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AFRPL-TR-71-47

ASPC Report No. 1623-26F

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FLUOROCARBON PROPELLANT FOR CONTROLLABLE SOLIDS

By

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Aerojet Solid Propulsion Company
Sacramento, California

TECHNICAL REPORT AFRPL-TR-71-47

May 1971

Air Force Rocket Propulsion Laboratory
Research and Technology Division
Air Force Systems Command
United States Air Force
Edwards, California

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FOREWORD

This is the final report issued under Contract F04611-70-C-0040 and covers the period from 1 June 1970 through 31 March 1971. This contract was monitored by the Air Force Rocket Propulsion Laboratory, Edwards, California. The Air Force Project Officer was Capt. Paul Jendrik.

This report is Aerojet Solid Propulsion Company Report No. 1623-26F

The work was performed by the Advanced Propellants Section under the supervision of Dr. R. L. Lou, within the Advanced Propellants and Chemicals Department, Dr. A. O. Dekker, Manager. The Principal Investigator was Dr. R. S. Bruenner.

This technical report has been reviewed and is approved.

Capt. Paul Jendrik
Project Officer
Air Force Rocket Propulsion Laboratory

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GLOSSARY

AP	Ammonium perchlorate
ATMP	Ammonium tetrametaphosphate
Avg.	Average
BDNPA	Bis-dinitropropyl acetal
BDNPF	Bis-dinitropropyl formal
BI blend	Bimodal ammonium perchlorate blend consisting of 50 parts 130μ average particle size AP and 50 parts 8μ average particle size AP.
BRA-101	Ballistic additive
BuNCO	n-butylisocyanate
CA-blend	Bimodal ammonium perchlorate blend consisting of 50 parts 8μ average particle size AP and 50 parts 180μ average particle size AP.
C-1	$(NC-CH_2-CH_2-)_2N-CH_2-CHOH-CH_2OH$
CD-blend	Bimodal ammonium perchlorate blend consisting of 30 parts 8μ average particle size AP and 70 parts 130μ average particle size AP.
CF-24	Fluoro-polyester
Conc.	Concentration
CSE-15	Fluoro-polyester
CTI	Cyclohexane trisocyanate
DPT	Double plate tensile
E_{eq}	Equilibrium modulus
E_o	Initial tangent modulus
Eq.	Equivalent
Eq. wt.	Equivalent Weight
Farris Optimal Blends	Multimodal blends calculated by Farris for minimum viscosity (see also Appendix to Glossary)
F-butanol	$H\text{---}(CF_2)_3CH_2OH$

GLOSSARY (cont.)

FC-9	Proprietary fluorocarbon plasticizer
FC-122	Proprietary bonding agent
FC-156	Proprietary bonding agent
FC-190	Proprietary wetting agent
FC-194	Proprietary wetting agent
FC-199	Proprietary wetting agent
FC-201	Proprietary bonding agent
FC-202	Proprietary bonding agent
FeAA	Ferric acetylacetonate
FEFO	bis(2,2-dinitro-2-fluoroethyl)formal
Freon 113	1,1,2-trichloro-1,2,2-trifluoro-ethane
g	Gram
GMRO	Glycerine-mono-ricinoleate
GTRO	Glycerine-tri-ricinoleate
HAA	Acetylacetone
HDI	Hexamethylene diisocyanate
HS	High speed; ammonium perchlorate grind with an average particle size of 26μ.
HT	Hexanetriol
IPDI	Iso-phorone-diisocyanate
ips	Inches per second
Isonate 143L	A commercial diisocyanate
k_o	Rate constant of uncatalyzed urethane reaction
k_2	Rate constant of catalyzed urethane reaction
kdyn	Kilodyn
k_p	Kilopoise

GLOSSARY (cont.)

KEL-F	Polymeric oil, based on trifluorochlore ethylene
LHT-240	Propyleneoxide-extended hexane triol
MA	Micro-atomized, ammonium perchlorate grind with an average particle size of 6-9μ.
MAPO	Tris-methylaziridine-phosphineoxide
MS	Medium speed; ammonium perchlorate grind with an average particle size of 70μ.
ml	Milliliter (cubic centimeter)
n	Burning rate pressure exponent
-NCO	Isocyanate group
NMR	Nuclear magnetic resonance
-OH	Alcoholic hydroxyl group
opt.	Optimal
P_{DL}	Deflagration limit pressure
P-33	Carbon black
phosphate plasticizer	$OP[-O-CH_2(CF_2)_4H]_3$
PPG	Polypropyleneoxide glycol
prop.	Propellant
Quadrol	Tetra-isopropanol-ethylenediamine
R_F	Fluorocarbon group
RRD	Rotary rounded (AP)
r_{200}	Burning rate at 200 psia
Silon S	Ultrafine SiO_2
SS	Slow speed; ammonium perchlorate grind with an average particle size of 130μ.
TDI	Tolylene diisocyanate
TEA	Tri-ethanolamine

GLOSSARY (cont.)

