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DOUBLE-BASE BINDER IMPROVEMENT

DR. W. E. BAUMGARTNER
DR. G. E. MYERS, et al

LOCKHEED PROPULSION COMPANY
A DIVISION OF LOCKHEED AIRCRAFT CORPORATION
REDLANDS, CALIFORNIA

TECHNICAL REPORT AFRPL-TR-69-13

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DOUBLE -BASE BINDER IMPROVEMENT

Dr. W. E. Baumgartner
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LOCKHEED PROPULSION COMPANY
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REDLANDS, CALIFORNIA

FOREWORD

This is the seventh Quarterly Report issued under Contract F04611-67-C-0078, "Double-Base Blnder Improvement," covering the period 1 September through 30 November 1968. This contract is assigned to Lockheed Propulsion Company, Redlands, California, and is monitored by Capt. William Anders, Alr Force Rocket Propulsion Laboratory, Edwards, California.

Technical effort under this contract has been performed by the following: Dr. W. E. Baumgartner, (Chemistry Department Manager); Dr. G. E. Myers, (Program Manager); W. S. Baker, (Prncipal Technical Investigator); Leo Asoaka, Waldemar Koehler, W. D. Allan, and Diane Burley.

Publication of this report does not constitute Alr Force approval of the report's findings and conclusions. It is published only for the exchange and stimulation of ideas.

William Ebelke
Colonel, USAF
Chief, Propellant Division

ABSTRACT

Investigation of means to improve the mechanical properties of slurry cast CMDB propellant has continued. Numerous small mixes have been cast into microdogbones and tested at 74°F in order to delineate the influence of several variables upon the tensile properties of isocyanate crosslinked systems. With well-dried and purified ingredients, complete incorporation of NC into crosslinked network occurs at isocyanate/NC hydroxyl ratios between 0.05 and 0.1 (prepolymer crosslinker weights well below 10 percent of the NC weight), and tensile properties also attain maximum values in the same region. This is despite the fact that isocyanate consumption occurs at about the same rate whether NC is present or not. Upon crosslinking with a TDI-capped polyester, stress is increased 50-100 percent and strain 10-15 percent as total polymer content (NC + crosslinker) is varied from 10 to 6 percent by weight of propellant (bimodal AP). Best properties are obtained with smaller particle size solids and/or with AP instead of HMX. The use of additives or precoated AP to enhance binder-solids bonding has not yet proven successful. Uncross-linked properties using the acetate derivative of NC are well below those using standard PNC, but crosslinking improves the properties with acetate to about those with crosslinked standard PNC.

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GLOSSARY

CaT-1000	TDI-capped polyester caprolactone, 1000 molecular weight
DBTDA	Dibutyltin diacetate
FNC	Fibrous nitrocellulose
HMDI	Hexamethylene diisocyanate
MIR	Multiple internal reflectance infrared
NC	Nitrocellulose
NOS	Naval Ordnance Station
PGA-TDI-1000	TDI-capped polyglycol adipate, 1000 molecular weight
PNC	Plastisol nitrocellulose
TDI	Toluene diisocyanate
TEGDN	Triethylene glycol dinitrate
TMETN	Trimethylolethane trinitrate
TPMTI	Triphenylmethane triisocyanate

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SECTION I

INTRODUCTION AND SUMMARY

The general objective of this program is to improve the mechanical properties of composite modified double base (CMDB) propellants, with particular emphasis upon those prepared by the slurry cast process.

Earlier results from this program and from other studies have led to the conclusion that major improvements in slurry cast CMDB propellant properties are most likely to be produced as a consequence of modifying two basic factors in such systems (Ref. 1). First is the usually extremely poor bonding between binder and solids which limits the useful properties of most CMDB propellants; the most fruitful approach here appears to involve the use of additives or filler pretreatments which provide chemical bonding between solid particle and binder (Refs. 2, 3). The second factor concerns the structure of nitrocellulose which inherently produces two undesirable effects:

- Strong NC intermolecular interaction with resultant difficulties in producing a homogeneous, well plasticized binder.
- A multitude of hydroxyl groups which, combined with the above, is believed to cause localized, high crosslink densities around NC particle peripheries during early stages of the gelation/crosslinking processes and in addition, undoubtedly causes a large amount of ring formation rather than intermolecular crosslinking.

The present approach towards improving these structurally imposed limitations involves the use of NC derivatives which reduce the effective functionality for crosslinking and alter the physical interactions among NC and plasticizer molecules. Derivatives now being examined include the acetate, the phenyl carbamate, and carboxymethyl.

Specific objectives of this reporting period included the following:

- Obtain "baseline" data outlining the effects of factors influencing the mechanical behavior of crosslinked slurry cast CMDB propellant containing a standard PNC form - with particular emphasis upon determining whether past emphasis on using comparatively large amounts of crosslinkers was indeed necessary or whether crosslinking efficiency could be increased to permit ballistically acceptable levels of inert crosslinker.
- Compare the above behavior with that produced by using the acetate derivative of NC in a PNC form. Extend to other derivatives as time permitted.

- Examine briefly the differences in behavior occasioned by the use of AP and HMX and initiate investigation of the influence of additives or filler pretreatments thereon.

To these ends, a large number of small (30-gram) mixes was prepared and cast in Teflon-lined molds to provide microdogbones* for mechanical testing at ambient (74°F) temperature. In this way numerous variables could be rapidly surveyed and an optimum range selected for subsequent larger mixes to be tested at various temperatures.

Most of the preceding work under this program was carried out with formulations similar to LPC-1005A nitroplastisol which contains 13.6 weight percent of nitrocellulose. During this report period, the range of propellant formulations was extended to lower NC levels, chiefly in the range of 6 to 10-percent NC. Although this change makes comparison with previous data difficult, it has two important advantages as follows:

- Formulations which could not be prepared at the 13.6-percent NC level because of rapid plasticization and short pot life can be mixed and cast without difficulty at the low NC levels, thus extending the practical range of comparisons. Propellants can be prepared containing very active plasticizers and it is possible to utilize NC modifications which have shown an unacceptably rapid plasticization rate at the 13.6-percent NC level.
- The smaller amount of NC and derivatives needed for the lower NC level formulations results in a significant material savings.

Results of these investigations are summarized as follows:

(1) Effect of crosslinking PNC with TDI-capped caprolactone

- Complete conversion of PNC into insoluble network occurs within an isocyanate to NC hydroxyl equivalence ratio of 0.05 to 0.1, corresponding to much less than 1-percent by weight of crosslinker (1000 molecular weight) in propellant.
- Stress and strain (74°F) are both increased by crosslinking (unimodal and bimodal AP, bimodal HMX) and reach maximum values in the above equivalence ratio range.
- For a bimodal AP system 74°F stress is increased 50 to 100 percent whereas it is increased 20 to 50 percent for a bimodal HMX system. Strain is increased at most by 10 to 15 percent. The greatest effect is observed at low total polymer content, e. g., 6 percent PNC plus crosslinker.

* $\frac{1}{4}$ by $\frac{1}{4}$ -inch cross section and 1-inch gage length

(2) Effect of isocyanate crosslinker structure

- No significant differences in ambient (74°F) properties were observed using two different TDI capping batches of polyester-caprolactone or a commercial TDI-capped polyglycoladipate.
- With unimodal AP, HMDI and TPMTI produced increased stress but decreased strain capabilities from zero to 0.1 equivalent ratios.
- With bimodal AP and without catalyst, TPMTI resulted in 74°F properties comparable to those produced with TDI-capped prepolymer.

(3) Effect of NC derivatives

- The acetate derivative attains complete gelation and produces maximum properties at almost the same equivalence ratio as does the standard NC.
- Although uncrosslinked properties of the acetate system at 74°F are well below those with standard NC, crosslinking improves the former to about the same values observed for the standard NC system; stress is slightly less for the acetate system but strain slightly greater.
- Compared with standard NC, an uncrosslinked phenylurethane NC produced lower strain but significantly higher stress while the uncrosslinked carboxymethyl NC produced very low stresses and strains.

(4) Binder-solids interaction

- HMX-loaded propellant exhibits a distinct yielding in its stress/strain response as a consequence of localized dewetting.
- In general the use of smaller particle size and/or of AP instead of HMX leads to distinct increases in ambient stress and somewhat lesser increases in strain.
- Binder/HMX tablet experiments were unsuccessful due to strong sorption of plasticizers by the tablets with consequent weakening of the tablets.
- Attempts to increase AP-loaded propellant mechanical properties by addition of C-1 or by using AP precoated with various chlorosilanes were unsuccessful.

(5) Isocyanate consumption by propellant ingredients

- Despite careful drying of all ingredients and alumina pre-treatment of plasticizers, significant consumption of isocyanate occurs in the absence of NC.
- Although crosslinking of NC still occurs below 0.1 isocyanate/NC hydroxyl, the above degree of side reactions demonstrates the necessity for careful purification of ingredients in order to obtain reproducible mechanical properties with crosslinked CMDB propellants.

SECTION II

PROGRESS

1. CMDB PROPELLANT; STANDARD PNC CROSSLINKED WITH TDI-CAPPED POLYESTERCAPROLACTONE (CaT-1000)

Baseline data* were obtained from 30-gram mixes using a Naval Ordnance Station (NOS) lot of plastisol nitrocellulose (PNC) and a TDI-capped polyestercaprolactone of 1000 molecular weight (CaT-1000). Small amounts of PNC were replaced with crosslinker to hold the total binder polymer content constant at selected levels. The equivalence ratio of isocyanate groups to NC hydroxyls (12.6-percent nitrogen NC) was varied from zero to 0.75, corresponding, for example, to weight percents from 10% NC/0% CaT-1000 to 6% NC/4% CaT-1000. (See formulations d and e of Table 1 for example.)

All ingredients were dried as well as possible (e.g., plasticizers down to ~0.02% H₂O, PNC to ~0.2%, AP to ~0.05%) and mixing was conducted in a dry box or controlled low humidity processing area. Plasticizers were purified prior to final drying by passage through alumina columns.

On selected propellant samples the consumption of isocyanate was followed by multiple internal reflectance infrared (MIR). In general, 72 hours at 140°F was found sufficient to consume all measurable isocyanate in propellant with or without catalyst. Measurements of binder sol/gel** contents were also conducted by repeated extraction of propellant samples in acetone; four days standing in acetone at room temperature with daily changes of solvent was found adequate to dissolve all ingredients except Al and insoluble, crosslinked polymer.

a. Properties at 10-Percent Total Polymer, AP Loaded

Stress and strain for a bimodal AP propellant (Formulation d, Table I) at varying crosslink ratios are shown in Figure 1; data for the binder itself are shown in Figure 2. These results are highlighted as follows:***

- As the NCO/OH ratio rises from 0 to 0.1, the propellant stress capability increases strongly but shows definite leveling off in the region of 0.1.

*Microdogbones ($\frac{1}{4} \times \frac{1}{4}$ -inch cross section and 1-inch gage length) were tested in triplicate at 74°F and 1 inch/minute crosshead rate. All strain values reported represent crosshead travel and original cross section, respectively, and unless otherwise stated are maximum stress and strain at maximum stress.

** Percent gel is defined as the percentage of total initial polymer (NC + crosslinker) which is acetone insoluble.

*** Similar behavior has been observed for propellants with unimodal AP (Formulation c, Table 1) and bimodal HMX (Formulation b, Table 1). The effects of solid type and size distribution are discussed in subsection II.4.

