanate (HDI) instead of TDI. The physical properties of the product are listed in Table I (Sample 2).

2. When the same procedure was repeated with 60 g. (0.05 mole) of polyformal prepolymer of molecular weight 1180, a polyurethane with similar physical properties was obtained (Sample 3, Table I).

C. Preparation of Plasticized Polyurethane Compositions - 1. The procedure given in B.2 was repeated, except that 10.5 g. butylcyclohexylphthalate

(BCPH) was added to the original mixture as a plasticizer, and 0.5 g. of di-*p*-phenylphenylenediamine and 0.05 g. of ferric acetylacetonate were used as catalysts. The properties of the resulting cured polymer are given in Table I (Sample 4).

2. The above procedure was repeated using 95.7 (0.05 mole) of the 1915 molecular weight prepolymer and 9.18 g. (0.01 mole) of castor oil as the cross-linking agent. Physical properties are listed under Sample 5 in Table I.

D. Mixing, Casting and Curing of Propellants - The propellant was mixed in a sigma-blade mixer. The order of addition of ingredients had little effect on the properties of the final propellant. For safety reasons, however, the ammonium perchlorate was added to the fuel binder ingredients, except for the diisocyanate. The latter was added portion-wise to the remainder of the propellant mix. This procedure was employed to increase pot life. The most important factors in the propellant mixing were the mixing temperature and the mixing time. The mixing temperature was governed primarily by the temperature-viscosity relationships of the particular prepolymer batch. Propellants containing up to 77.8 percent oxidizer were cast through a "bayonet" with 1/16 in. to 1/8 in. wide slits into an evacuated, vibrated mold. Propellant containing 80% oxidizer was cast by applying 20 psig nitrogen pressure to the casting feed can. The propellant and casting equipment were maintained at 70-75°C during casting. The measured densities of the propellants were 0.063, 0.061, and 0.058 lb/in.³ at 80, 77.8, and 75 wt% ammonium perchlorate respectively. These densities represent 98.5, 97, and 95% of the theoretical densities. Grains were cured at 75 to 80°C for 16 to 44 hours; a satisfactory cure was generally obtained in 20 hours at 80°C.

REFERENCES

1. See, for example, L. F. and M. Fieser, "Organic Chemistry", D. C. Heath and Co. 3rd ed. (1956) p. 215.
2. J. W. Hill and W. H. Carothers, J. Am. Chem. Soc., 57, 925 (1935).
3. Picatinny Arsenal Technical Report No. 1401, Rev. 1.

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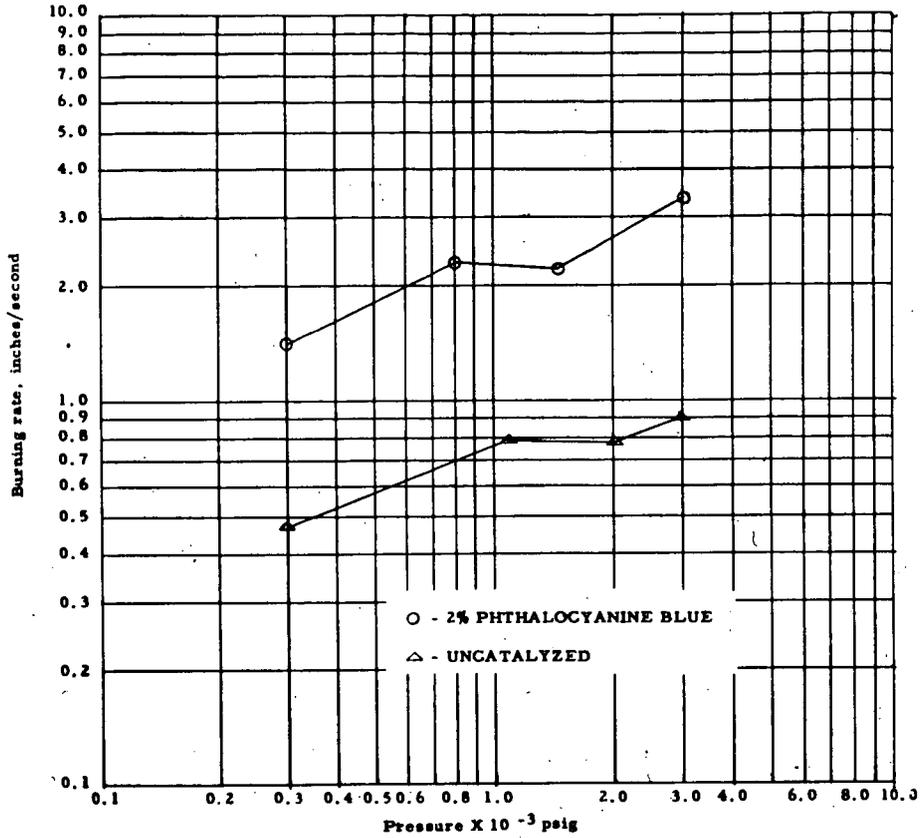


Fig. 1.-BURNING RATE OF CATALYZED AND UNCATALYZED ACETYLENIC POLYURETHANE PROPELLANT COMPOSITIONS CONTAINING 80 PERCENT AMMONIUM PERCHLORATE