TEPAN 3:2	Bonding agent
TMDI	Trimethylhexamethylenediisocyanate
TMP	Trimethylolpropane
TP-340	Propyleneoxide-extended trimethylolpropane
UFAP	Ultrafine AP, ammonium perchlorate grinds with average particle sizes $\leq 3\mu$
UG	Unground ammonium perchlorate with an average particle size of 180μ
$v_{2,m}$	Volume fraction of network rubber in an equilibrium-swollen elastomer
$v_{2m,u}$	Volume fraction of network rubber in an equilibrium-swollen elastomer, unplasticized.
v_o	Volume fraction of network rubber in a plasticized (including other extractables) elastomer
Viton A	
vol.	Volume
VPO	vapor phase osmometry
wt.	weight
XD	crosslink density, moles crosslinks/g binder
XIII-diisocyanate	$O_2N\text{-}N(CH_2CH_2\text{-}NCO)_2$
Zonyl E-7	Condensation product of pyromellitic anhydride and a mixture of C_5/C_7 trihydrofluoroalcohols
Zonyl E-91	ester of d,l-camphoric acid and C_7 trihydrofluoroalcohol (duPont)
+32	Ammonium perchlorate with an average particle size of 600μ
+48	Ammonium perchlorate with an average particle size of 400μ
ϵ_m	% elongation at maximum stress
Ø-NCO	phenylisocyanate
σ_m	Maximum stress, psi

APPENDIX TO GLOSSARY

GRINDS AND BLENDS OF AMMONIUM PERCHLORATE USED ON THIS PROGRAM

a. Grinds of AP:

Designation	Mean Particle Size, μ
MA (microatomized)	6-9
HS (high speed)	26
MS (medium speed)	70
SS (slow speed)	130
UG RRD (unground, rotary rounded)	180
+48 RRD (larger than 48 mesh, rotary rounded)	400
+32 RRD (larger than 32 mesh, rotary rounded)	600

b. Blends of AP:

BI	MA:SS = 50:50
CA	MA:UG = 30:70
CD	MA:SS = 30:70

Farris Optimal Blends: Multimodal blends, calculated by Farris* for minimum viscosity.

Optimal bimodal blend** : Fine: coarse = 30:70
Optimal trimodal blend**: Fine: medium: coarse = 17.5:30.5:52.0

Particle sizes are not specified other than that they should be different by about a factor of ten (or higher) for best results. For trimodal blends this is not always possible and one has to settle for smaller spacings of particle sizes.

This means that for one Farris optimal blend there is a choice of different grinds one can use. For example, an optimal bimodal blend can be composed of 30 parts MA and 70 parts UG ("CA"-blend) or 30 parts MA and 70 parts SS ("CD-blend") etc.

The same is true for optimal trimodal blends. Examples of compositions of such trimodal blends used on this program are given below:

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* R. J. Farris, Trans. Soc. Rheol. 12, 281 (1968).

** For 80 vol. % solids

APPENDIX TO GLOSSARY (cont.)

Example No.	Fine 17.5	Medium 30.5	Coarse 52.0
1	UFAP, coated (0.6μ)	MA	MS
2	UFAP (3μ)	HS	UG RRD
3	UFAP (3μ)	MS	UG RRD
4	MA	MS	UG RRD
5	MA	MS	+48 RRD
6	MA	SS	UG RRD
7	MA	SS	+48 RRD
8	MS	UG RRD	+32 RRD

The examples show that in extreme cases (#1 and 8) the very same grind (MS AP) was used as "coarse" particle size in Example #1, but as "fine" particle size in Example #8.

Aerojet Solid Propulsion Company

SUBJECT: Final Report - "Fluorocarbon Propellant for Controllable Solids"

TO: Air Force Rocket Propulsion Laboratory
Attention: Captain Paul Jendrek (RPCS)
Edwards, California

I. INTRODUCTION

This is the Final Report submitted in fulfillment of the requirements of Contract F04611-70-C-0040. This report covers the period 1 June 1970 through 31 March 1971.