TABLE I
BASIC PROPELLANT FORMULATIONS

Ingredient	Weight Percent				
	a	b	c	d	e
PNC + Crosslinker	10.00	10.00	10.00	10.00	6.00
TEGDN	9.15	9.15	9.15	9.15	10.60
TMETN	16.35	16.35	16.35	16.35	18.90
Ethyl centralite	0.495	0.495	0.495	0.495	0.495
DBTDA	0.005	0.005	0.005	0.005	0.005
HMX (Type A)	46.00	30.70	--	--	--
HMX (Type E)	--	15.30	--	--	--
AP (Type II, I)	--	--	46.00	30.70	30.70
AP (9 μ)	--	--	--	15.30	15.30
Al (H-5)	18.00	18.00	18.00	18.00	18.00

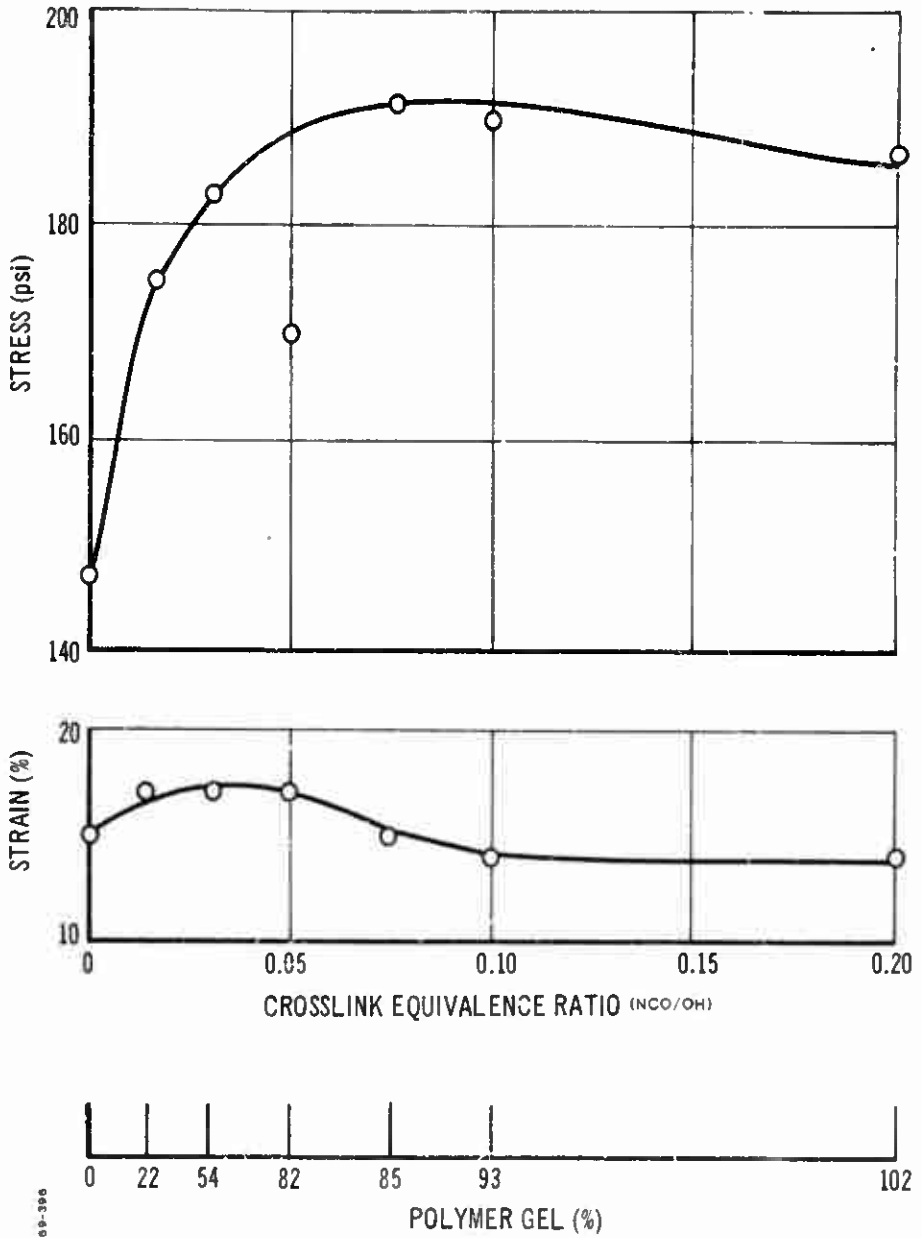


Figure 1 Propellant Tensile Properties, 10-Percent Total NC plus CaT-1000, Bimodal AP, 74°F (Formulation d, Table I)

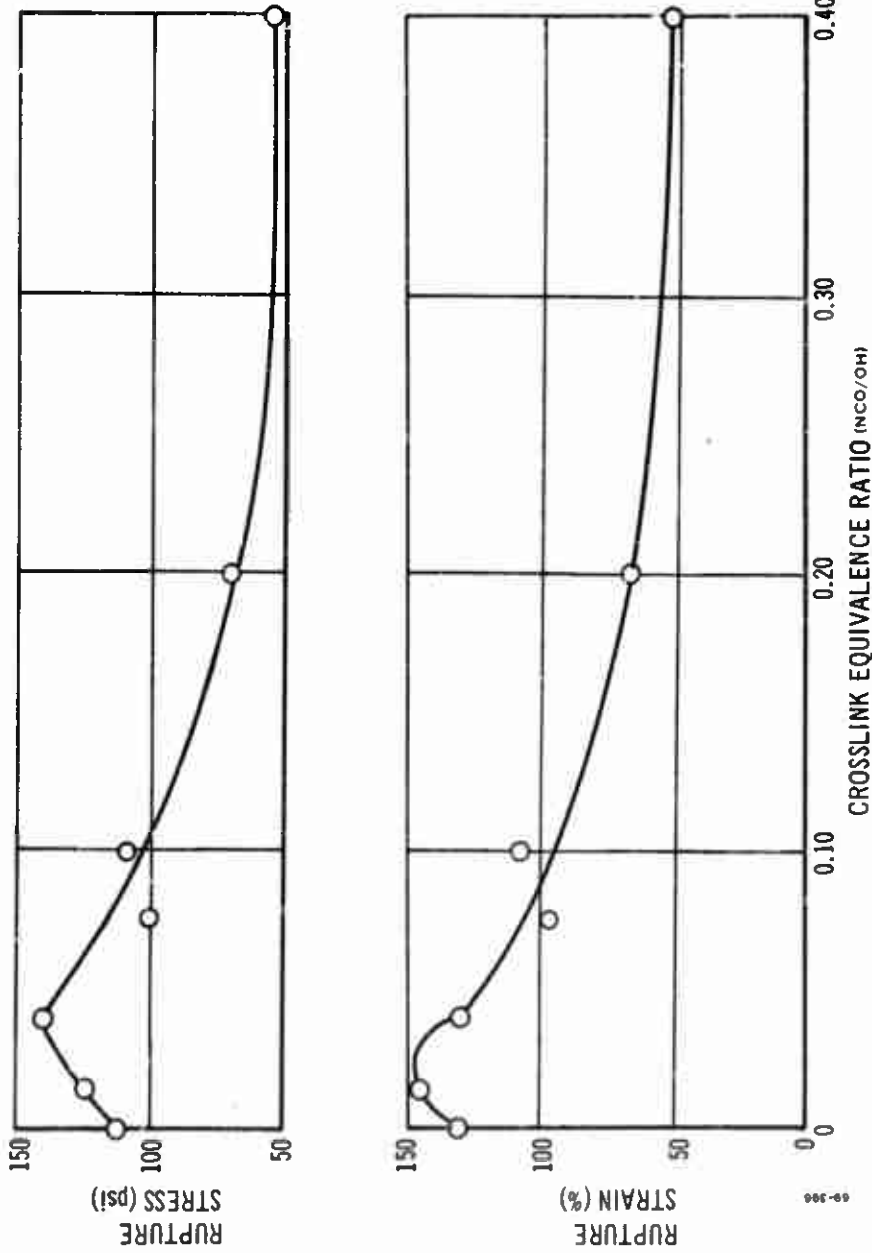


Figure 2 Binder Tensile Properties, CaT-1000 Cross-linked (Basic Formulation as in a, Table 1)

- Concurrently the propellant strain capability shows initial increase and appears to maximize at about 0.05 equivalence ratio.
- Binder properties appear to reach maximum values at somewhat lower equivalence ratios, both stress and strain falling off after that point.
- Paralleling the above behavior, the gel content increases very rapidly with increasing crosslinker content, attaining 100 percent between 0.05 and 0.1 equivalence ratio. Despite probable side reactions (see subsection II.5), therefore, complete conversion of the NC into crosslinked network occurs below one-percent crosslinker content in the propellant, such levels being entirely acceptable from a ballistic point of view. Note, that 0.1 equivalence ratio is still 5 to 10 fold greater than the theoretical quantity required to achieve incipient gelation of the NC in the absence of all side reactions. Considering the comparatively rapid consumption of isocyanate in the absence of NC (subsection II.5), however, only a fraction of the crosslinker present must actually be effectively employed. This would seem to argue for relatively rapid and uniform penetration of the NC particles by this crosslinker, with minimal degrees of ring formation.

Thus, this particular system results in acceptably efficient crosslinking with appreciable increases in stress, but the magnitude of the strain increase is disappointingly small (only 3 to 4 absolute percent for either the HMX or AP propellant). It was hoped that added strain capability could be achieved by decreasing the polymer content at constant total binder content while still retaining satisfactory stress capability by virtue of crosslinking. Pertinent experiments are summarized in the following section.

b. Effect of NC/Plasticizer Ratio (Total Polymer Content)

Propellant formulations were tested at the 10, 8, 7, and 6-weight percent total polymer level. As the polymer content dropped, the plasticizer level correspondingly increased such that the polymer/plasticizer ratio decreased from 0.40 to 0.21. Formulations were otherwise as listed in Table I.