II. OBJECTIVE

The objective of this program was to determine the feasibility of formulating a propellant of equivalent or superior ballistic properties with improved processing and mechanical properties for controllable systems using the new 3M fluorocarbon prepolymer FC-2202.

III. SUMMARY

TASK I: CHARACTERIZATION OF FC-2202

Analytical Data: FC-2202, lot 5, was characterized by elemental analysis, equivalent weight (through isocyanate method and NMR end group analysis), molecular weight (by VPO), average functionality, impurities (trace metals, water content), viscosity at 25 and 71°C, density at 25°C and volatiles. Significant in respect to binder quality is that the functionality of the FC-2202 is nearly exactly two.

Reactivity: Reactivity of FC-2202 with isocyanate was measured in terms of second order rate constants and compared with those of fluorobutanol and n-butanol. At the same time different catalysts were evaluated, such as ferric acetylacetonate (FeAA) and its tri- and hexafluoro derivatives and tin catalysts (dibutyltindiacetate). FC-2202 responds normally to those catalysts and systems of catalyst and moderator, e.g. FeAA and acetylacetone. In FeAA catalyzed systems with Freon 113 as a solvent, FC-2202 reacts 2-3 times faster with aliphatic or aromatic isocyanates than aliphatic alcohols. Reaction rate of FC-2202 with aliphatic isocyanate in this system is nearly three times faster than with aromatic isocyanate. In a binder system the rate was only about 1/4 of that in Freon 113.

Compatibility: Compatibility studies of FC-2202 with binder ingredients showed that crosslinkers like low molecular weight polymer triols (TP-340) are soluble. All isocyanates investigated are insoluble in FC-2202, but become soluble (most of all HDI) with certain fluorocarbon plasticizers (FC-9), with catalytic amounts of FeAA, HDI forms a clear solution with FC-2202 and FC-9 (20%).

TASK II: GUMSTOCK STUDIES

On gumstock studies with FC-2202 it was found that the highest modulus occurred at an NCO/OH equivalent ratio of 1.00, confirming the equivalent weight of FC-2202.

Unplasticized FC-2202 Binders: With unplasticized FC-2202 binder series, paralleled by corresponding PPG binder series, the characteristics of FC-2202 elastomers were determined.

The fluorocarbon binders show a higher stress relaxation, lower equilibrium moduli, lower swelling and higher extractables than the corresponding

PPG binders. Physical properties are similar with TP-340 as crosslinker, but with CTI softer elastomers are obtained with FC-2202. The binder swelling data indicated that the percentage of extractables increases with decreasing crosslink density, but is relatively higher than experienced with well-defined polyether polyurethanes. Also, $v_{2,m}$ values are unusually high. If stress relaxation as well as extractables, are plotted as function of actual crosslink density (as expressed through equilibrium modulus), they are represented by a single curve for both FC-2202 and PPG elastomers. The only exception is the stress relaxation curve for CTI-crosslinked FC-2202, which does not coincide with the curves for TP-340 crosslinked FC-2202 and PPG binders.

Plasticized FC-2202 Binders: Two fluorocarbon plasticizers were evaluated as cosolvents for isocyanates. One, a fluorocarbon phosphate, was ruled out, because it deactivated the curing catalysts (except tin catalysts) and was exuded from the cured binder even at lower concentrations, which was not the case for the other plasticizer (FC-9) at 20%.

From these studies, an FC-2202 elastomer plasticized with 20% FC-9, crosslinked with TP-340 and cured with HDI (FeAA/HAA as the catalyst system) emerged as the most promising propellant binder.

TASK III: PROPELLANT STUDIES

75 Vol.% Checkpoint: The first propellants made contained only 75 vol.% AP, and served as a checkpoint. It was found that viscosity requirements could be met only with propellants containing TP-340 as crosslinker, but not with CTI. The proper NCO/OH ratio to use in a propellant was also 1.00. Further increase of solids was, however, only possible through the use of wetting agents or bonding agents with wetting properties.

Wetting Agents: A series of excellent wetting agents was available, but all interfered with the cure reaction. Others became inefficient in the last stages of processing. In combination with bonding agents they lost their wetting properties completely.

Bonding Agents: The solution to the processing problem was found with bonding agents, which, during the last stages of mixing, act like wetting agents, they also improve the physical properties of the cured propellant. At 82% solids viscosity requirements were easily met with a 40:30:30/MA:SS:+48 blend.

Optimal AP Blends and Solids Loadings: Further improvements in processing were possible by using proper bimodal and trimodal AP blends, which allowed to make castable propellants even at 86% solids (83.7 vol.%). Without bonding agents, however, viscosity requirements could not be met with these blends at 82% solids.

Ballistic Properties: Burning rates obtained first with epoxy-resin coated propellant strands indicated that rather wide variations of solid loadings and particle size of AP produced only minor changes of slope and burning rate. The use of ballistic additives like BRA-101, however, raised the pressure exponent to 0.80. The validity of these results is questionable because of faster burning at the propellant/restriction interface.

Burning rate strands with Viton A coating did not sustain burning at 200 psia. The surface conditions of the recovered strands indicate that the burning surface regression is more uniform with the inert Viton-A restriction. With Viton A/epoxide coatings, solid strands burning rate data could be obtained, which showed that r_{200} is well below the specified limit for propellants with coarser (Farris optimal trimodal blend, MA/SS/+48) as well as with finer (CD-blend, MA/SS) particle size AP. The data indicate a very high slope (close to 1) for the propellant with the coarser blend in contrast to the one with the finer blend (n = 0.8). It is felt, however, that the strand data for this type of propellant might not represent the burning rate in a motor. This probably also applies to P_{DL} data. P_{DL} tests at a depressurization rate of 7 psi/sec showed extinguishment of propellants to occur at 230-250 psig. The tests used 1/2 inch diameter unrestricted strands.

Adjustments of Propellant Composition for Optimal Viscosity and Physical Properties: With optimal bimodal AP blend (CD) and crosslink densities between 3.25×10^{-5} to 3.5×10^{-5} moles crosslinker/g binder both viscosity and physical properties requirements could be met at 82% solids loading.

With optimal trimodal blends both requirements could not be met at the same time. Only with the use of HDI/TDI mixtures (ratios not lower than 60:40) it became possible to improve physical properties and still stay below the viscosity limits, though, inevitably, longer cure times were required. An HDI/TDI ratio as high as 80:20 was selected for optimal balance of mechanical properties and viscosity.

TASK IV: DEMONSTRATION PHASE

Based on the formulation studies, a propellant with 82% trimodal AP (Farris optimal, MA:SS:+48 RRD = 17.5:30.5:52) and a mixture of HDI/TDI (80:20) as curative was singled out for scale-up. First a pilot batch of 400g of propellant was made to learn about possible scale-up effects. The only change necessary was an increase in catalyst concentration for the three follow-up 1800g batches. Potlife measured as the time to reach the specified viscosity was about 10 hrs for a shear of 30 Kdynes/cm^2 and 12 hrs for 5 Kdynes/cm^2 with a spread of 1-1/4 to 1-1/2 hr at the specified viscosity.

The physical properties as an average over all three batches were: $\bar{\sigma}_m = 91.4$, $\bar{\varepsilon}_m = 38.0\%$ and $\bar{E}_o = 658$. Standard deviation from the mean value was $\pm 10\%$ for $\bar{\varepsilon}_m$, but higher for $\bar{\sigma}_m$ and $\bar{E}_o$.

Burning rates at 200 psia measured with 1/2" x 1/2" x 3" strands, coated with Viton A and epoxy-resin were 0.076 ips and the slope 1.00. Experimental propellant density was 1.886 g/ml, which is only slightly different from the calculated one (1.883 g/ml), indicating that no substantial cure shrinkage occurred.

TASK V: PROPELLANT LINER BOND

Five different liners were tested with FC-2202 propellant as to their bond strength. One liner was based on polyether polyurethane, the other four on FC-2202 elastomers. The best properties were obtained with a TP-340/FC-156/FC-9/FC-2202/HDI/FeAA/HAA liner containing 30% iron oxide as a filler. Bond strength with double-plate tensile specimens was 73.4 psi without and 92.4 psi with washcoat, and with peel specimens it was 12.6 and 13.3 psi, respectively.

IV. TECHNICAL DISCUSSION

A. TASK I: CHARACTERIZATION OF FC-2202, LOT 5.

1. Analytical Data:

Data furnished by 3M comprise the elemental analysis and the equivalent weight determined by the phenylisocyanate method (=1032). On this program, the equivalent weight was determined by an end group ($-CH_2OH$) analysis with NMR by measuring the methylene proton peak, using $CHCl_3$ as an internal standard, and comparing the -OH proton peak with the methylene proton peak, thus arriving at an equivalent weight of 1027. Also, the molecular weight of the material was obtained by VPO with Freon 113 as a solvent, yielding a value of 2051. These results give an average functionality of nearly exactly 2.0. If by the nature of the FC-2202 synthesis functionalities higher than two for individual molecules can be excluded, this result would indicate that there is essentially no functionality distribution, but only a strict difunctionality.