Data for the bimodal AP systems are shown in Figures 1, 3, 4, and 5 as a function of crosslink equivalence ratio. Figure 6 summarizes

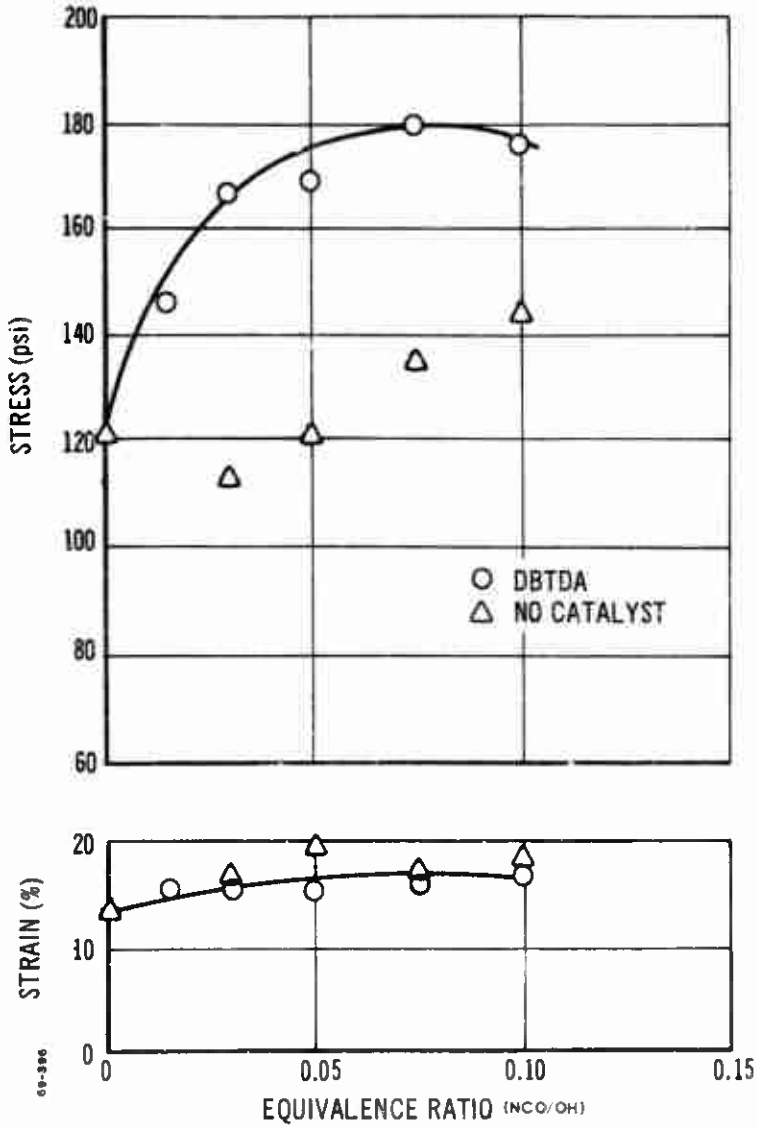


Figure 3 Propellant Tensile Properties, 8-Percent Total NC plus CaT-1000, Bimodal AP, 74°F

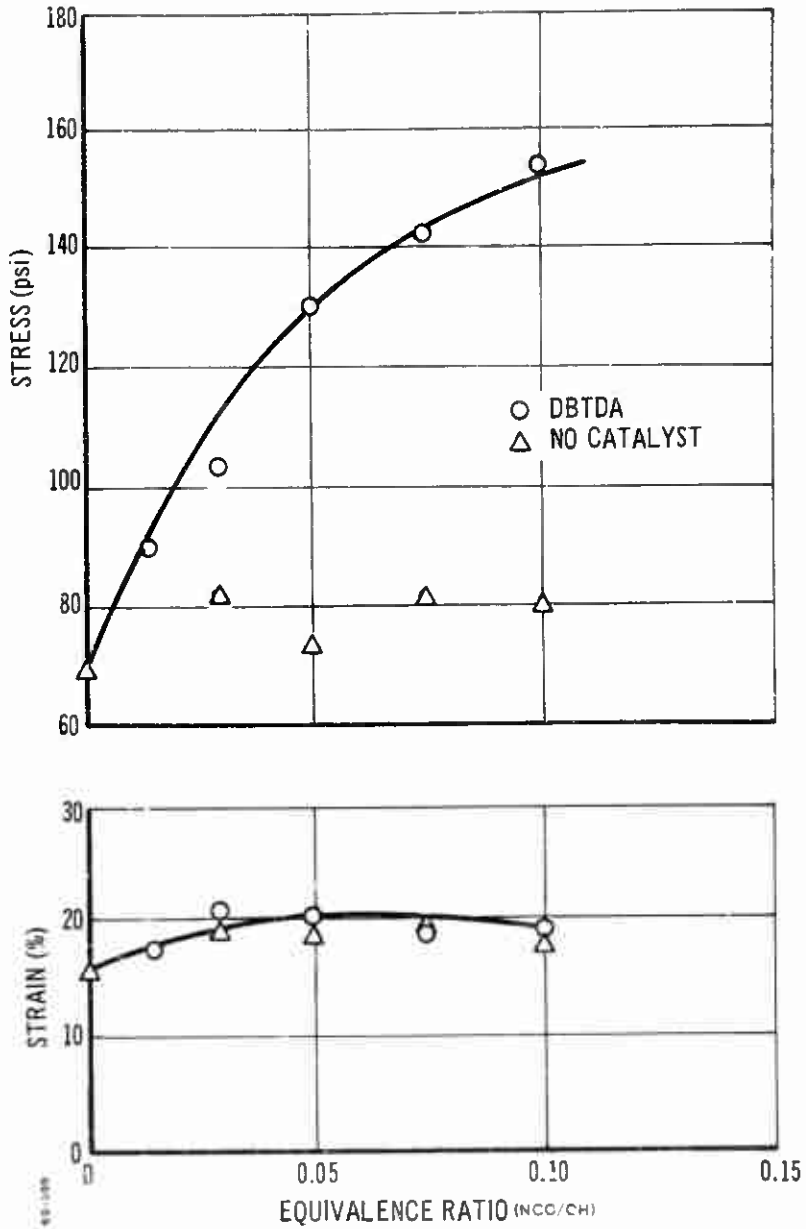


Figure 4 Propellant Tensile Properties, 7-Percent Total NC plus CaT-1000, Bimodal AP, 74°F

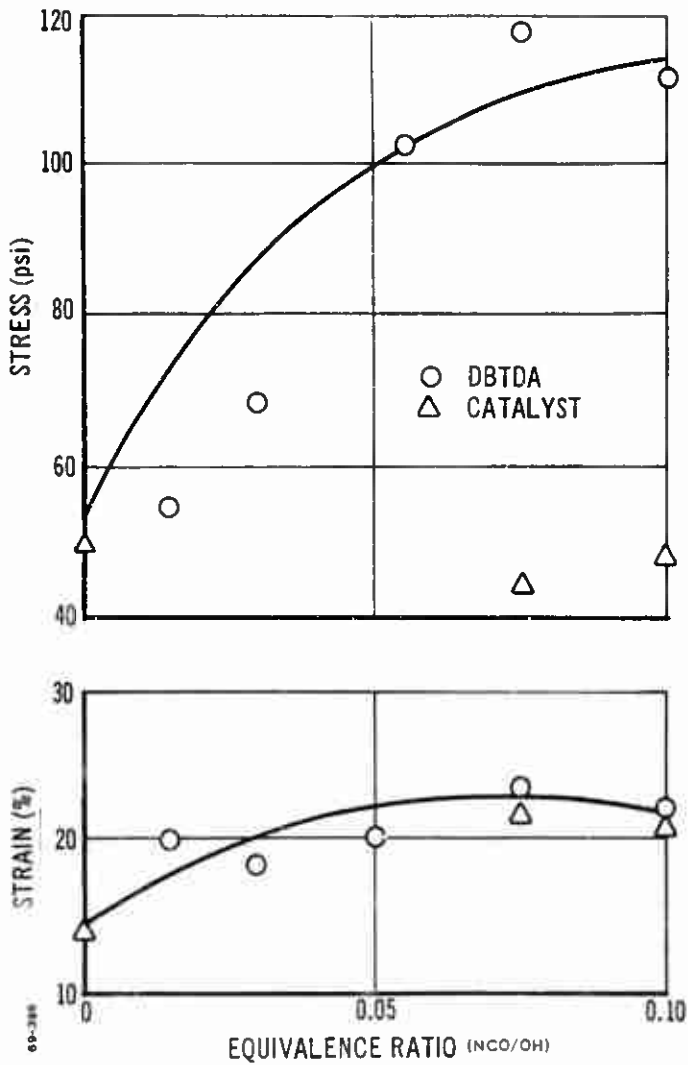


Figure 5 Propellant Tensile Properties, 6-Percent Total NC plus CaT-1000, Bimodal AP, 74°F

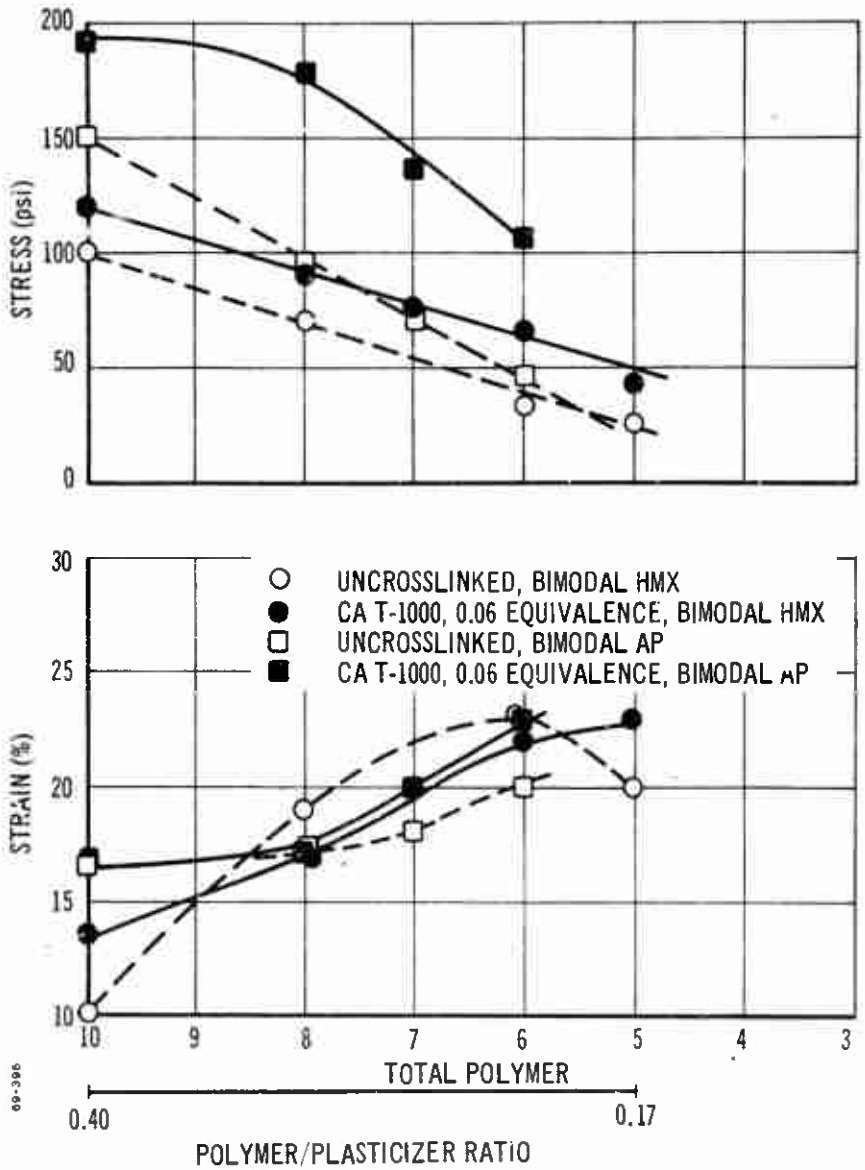


Figure 6 Propellant Tensile Properties as a Function of Polymer/Plasticizer Ratio

these properties and those for a bimodal HMX system at a fixed equivalence ratio of 0.06.*

For the AP system stress is increased 50 to 100 percent by crosslinking whereas the increase is only 20 to 50 percent for the HMX system. The effects upon strain are less clear-cut but amount perhaps to 10 to 15 percent relative strain increase for the AP system at the lowest polymer content. Probably the most worthwhile effect of crosslinking is at the low polymer level where an essentially useless propellant (too low stress) attains a useful stress capability (AP system) without loss of strain capability. Such a system would be particularly interesting for high energy application, assuming that its mechanical properties remained acceptable over the necessary temperature range. From an absolute point of view these ambient stress and strain values are, of course, not exceptional and greater improvement still is desirable.