The reported lot to lot variation of FC-2202 reactivity(1) could have been caused by trace metals, however, in Lot 5 no trace metals were detected by emission spectrographic analysis.

When the FC-2202 was heated to 130°C at 0.5mm Hg some reflux was noticed, which could be distilled over and amounted to about 6%. From the IR spectra of distillate and residue (Figure 1) it can be seen that the C-H as well as the O-H peaks are stronger with the distillate indicating that the distillate is nothing but low molecular weight FC-2202.

---

(1) Hercules Report on Contract F04611-69-C-0063.

TABLE 1

CHARACTERIZATION OF FC-2202, LOT 5

1. Elemental Analysis*

C	20.2%
F	60.1%
H	0.3%
O (by difference)	19.4%

2. Equivalent Weight: (a) by isocyanate method*: 1032
   (b) by NMR end group analysis: 1027
3. Molecular weight by VPO: 2051
4. Average functionality by molecular weight/equivalent weight: 2.0
5. Impurities: (a) Trace metals by emission spectrography: None
   (b) Water by Karl Fischer analysis: 0.015% (≈ 2 equiv. %)
6. Viscosity at 25°C: 89 cp
   71°C: 17.1 cp
7. Density at 25°C: 1.807 g/ml
8. Volatiles at 0.5 mm Hg and 100°C for 1 hr: 0.63%

---

* Data supplied by 3M Co.

Other routine tests run with FC-2202 include measurements of density, viscosity at ambient and elevated temperature,and water content. A summary of all pertinent data is found in Table 1.

2. Reactivity of FC-2202

The reactivity of FC-2202, Lot 5, was evaluated with the proposed FeAA/HAA (see glossary for description) and other catalyst systems. The reactions were run in Freon 113 with FC-2202 (0.2N) and butylisocyanate (BuNCO), 0.1N. Concentration of -NCO was measured by the absorbance of the NCO band at 2272 cm^{-1}. Reactivities are expressed in terms of customary second order rate constants. However, it should be kept in mind that they are not real constants since the reaction is not true second order and may change at higher extents of reaction.(2-4) Figure 2 presents the results in graphic form. It shows that the system behaves essentially like others with aliphatic alcohols which can be described by a general equation:(2)

$$k_2 = k_o + A \{ \sqrt{([HAA] + a)^2 + 4ac} - ([HAA] + a)\}$$

where k_2 = second order rate constant.

k_o = rate constant of the uncatalyzed reaction.

[HAA] = acetylacetone concentration.

c = Ferric acetylacetonate (FeAA) concentration.

A and a = constants, characteristic for the given system.

---

(2) R. S. Bruenner and A. E. Oberth, J. Org. Chem. 31, 887 (1966)
(3) A. E. Oberth and R. S. Bruenner, J. Phys. Chem. 72, 845 (1968)
(4) A. E. Oberth and R. S. Bruenner, I & EC Fundamentals, 8, 383 (1969)

TABLE 2

PSEUDO SECOND ORDER RATE CONSTANTS, k_2, OF THE URETHANE REACTION IN FREON 113 AT $\approx$ 27°C

Alcohol (0.2N)	Isocyanate (0.1N)	FeAA Conc.	k_2, eq^{-1} min^{-1} 1
FC-2202	BuNCO	-	0.001 to 0.002
FC-2202	ϕ-NCO	-	0.004
F-butanol*	ϕ-NCO	-	0.002
n-butanol	ϕ-NCO	-	0.031
FC-2202	BuNCO	1×10^{-4} M	1.1
F-butanol	BuNCO	1×10^{-4} M	1.0
n-butanol	BuNCO	1×10^{-4} M	0.4
FC-2202	ϕ-NCO	1×10^{-4} M	0.4
F-butanol	ϕ-NCO	1×10^{-4} M	0.6
n-butanol	ϕ-NCO	1×10^{-4} M	0.2

---

* $H(CF_2)_3CH_2OH$

From the point of intersection of the experimental curves, the constants A and a of the system were computed. With $k_o = 0.25 \times 10^{-3}$, $A = 8.885 \times 10^{3}$ and $a = 0.83 \times 10^{-4}$ the solid curves in Figure 2 were calculated, which represent all experimental points fairly well.

The FeAA/HAA system is therefore applicable to the FC-2202/isocyanate reaction. In general the catalyzed reaction of alcohols $R_F - CH_2OH$ with isocyanates seems to be even faster than with primary aliphatic alcohols with both aliphatic and aromatic isocyanates as shown in Table 2, but the uncatalyzed rate, at least with phenylisocyanate, is considerably lower than the one with n-butanol.

Rates were also run in a system, which comes close to an actual binder composition, namely FC-2202, HDI (OH/NCO = 2, $C_{OH} = 1.06$ N, $C_{NCO} = 0.53$N) and 30 wt. % of $H_9C_4\text{-}CH(C_2H_5)\text{-}COO\text{-}CH_2\text{-}(CF_2)_8H$ (plasticizer FC-9). This mixture forms a clear solution at room temperature without prereaction. With 0.25×10^{-4} M FeAA k_2 was 0.13 eq^{-1} min^{-1} 1, which is only 1/4 of that found in Freon.

Attempts were also made to obtain rates by measuring the change of the refractive index (n) with increasing extent of reaction. However, Δn between the initial system and the final system was so small (=0.0030) that accurate measurements were not possible.

Catalyst evaluation with FC-2202 was continued with catalysts other than ferric acetylacetonate (FeAA) under the same conditions (BuNCO 0.1N and FC-2202 0.2N in Freon 113, catalyst concentration 5 x 10^{-5}M).

Trifluoro-FeAA and hexafluoro-FeAA were about as effective as FeAA (k_2 for both was 0.5, for FeAA 0.6), dibutyltindiacetate was somewhat slower (k_2 = 0.2) at this concentration.

It was tried to determine the reaction rate of CTI with FC-2202, but no common solvent could be found. Instead, hexafluorobutanol was used with CTI in benzene as a common solvent. In this solvent the rate constant was 0.5 and about twice the value for n-butanol under identical conditions. Further catalyst evaluations were done in connection with gumstock studies.

3. Compatibility Studies

The unique solubility characteristics of FC-2202 required a more extensive study of its compatibility with other binder ingredients as well as with solvents. Only Freon 113 has been found to be a good solvent,which is required to be completely miscible with FC-2202. Some of the solvents, however, seem to be partially soluble in FC-2202, whereas the solubility of FC-2202 in these solvents is practically nil. As binder ingredients, the compounds investigated were called soluble if about 10-20% would dissolve in FC-2202 regardless of the existence of a miscibility gap. Results are summarized in Table 3 with some typical examples listed in each group. It is seen that all ingredients proposed for binders are soluble except the isocyanates. Added to this list are some triols, usable as crosslinkers, like TP-340, which has an equivalent weight of only 101. In Table 4 some prospective plasticizers are found with their compatibility (+ for positive) and their effectiveness as cosolvents for HDI as well as their densities listed. It seems that only plasticizer #1 (FC-9) and #2 (phosphate) are usable.

B. TASK II: GUMSTOCK STUDIES WITH FC-2202

1. Equivalent Weight by Maximum Modulus

First, a binder series was made to check on the equivalent weight and/or to find out whether side reactions would occur which would consume some isocyanate. Table 4 shows the composition of the binder with which NCO/OH ratios of 0.95, 1.00 and 1.05 were used.* Judging from both the modulus and the swelling data, the optimum ratio is approximately 1.00 indicating negligible side reactions and also confirming the equivalent weight.

For further information on FC-2202, evaluation of crosslinkers and correlation between minibone samples and regular Instron bars, four series of binders were made with varying crosslinker concentration in each series and no plasticizer.*

(1) FC-2202/HDI, crosslinker CTI, catalyst FeAA

(2) FC-2202/HDI, crosslinker TP-340, catalyst FeAA

(3) PPG/HDI, crosslinker CTI, catalyst FeAA

(4) PPG/HDI, crosslinker TP-340, catalyst FeAA

---

* After addition of the catalyst the ingredients form a clear solution on heating to about 60°C. After this the liquid binder is degassed and cast in minibone molds, vibrated and cured at 60°C.

Without plasticizer it took a few minutes at 70-80°C for the binder to become homogeneous.

TABLE 3

COMPATIBILITY OF DIFFERENT TYPES OF COMPOUNDS WITH FC-2202

a. Solvents: None but Freon 113

b. Cure Catalysts: FeAA, dibutyltindilaurate (very sparingly), soluble

c. Curatives (isocyanates): all insoluble

Examples: HDI, TDI, TMDI, IPDI, XIII-diisocyanate, CTI

d. Triols: glycerine, HT, TMP, GMRO, GTRO, TEA, fluorinated triols insoluble:

LHT-240, TP-340 and similar ones (e.g. quadrol), sufficiently soluble

e. Bonding Agents: C-1 insoluble
TEPAN 3:2 soluble

f. Wetting Agents: FC-190 soluble

g. Other Prepolymers: fluorinated prepolymers (CSE-15, CF-24) not soluble at 30%.
PPG soluble to a certain extent

h. Other Compounds: MAPO, tetrabutyloxamide, tetramethylurea, dimethylformamide, dibutylformamide, H_3C-NH-CH_2CH_2-CN soluble to a certain extent.