2. CMDB PROPELLANT; EFFECT OF ISOCYANATE CROSSLINKER STRUCTURE WITH STANDARD PNC

a. TDI-Capped Prepolymers

No significant differences in behavior have been observed at ambient with propellant (Formulation d of Table I) prepared using two different TDI-capping batches of the polyester caprolactone or using a commercial TDI-capped polyglycol adipate (PGA-TDI-1000, CPR Division of Upjohn). The stress/strain/equivalence ratio curves with PGA-TDI-1000, like those with CaT-1000, show increasing yield stress as the NCO/OH equivalence rises toward 0.1. Maximum strain for the PGA-TDI system appears to be at an equivalence value of about 0.05 which is slightly lower than the optimum of 0.075 found for the CaT-1000 system. Throughout the series of mixes with these two crosslinkers, comparison mixes prepared without a catalyst showed less well defined trends than the catalyzed analogs, most often exhibiting substantially lower stress with little change in strain as the equivalence ratio increased.

b. Effects of Lower Molecular Weight Crosslinkers

Figures 7 and 8 present the results for mix series at 8 and 6-percent NC in which hexamethylene diisocyanate (HMDI) was used as the crosslinker (unimodal AP, formulation c, Table I). Again, stress increased rapidly with increasing equivalence ratio, but in contrast to the CaT-1000

*It should be noted that the strain values for uncrosslinked systems in Figure 6 are averages from several small mixes and are somewhat higher than the zero equivalence values in Figures 1, 3, 4, and 5. Repetition of any series of mixes over the equivalence range usually resulted in some shift of the strain scale. This shift was much more pronounced at the zero equivalence point and hence the summary Figure 6 employs average values there.

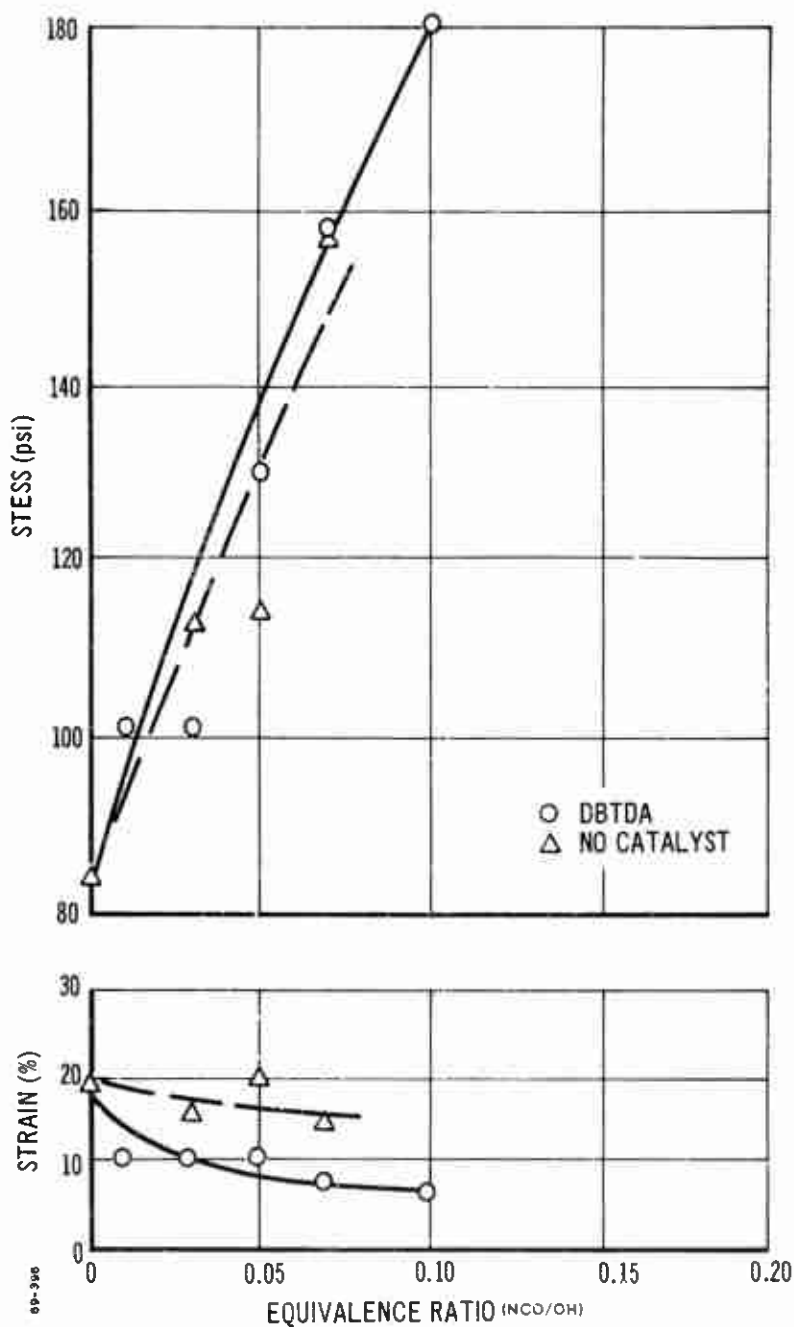


Figure 7 Propellant Tensile Properties, 8-Percent PNC, HMDI, Unimodal AP, 74°F

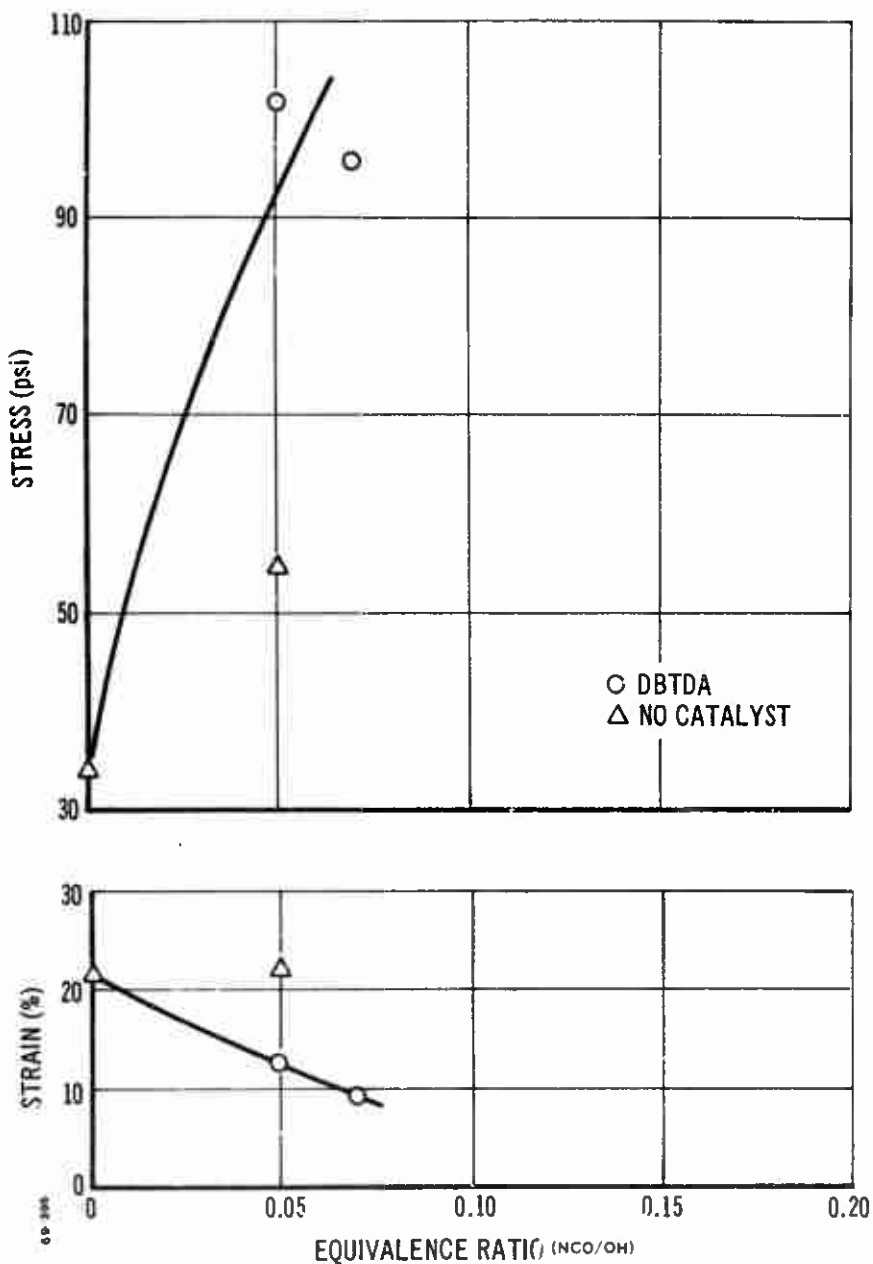


Figure 8 Propellant Tensile Properties, 6-Percent PNC, HMDI, Unimodal AP, 74°F

systems, the lower molecular weight HMDI caused decreases in strain at all equivalence ratios tested. Several mixes prepared without catalyst also resulted in increased stress with less reduction in strain.

Figures 9, 10, and 11 represent similar series at the 10, 8, and 6-percent PNC level with triphenylmethane triisocyanate (TPMTI) as crosslinker. Effects generally similar to those with HMDI are evident, despite the considerable scatter.

Figures 12 and 13 show the effects on NOS PNC propellant of adding TPMTI as crosslinker without a catalyst at binder polymer levels of 10 and 7 weight percent with bimodal AP. The optimum equivalence ratio appears to be about 0.05, yielding stress/strain values of 244 psi/18% and 146 psi/19.5%. The use of a catalyst in two comparison mixes caused significant decreases in stress with little effect on strain. The results here for the 10-percent binder level are markedly superior to those for the 10-percent series containing TPMTI with DBTDA catalyst (Figure 9). However, the latter series used unimodal AP whereas the mixes for Figure 12 were made with the AP blend. Since the values for the AP blend are comparable to those for the catalyzed CaT-1000 system (Figures 1 and 4), further tests are planned to clarify the relative merits of TPMTI as crosslinker. Preliminary data, for example, with NOS PNC/polyestercaprolactone diol (non TDI-capped CaT-1000)/uncatalyzed TPMTI show ambient properties superior to any others observed; additional mixes are in progress.

Reasons for some of the differences being observed with these low molecular weight crosslinkers are not obvious at this time. With both HMDI and TPMTI, MIR measurements performed upon propellant slices after a 72-hour cure at 60°C indicated no measurable isocyanate groups remaining whether or not catalyst was included in the formulation, although it must be kept in mind that the MIR technique has difficulty picking up the last 10-percent or so of isocyanate. Gel content measurements are in progress upon selected samples from these series.

3. CMDB PROPELLANT WITH NITROCELLULOSE DERIVATIVES

As discussed in Section 1, the rationale for investigating the effects of NC derivatives resides primarily in the belief that the abundance of NC hydroxyl groups may well produce several undesirable results. Very briefly, these are:

- The very high local concentrations of both hydroxyls and crosslinker groups existing during early stages of cure and dispersion of the NC could cause extreme inhomogeneity in final crosslink density and even inhibit dispersion of the NC particles.
- The probability is high that a given crosslinker molecule will react with two hydroxyls on the same NC molecule to form ring structures.