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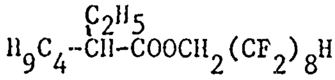
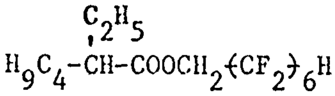
Table 4

COMPATIBILITY OF PLASTICIZERS WITH FC-2202 AND THEIR EFFECTIVENESS AS COSOLVENTS FOR HDI

No.	Plasticizer	Solubility of Plasticizer: Ambient Temp.	Solubility of Plasticizer: Elevated Temp.	Solubility of HDI in FC-2202 + 30% Plasticizer: Ambient Temp.	Solubility of HDI in FC-2202 + 30% Plasticizer: Elevated Temp.	Approx. Density
1	FC-9,  $H_9C_4\text{-}\overset{C_2H_5}{CH}\text{-}COOCH_2(CF_2)_8H$	+	+	-	+ ∿50°C	1.47
2	$OP[-OCH_2(CF_2)_4H]_3$	+	+	-	+ ∿60°C	1.70
3	FC-7,  $H_9C_4\text{-}\overset{C_2H_5}{CH}\text{-}COOCH_2(CF_2)_6H$	+	+	-	-	1.365
4	3M's L-2347	+	+	-	-	1.82
5	3M's L-2348	-	+ ∿40°C	-	+ ∿40°C	1.54
6	$[(CH_2)_2COOCH_2(CF_2)_6H]_2$	-	+ "	-	+ ∿50-60°C	1.69
7	$[CH_2\text{-}COOCH_2(CF_2)_6H]_2$	-	+ "	-	+ ∿60°C	1.73
8	Zonyl E-91	-	+ "	-	+ ∿60°C	1.60
9	Zonyl E-7	-	- "	-	-	1.75
10	FEFO	-	- "	-	-	1.60
11	BDNPA/F	-	- "	-	-	1.36-1.415
12	KEL-F, Grade KF-3	-	+ ∿60°C	-	-	

The PPG series were made for comparison with the FC-2202 binders and for the minibone/Instron bar correlation. As seen from Table 6, the latter correlation holds fairly well and shows that meaningful data can be derived from minibone samples.

Above binder series yielded information about stress relaxation, equilibrium modulus and other mechanical properties, crosslink densities, extractables and swelling, and type of prepolymer. These results will be discussed in the following.

2. Stress Relaxation

Relative stress decay* usually increases with increasing chain length between crosslinks. If significant amounts of dangling chains (attached to the elastomer network) are present, the relative stress decay decreases and thus helps to identify such structures.

In Figure 3 the stress decay for above binders is shown as function of the molecular weight between crosslinks, which is proportional to the chain length between branch points as long as no dangling chains are present (calculated from the crosslinker concentration used). Each binder type (FC-2202 and PPG) is represented by a single curve, regardless of crosslinker (CTI or TP-340). Since the PPG is essentially difunctional with only very small amounts of monofunctional material, it can be assumed that the FC-2202 is also free from monofunctional species,

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* Measured as $\frac{\sigma_1 - \sigma_{20}}{\sigma_1}$ x 100, where σ_1 and σ_{20} are the stresses after 1 min and 20 min respectively at about 20% elongation.

TABLE 5

EFFECT OF DIFFERENT NCO/OH RATIOS ON BINDER PROPERTIES

Composition of Binder with NCO/OH = 1.00		
	CTI	1.06%
	HDI	4.08%
	FC-2202	64.86%
	FC-9	30.00%
	FeAA	1.5×10^{-3}%

	NCO/OH	σ_m, psi	ε_m, %	E_o, psi	v_{2m}*
Physical Properties	0.95	3.5	825%	0.5	0.197
	1.00	17.6	480%	8.5	0.278
	1.05	12.0	365%	3.7	0.275

---

* $$v_{2,m} = \frac{\text{vol. of network rubber}}{\text{vol. of network rubber + vol. of solvent}}$$

at equilibrium swelling.