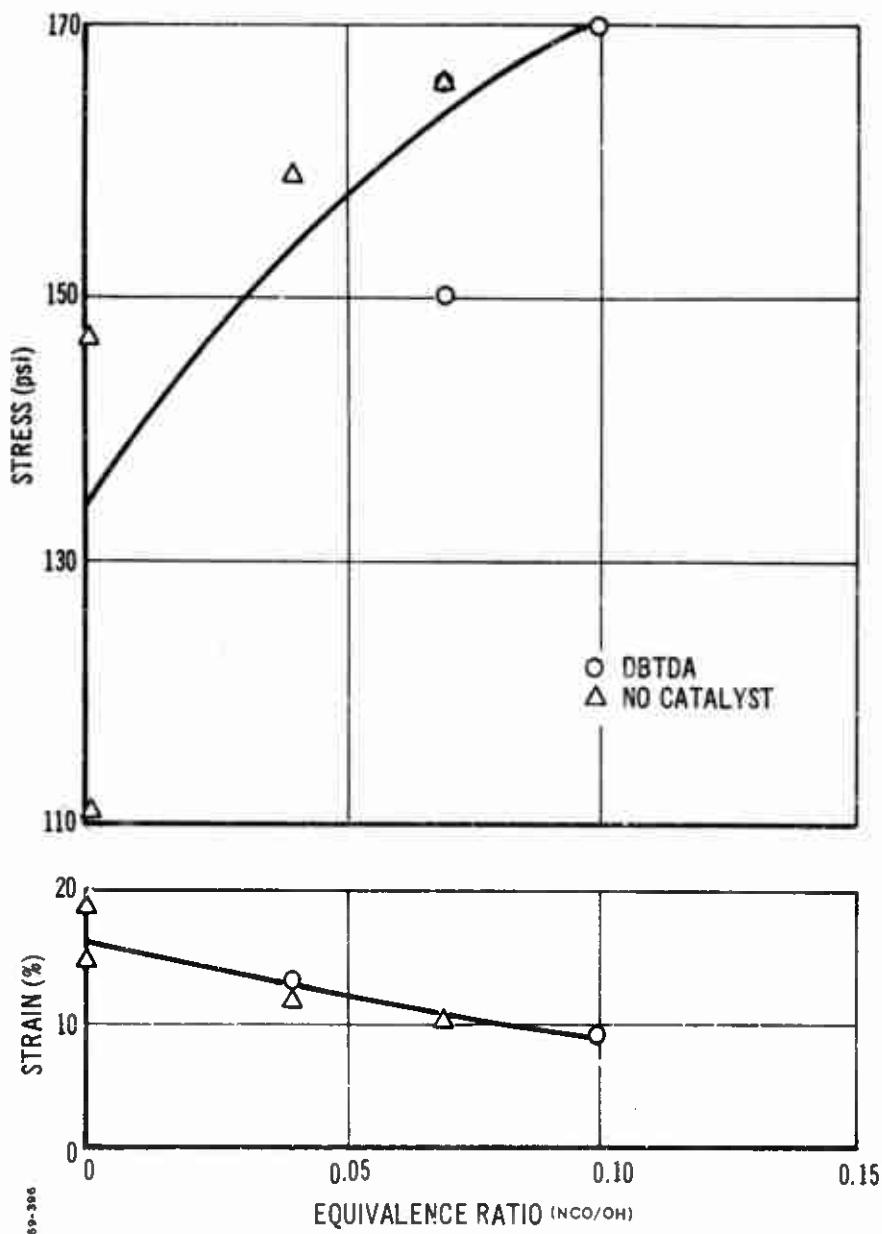


Figure 9 Propellant Tensile Properties, 10-Percent PNC, TPMTI, Unimodal AP, 74°F

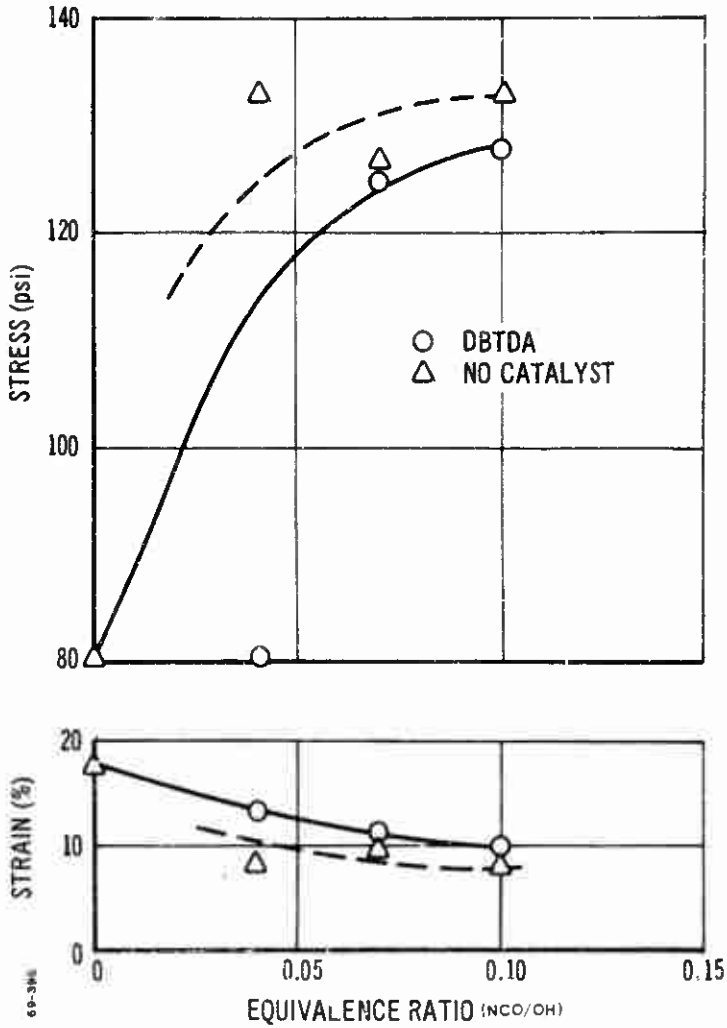


Figure 10 Propellant Tensile Properties, 8-Percent PNC, TPMTI, Unimodal AP, 74°F

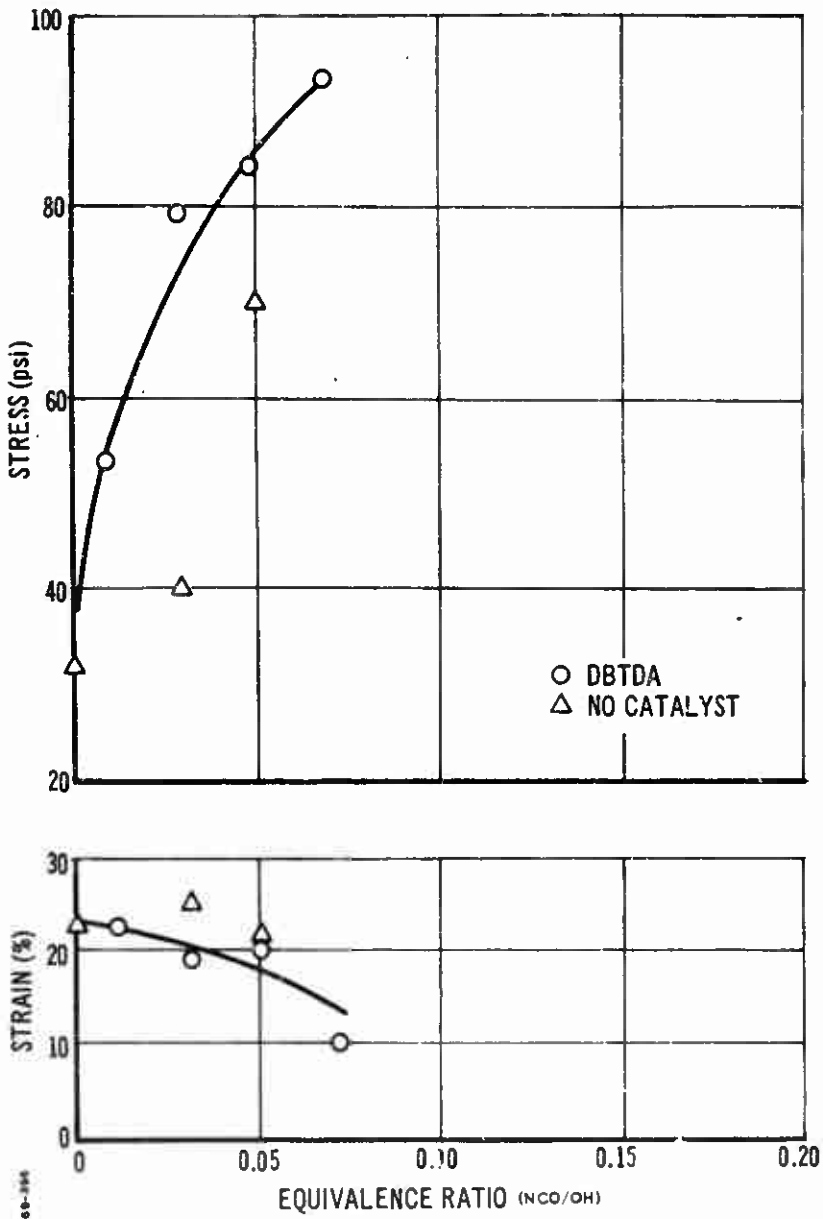


Figure 11 Propellant Tensile Properties, 6-Percent PNC, TPMTI, Unimodal AP, 74°F

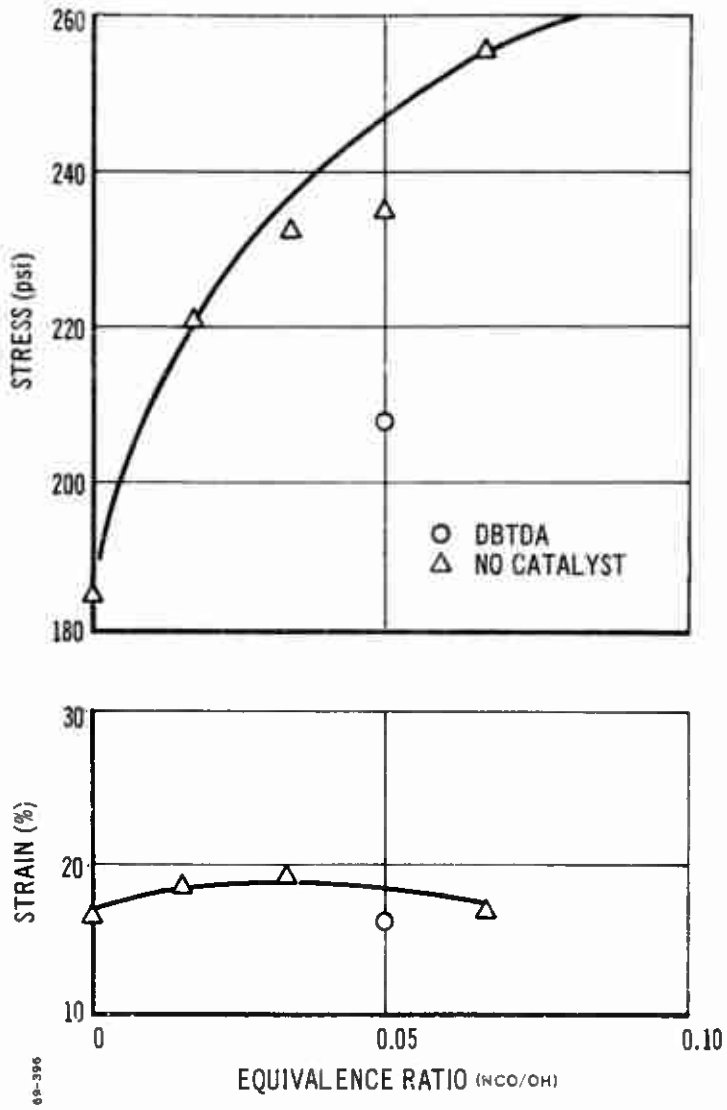


Figure 12 Propellant Tensile Properties, 10-Percent PNC, TPMTI, Bimodal AP, 74°F

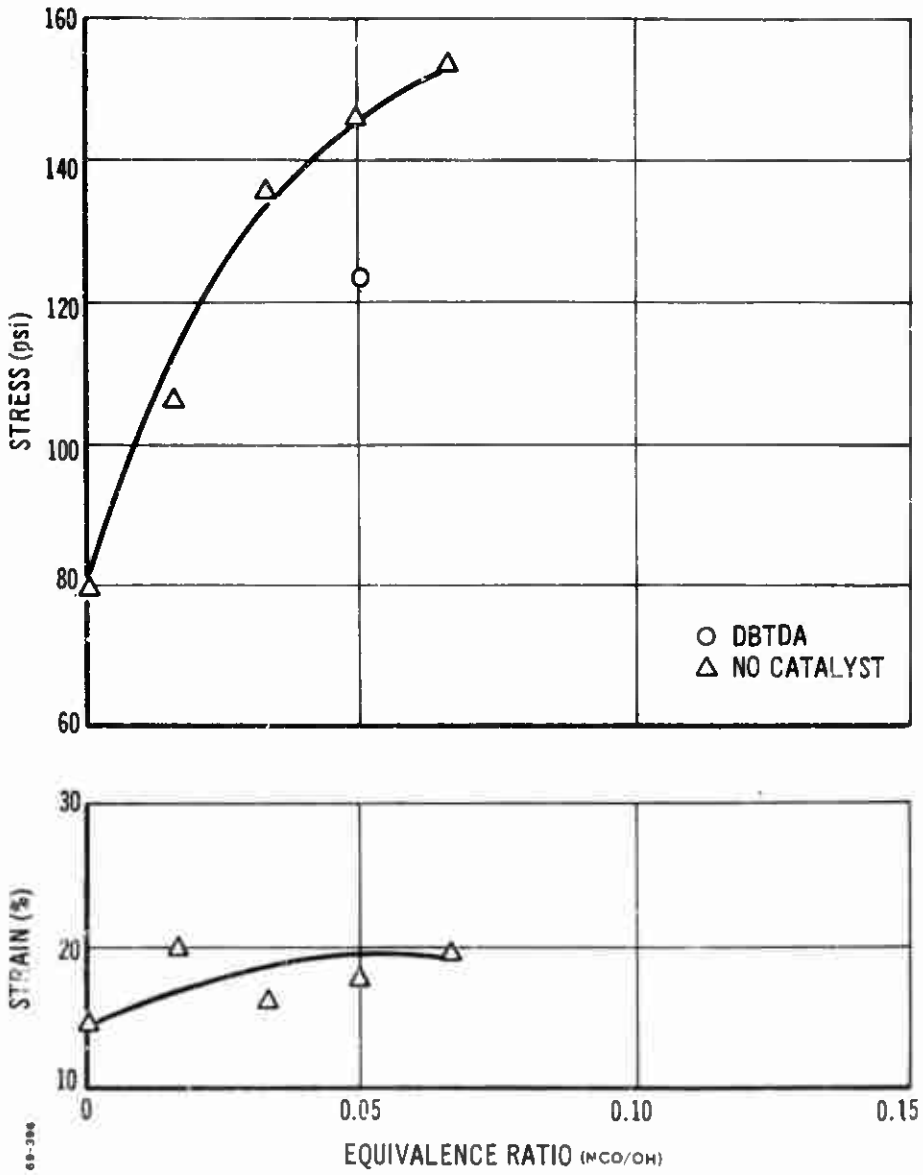


Figure 13 Propellant Tensile Properties, 7-Percent PNC, TPMTI, Bimodal AP, 74°F

- The strong hydrogen bonding between NC molecules makes complete solution of the NC difficult and may inhibit effective plasticization.

To reduce the possibility of these occurrences, various derivatives of NC have been synthesized wherein a substantial fraction of the original hydroxyls is converted to other chemical groups. In this program to date, the derivative which has received the most attention is a nitrocellulose acetate in which approximately one-third of the hydroxyls were reacted with acetic anhydride.

a. Nitrocellulose Acetate

Details concerning the synthesis of this material were reported in Quarterly Progress Report No. 4 (Ref. 4). Analysis was conducted by infrared using the adsorption at 1760 cm^{-1} characteristic of the C=O group. About 900 grams of the derivative was synthesized from Hercules 30-second FNC. Part of this material was converted to PNC form, yielding approximately 200 grams of final product. The conversion yield was only 55 percent because of equipment malfunctions during conversion operations. Microscopic examination and plasticization (photometer) tests showed the product to be comparable to PNC prepared from Hercules 5-second nitrocellulose. The remaining supply of the derivative was dissolved in nitromethane for further conversion as needed.

Figure 14 presents a comparison of ambient microdogbone tensile properties for CMDB propellant (bimodal AP, formulation d of Table I) containing NOS and acetate PNC, as a function of CaT-1000 equivalence ratio. Both the unmodified NC and the acetate NC systems reach optimum properties, and complete incorporation of NC into elastomer, by an equivalence ratio of 0.05 to 0.075, despite the decreased number of reactive hydroxyls present in the acetate derivative. Although the uncrosslinked properties of the acetate system are much inferior to those with the NOS PNC, crosslinking improves the former to about the same performance exhibited with the NOS material. The use of FeAA instead of DBTDA as catalyst results in poorer stress and strain values.

Additional comparisons have been performed at the 8 and 6-percent total polymer level using PGA-TDI-1000 as crosslinker and unimodal AP. In general, the results paralleled those in Figure 14; Table II summarizes the values existing at the approximate point of maximum ambient strain.

In all of these series, the NC acetate had somewhat lower stress and about 2 to 3-percent greater absolute strain than NOS PNC analogs. Comparison mixes without a catalyst showed less well defined trends than appeared with catalyzed analogs but usually possessed substantially lower stress with little change in strain from that of a crosslinked system.

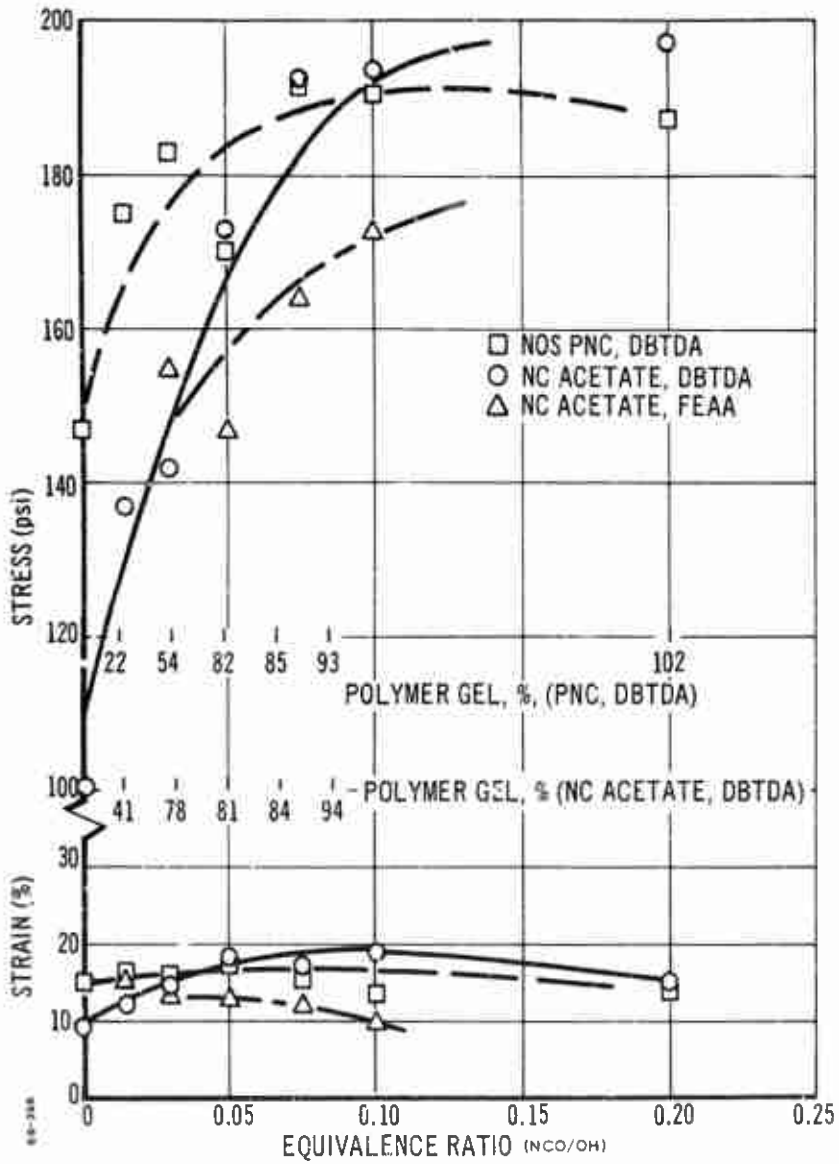


Figure 14 Comparison Between NOS and Acetate PNC, 10-Percent Total NC plus CaT-1000, Bimodal AP, 74°F

TABLE II
 AMBIENT TENSILE PROPERTIES WITH NOS AND
 ACETATE PNC AT POINT OF MAXIMUM STRAIN

NC	Binder Polymer (wt %)	Crosslinker	Equivalence Ratio (NCO/OH)	Stress (psi)	Strain (%)
NOS PNC ^(a)	10	CaT-1000	0.075	188	16.7
NC acetate ^(a)	10	CaT-1000	0.075	182	19.3
NOS PNC ^(b)	8	PGA-TDI	0.050	108	20.0
NC acetate ^(b)	8	PGA-TDI	0.050	80	22.0
NOS PNC ^(b)	6	PGA-TDI	0.070	74	22.3
NC acetate	6	PGA-TDI	0.070	68	24.7

(a) Formulation d, Table I with bimodal AP

(b) Formulation c, Table I with unimodal AP

Thus, the acetate derivative does not show a strong advantage over unmodified PNC at ambient temperature. However, the possibility that a greater improvement will be realized at other temperatures is being investigated with larger mixes to determine mechanical properties over the full range of -40 to 140°F.

b. Phenylurethane and Carboxymethyl Derivatives

A phenylurethane derivative has been prepared at a degree of substitution of about 0.2 by reaction of phenyl isocyanate with Hercules 30-second FNC. A carboxymethyl (0.06 degree of substitution) nitrocellulose was supplied by Naval Weapons Center. These were both converted to plastisol form in small batches.

Initial tests of the effect of these derivatives upon propellant behavior were conducted at the 6-percent polymer level without crosslinker. Results are summarized in Table III for propellant prepared from four different synthesis lots of NC phenylurethane and from two different plastisol conversion samples of carboxymethyl nitrocellulose.

Although the strain capability of all four of the phenylurethanes was significantly lower than that of the NOS PNC control, their distinctly higher stress values are encouraging. Microscopic examination of the converted PNC forms of these samples showed that No. 4 consisted of extremely large particles, many greater than 100 μ diameter, and, therefore, cannot be considered representative. Differences in the particle sizes of the other three samples were small.

TABLE III

EFFECT OF PHENYLURETHANE AND CARBOXYMETHYL NC
DERIVATIVES UPON UNCROSSLINKED PROPELLANT
TENSILE PROPERTIES (74°F)

<u>NC Type</u>	<u>Stress (psi)</u>	<u>Strain (%)</u>
NOS PNC (control) ^(a)	39	22.6
NC phenyl urethane		
No. 1	74	14.0
No. 2	88	17.8
No. 3	118	16.2
No. 4	17	17.0
Carboxymethyl nitrocellulose		
No. 1	18	8.0
No. 2	26	8.7

^(a) 6-percent NC, 29.5-percent plasticizers, unimodal AP

Infrared examination of the first three phenylurethane showed distinctive differences for the No. 3 sample, its absorption of 1755 cm^{-1} being substantially less and absorptions at 1730, 1600, and 1545 being stronger than for samples No. 1 and 2. A brief examination of the phenylurethane synthesis conditions has been initiated to establish those necessary to duplicate Sample No. 3 for more extensive evaluation in crosslinked mixes.

Whether the very poor properties with the carboxymethyl derivative are a consequence of its relatively low molecular weight* or of inherently poor interaction with plasticizers and/or solids cannot yet be stated. This should be established at least in part by crosslinking studies now in progress.

4. BINDER-SOLIDS INTERACTION

Earlier studies in this program involved a comparison between slurry cast and base grain propellants of identical composition, and it was concluded that a major contributing factor to the poorer mechanical properties of the slurry cast system was poor binder-solids adhesion. The strong influence of this phenomenon upon propellant mechanical properties is amply illustrated by Figures 6, 15, and 16.

* Reduced viscosity in acetone ($1/2$ percent at 25°C) is 1.16 compared with 3.4 for NOS PNC.

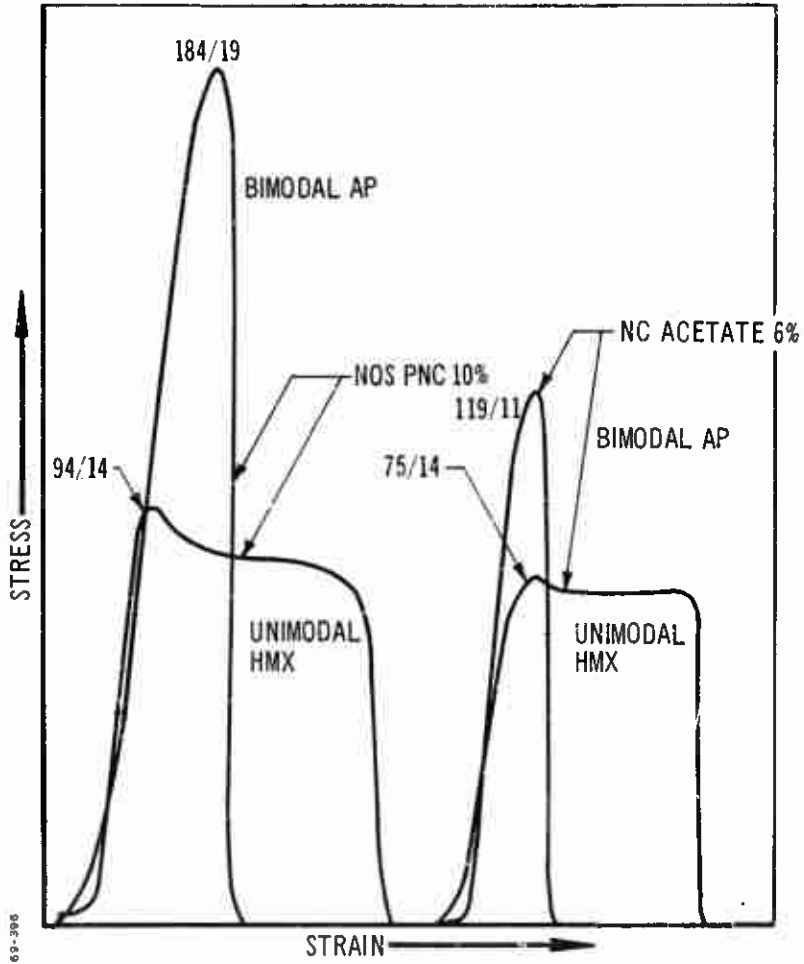


Figure 15 Representative Stress-Strain Curves at Ambient Temperature for Crosslinked AP and HMX-Filled Propellant

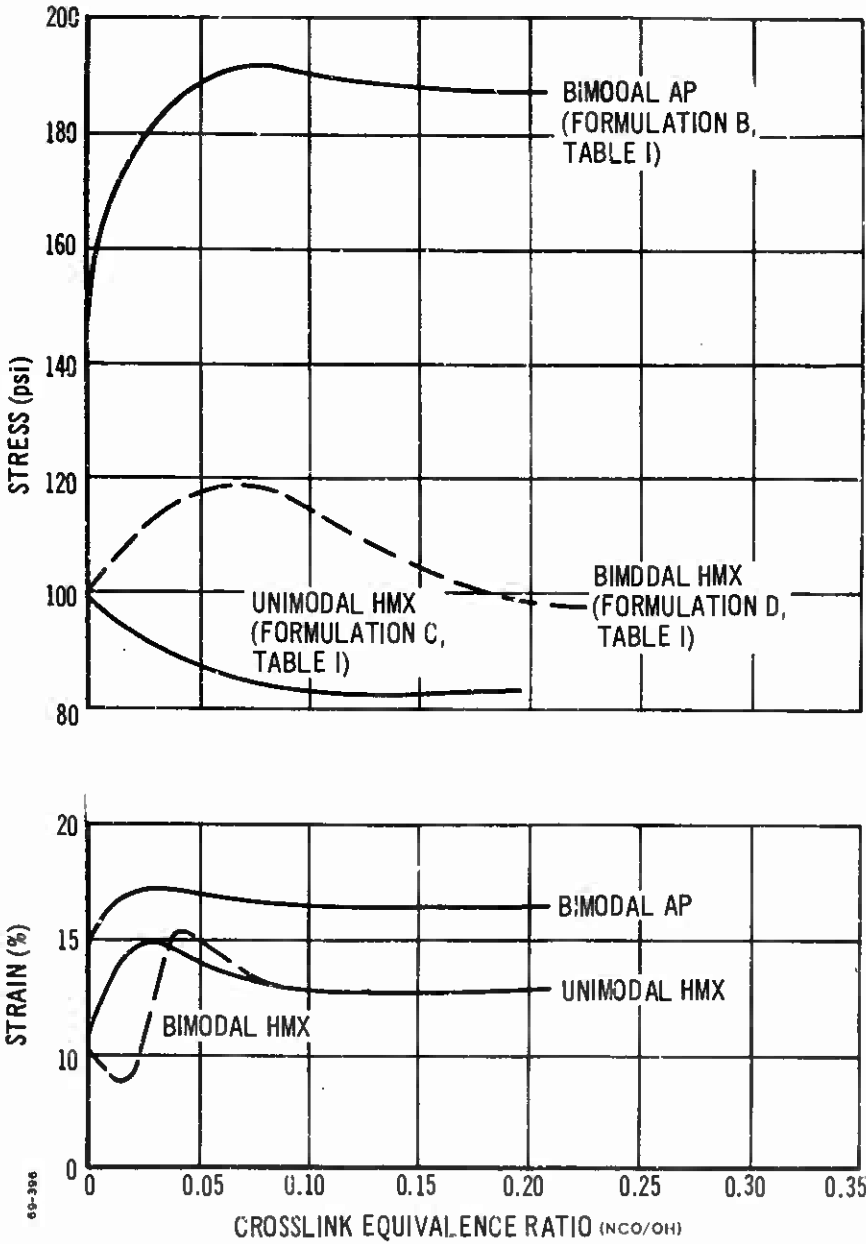


Figure 16 Effect of Solids Type and Size Distribution Upon Ambient Tensile Properties (10-Percent Total PNC plus CaT-1000)

Figure 15 presents representative stress/strain curves obtained at 74°F for HMX and AP loaded propellants prepared with both NOS and acetate PNC. The distinctive differences between the HMX and AP systems are presumed to be the consequence of lower adhesive strength between HMX and binder than exists between AP and binder, resulting in localized dewetting and a pronounced yield point in the HMX propellant. Since the stress and strain at rupture in such a system are representative of extensively dewetted propellant, all values reported herein for HMX propellant are those observed at the yield point, even in those occasional cases where the rupture load exceeds that at the yield point.

Figure 16 illustrates the effect of solids type and size distribution upon observed stress and strain as a function of crosslink equivalence, while Figure 6 presented similar effects as a function of total polymer concentration. In general, the use of smaller particle size and/or of AP instead of HMX leads to distinct increases in stress values and somewhat lesser increases in strain values.

As reported earlier (Ref. 1), the poor adhesion between AP and double base binder was also demonstrated by measurements of peel strength using a propellant model consisting of binder cast and cured against pressed AP tablets. For the majority of samples tested, the peel time was too short to permit meaningful comparisons even at very small loads, and distinctions could not be recognized between binders containing varied NC/plasticizer ratios. However, the peel time for a binder crosslinked with CaT-1000 was approximately three times that for the uncrosslinked control. Additional tests are planned with other crosslinkers and NC derivatives to establish whether measurable differences exist.

An attempt to carry out the same test with discs of pressed HMX was not successful because the tablets absorbed plasticizers during cure and were weakened to the point where they could not be mounted in the test fixture without extensive damage. It is not known whether the lack of physical integrity of the HMX discs is due to poor compaction in forming the tablets or to an inherent tendency of HMX to be softened by nitrate ester plasticizers. Reported improvements in HMX propellant behavior using HMX precoated with polyisocyanates (Ref. 2) may be a consequence of increased adhesion plus retention of HMX particle strength because of a coating relatively impermeable to nitrate esters. It is perhaps pertinent in this connection to note that preheating HMX in the nitrate esters prior to actual propellant mixing results in significantly lower stress and strain values both at yield and at rupture.

Efforts to improve the bonding between solids and binder have as yet been rather limited in this program. Small mixes have been tested, for example, containing AP plus the compound C-1 (2,3 dihydroxypropyl bis-2-cyanoethylamine) which is reputed to improve the behavior of isocyanate-cured HTPB propellants (Ref. 3). Not surprisingly, no real changes in CaT-1000 formulations were observed, presumably as a consequence of the high polarity of the nitrate ester binder with resultant low adsorption of C-1 upon the AP particles (Refs. 2, 3). It will be of interest to examine the effectiveness of pretreating AP with C-1 and polyisocyanate in a nonpolar solvent.

A series of AP samples treated with a variety of chlorosilanes was made available by another program and incorporated into small mixes. The organic substituents of these silanes included phenyl, methyl, ethyl, and vinyl groups. The treated AP's all showed markedly decreased wettability and rates of solution in water. However, in the propellant mixes they all caused significant reductions in both stress and strain. No further work with these relatively nonpolar substituents as coatings for AP is planned, but it can be anticipated that molecules containing highly polar and reactive groups may have a beneficial effect on mechanical properties.

5. ISOCYANATE REACTIONS WITH PROPELLANT INGREDIENTS OTHER THAN NC

One primary objective of the crosslinking studies was to increase the efficiency of utilization of crosslinkers to prevent losses in ballistic performance. Therefore, initial efforts were concentrated upon establishing the degree of ingredient purity required to minimize consumption of isocyanate crosslinker by undesirable reactions, e. g., with H_2O or un-nitrated plasticizer hydroxyls. Rates of isocyanate consumption were followed by infrared in numerous ingredient/isocyanate/catalyst mixtures. Pertinent data are summarized in Figure 17 and in the following comments:

- During a typical propellant cure cycle (e. g., 72 hours at $60^\circ C$), a significant fraction of the isocyanate groups disappears in the absence of NC when catalyst is present. This is in spite of the facts that (1) plasticizers are pretreated by passage through alumina until no measurable hydroxyls are observed by infrared, and (2) all ingredients are carefully dried, e. g., PNC and AP heated in vacuo at $60^\circ C$ for 48 hours.
- "Propellant" without NC consumes isocyanate at about the same rate as when NC is present, and the loss is nearly complete after 72 hours at $60^\circ C$ (Curves H and I).
- Subsequent addition of CaT-1000 and more catalyst to the above reacted "propellant" (Curve H) results in very rapid consumption of isocyanate (Curve J). Similar pre-reaction with trimethylsilyl reagents likewise gave no improvement.
- Results at $50^\circ C$ are analogous to those at $60^\circ C$.
- FeAA and DBTDA produce similar effects.

These effects may be assumed to be caused by one or more of the following:

- Moisture adsorbed on the solids. This may contribute to more rapid losses observed in the presence of solids but obviously does not account for the effects in purified plasticizer. While plasticizers are dried down to about 0.02 percent H_2O , AP and NC cannot generally be dried below 0.05 percent and 0.2 percent H_2O , respectively.

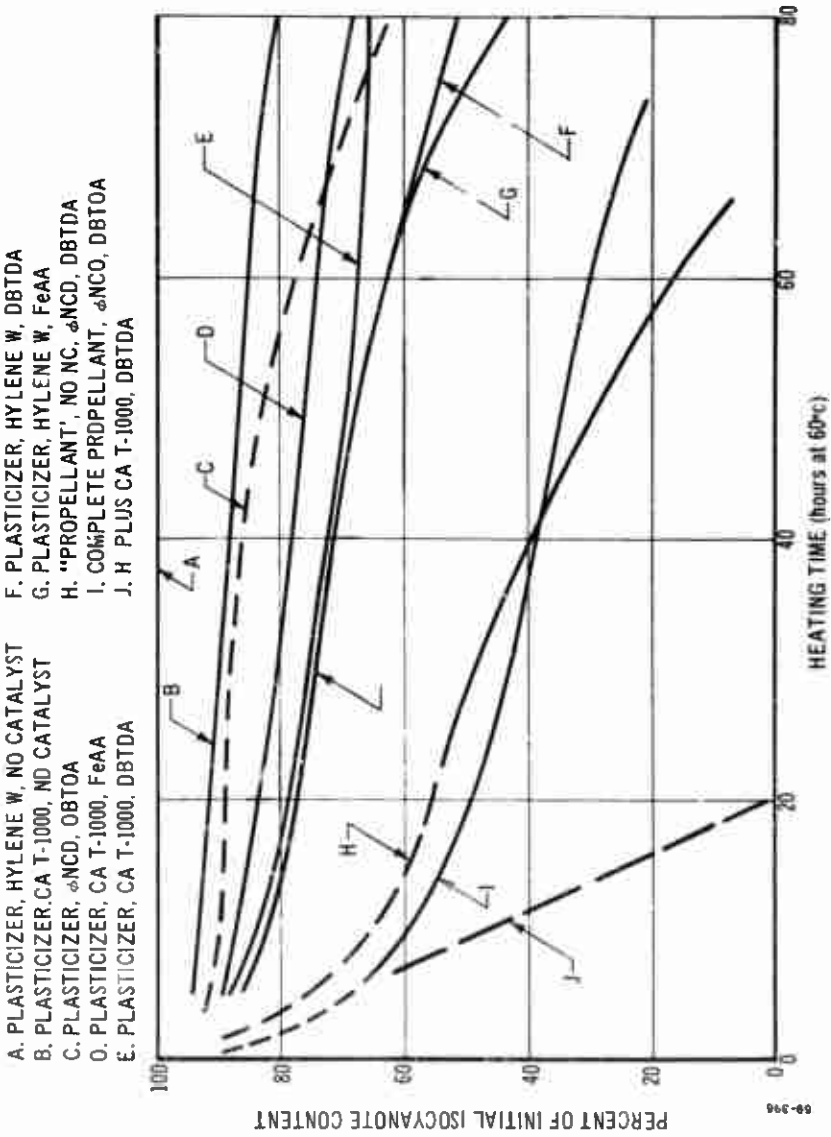


Figure 17 Isocyanate Consumption in Propellant and Ingredients (Initial Composition Corresponds to 0.1 Equivalence Ratio, Formulation d, Table I)

- Reaction with presently unknown impurities in the plasticizers. The pre-reaction experiments would seem to have minimized this possibility, however.
- Reaction with hydroxyls produced in situ by de-esterification of the nitrate esters and/or hydrolysis of urethane, perhaps catalyzed by the DBTDA and FeAA.
- Homo reactions, especially with the TDI-capped polyester (CaT-1000) which contains urethane linkages capable of allophanate formation. The literature generally reports such reactions to be slow at these temperatures although some evidence indicates catalysis of isocyanate reactions by increasing concentrations of reaction products (Ref. 5).
- The above homo reactions might include isocyanate dimerization which could be reversible and hence still leave the isocyanate available for NC crosslinking. To check this possibility, propanediol was added to a pre-reacted plasticizer/ δ NCO/DBTDA solution. The pre-reaction was conducted at 60°C for 144 hours at which time approximately 85 percent of the isocyanate absorptivity at 2270 cm^{-1} had disappeared. Upon addition of propanediol at room temperature the remaining isocyanate quickly reacted; thereafter no further reduction in diol content occurred during heating for 75 hours at 60°C. Thus the initial reaction products could not be effective for further crosslinking reactions.

Although the observed reductions of isocyanate have not been explained satisfactorily, it is believed that the isocyanate losses in plasticizers without NC are the result of reactions with small amounts of unremoved impurities and water in the propellant ingredients. These side reactions have not been examined any further since it was found that complete conversion of NC to insoluble gel could still be attained at very low weight percent crosslinker, as long as all ingredients were purified and very well dried. Under such conditions it is not too surprising that crosslinker equivalence ratios below 0.1 should be sufficient when it is considered that an average NC molecule of 55,000 molecular weight contains about 100 hydroxyl groups. Nevertheless these studies demonstrate the necessity for reproducible purification of ingredients and go far towards explaining the lack of reproducibility in much previous work upon CMDB crosslinking.

SECTION III

CONCLUSIONS AND FUTURE WORK

The studies reported herein have demonstrated that with the use of well-purified ingredients the nitrocellulose in CMDDB propellant can be crosslinked to an optimum crosslink density at crosslinker contents well below 1 percent by weight of propellant. Of the systems examined, the best ambient mechanical properties were obtained using small particle size AP and a TDI-capped polyester crosslinker at isocyanate/NC hydroxyl equivalence ratios between 0.05 and 0.1.

The greatest improvement in ambient properties due to crosslinking appears to be with a 6-percent total polymer system (Formulation e, Table I), observed values of stress and strain being about 105 psi and 23 percent respectively, corresponding to greater than 100 percent improvement in stress and 20 percent in strain over those for the corresponding uncrosslinked system*. In effect, crosslinking has elevated the ballistically interested low polymer content formulations from ones that are totally useless or marginal to ones that should be useable. On the other hand, the absolute levels of stress and particularly strain are only moderately good and further improvement would be highly desirable, especially since it can be anticipated that the above values may change for the worse at low or high temperatures.

Results to date have indicated that distinct differences in the behavior of NC can be obtained by using relatively easily prepared NC structural modifications. Although the best crosslinked propellant properties with the acetate derivative at 74°F do not differ greatly from those with standard PNC, the degree of improvement upon crosslinking the acetate is distinctly greater than it is for the NOS PNC. The high stress values obtained with the uncrosslinked phenylurethane derivative may also provide opportunity for attaining very good properties in crosslinked systems. It remains to be seen, of course, how all these comparisons fare at high and low temperatures.

Although the utilization efficiency of isocyanate crosslinkers is very low in comparison with more usual polyurethane systems, it is still several-fold better than much past work had indicated. (Ref. 6 for example). Despite the high degree of side reactions undoubtedly still present, the NC is definitely converted virtually completely to an insoluble network. This is definite indication that the crosslinking (and catalyst) molecules are able to penetrate and react throughout the PNC particles (standard material or acetate derivative). Nevertheless it still seems probable that crosslink densities will be greater around PNC particle surfaces than in their centers. Since the present acetate derivative (degree of substitution of about 2.5 nitrates and 0.2 acetates) readily crosslinks fully, it may well be that higher acetate substitution would lead to more uniform crosslinking and improved properties.

* Note again that these are crosshead values for cast microdogbones.

Obvious questions still remain to be answered and these include the following:

- Are the NC compounds presently being examined those which will produce the desired degree of mechanical property improvement in crosslinked systems over a wide temperature range? (The same derivative at higher degrees of substitution or quite different derivatives may ultimately prove more beneficial.)
- Can worthwhile improvement in mechanical properties be obtained with either standard NC or derivatives by the use of selected additives to enhance binder-solids adhesion without undue influence upon the crosslinking process?

During the ensuing quarter of this program efforts will be directed primarily towards answering the above questions as fully as time permits. As in the past, preliminary observations will be made using microdogbones tested at ambient and/or using the binder/tablet technique. Final demonstrations of property changes will involve testing of miniature JANAF's from -40 to 140°F.

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Unclassified

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Lockheed Propulsion Company P. O. Box 111 Redlands, California 92374		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE DOUBLE-BASE BINDER IMPROVEMENT			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Seventh Quarterly Technical Report covering period 1 Sept. through 30 Nov. 1968			
5. AUTHOR(S) (First name, middle initial, last name) Dr. Walter E. Baumgartner, Dr. George E. Myers			
6. REPORT DATE 6 January 1969	7a. TOTAL NO. OF PAGES 38	7b. NO. OF REFS 6	
8a. CONTRACT OR GRANT NO. F04611-67-C-0078	9a. ORIGINATOR'S REPORT NUMBER(S) LPC Report No. 829-Q-7		
b. PROJECT NO. 3148	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)		
c. PBSN 623148	AFRPL-TR-69-13		
d.			
10. DISTRIBUTION STATEMENT Qualified requesters may obtain copies of this report from DDC.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Air Force Rocket Propulsion Laboratory Research and Technology Division Air Force Systems Command United States Air Force, Edwards, Calif.	
13. ABSTRACT Investigation of means to improve the mechanical properties of slurry cast CMDB propellant has continued. Numerous small mixes have been cast into microdogbones and tested at 74°F in order to delineate the influence of several variables upon the tensile properties of isocyanate crosslinked systems. With well-dried and purified ingredients, complete incorporation of NC into cross-linked network occurs at isocyanate/NC hydroxyl ratios between 0.05 and 0.1 (prepolymer crosslinker weights well below 10 percent of the NC weight), and tensile properties also attain maximum values in the same region. This is despite the fact that isocyanate consumption occurs at about the same rate whether NC is present or not. Upon crosslinking with a TDI-capped polyester, stress is increased 50-100 percent and strain 10-15 percent as total polymer content (NC + crosslinker) is varied from 10 to 6 percent by weight of propellant (bimodal AP). Best properties are obtained with smaller particle size solids and/or with AP instead of HMX. The use of additives or precoated AP to enhance binder-solids bonding has not yet proven successful. Uncrosslinked properties using the acetate derivative of NC are all below those using standard PNC, but crosslinking improves the properties with acetate to about those with crosslinked standard PNC.			

DD FORM 1473

FORM
1 NOV 65

-37-

Unclassified

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Double-base propellants						
Slurry cast and base grain systems						
Plasticizers						
Crosslinking						
Nitrocellulose derivatives						