TABLE 6

COMPARISON OF MINIBONES WITH REGULAR INSTRON BARS

Binder	Moles x-linker per g binder	Sample	E_o	σ_m	ε_m	Stress Decay, %
TP-340/HDI/PPG	0.25×10^{-4}	Minibone*	31	77**	1185**	30.6
	0.25×10^{-4}	Regular	34	44	796	26.7
	0.5×10^{-4}	Minibone*	61	90	445	8.9
	0.5×10^{-4}	Regular	57	67	437	10.7
	1.0×10^{-4}	Minibone*	104	71.5	140	2.4
	1.0×10^{-4}	Regular	109	65	135	2.9
CTI/HDI/PPG	0.25×10^{-4}	Minibone	21	--	--	38
	0.25×10^{-4}	Regular	21	34	770	29
	0.5×10^{-4}	Minibone	77	--	--	9.6
	0.5×10^{-4}	Regular	52	61	228	6.1
	1.0×10^{-4}	Minibone	110	--	--	2.2
	1.0×10^{-4}	Regular	82	52	99	2.3
	1.5×10^{-4}	Minibone	174	--	--	1.5
	1.5×10^{-4}	Regular	174	70	65	1.0

---

* σ_m and ε_m measured after extraction of solubles with benzene and redrying.

** Bar slipped through jig.

judging from the even higher relative stress relaxation (which may be one of the pecularities of the fluorocarbon binders). If monofunctional and zero-functional species are practically nonexistent in FC-2202, then there is also no functionality distribution, because the average functionality is two.

If stress relaxation data would be plotted vs. the actual crosslink density or the equilibrium modulus (corrected for extractables(5)), which is proportional to it, a single curve should result. As shown in Figure 4 this is actually true for the two PPG crosslink density series and for the FC-2202 elastomer crosslinked with TP-340. The CTI crosslinked FC-2202 elastomers again are different; their data points fall on a separate curve. This difference was also found otherwise (see physical properties) and may be connected with the initial insolubility of the CTI crosslinker in FC-2202, which can change the network structure, in particular the distribution of chain lengths between crosslinks.

3. Equilibrium Modulus

According to rubber theory the equilibrium modulus is proportional to crosslink density, or concentration of crosslinker in case of exact stoichiometry, complete reaction and difunctionality of the prepolymer. If the extrapolated curve does not pass through the origin, the average functionality is likely to be different from two. The curves for the two PPG binders in Figure 5 are fairly linear at higher crosslinker concentrations and the extrapolated linear part intersects the abscissa near the origin. However, the curves for the FC-2202 binders are quite

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(5) A. E. Oberth and R. S. Bruenner, J. Pol. Sci., Part A-2, 8, 605 (1970).

different; not only is their slope much lower, but they are also not linear, which does not allow a reliable extrapolation.

This discrepancy becomes even more obvious, when the theoretical crosslink density (based on concentration of crosslinker) is plotted against the crosslink density as derived from equilibrium modulus and corrected for extractables,(5) Figure 6. The dashed line in Figure 6 corresponds to the ideal correlation. It is known that at higher crosslinker concentration deviations occur like those seen for PPG binders, but the strong deviations found with FC-2202 binders are quite unusual; such differences might be more fundamental and point to some effects which are not considered in simple rubber theory, and which are related to the nature of the fluorocarbon chains.

4. Extractables

Even in most carefully prepared polyurethane elastomers some extractables are found, i.e., material which is not part of the elastomer network. At low crosslinker concentration the extractables increase sharply as seen in Figure 7. Again PPG and FC-2202 elastomers are different, with higher percentages of extractables found with the latter, but the two FC-2202 elastomers show differences as well; the CTI crosslinked rubber has more extractables than the TP-340 crosslinked one. In PPG binders the type of crosslinker apparently does not make any difference within experimental error.

Plotting extractables vs. the actual crosslink density or the proportional equilibrium modulus (corrected for extractables) would probably be more meaningful. As shown in Figure 8, such a plot results indeed in a single curve for all four polymer series and thus allows a unified presentation of data.

5. Swelling

The rubber fraction in elastomers swollen to equilibrium, v_2, is also a function of crosslink density, but, in addition, of the swelling agent (solvent), which is characterized by Huggins interaction parameter μ. From equilibrium modulus and v_2 this parameter can be evaluated; for PPG binders with benzene as solvent μ is about 0.3. Its value increases with less swelling solvents. Figure 9 shows that v_2 values for PPG binders are slightly lower from what is expected for the indicated crosslinker concentration and Huggins parameter.

If one assumes that the relation holds for FC-2202 binders with Freon 113 as a swelling agent, then abnormally high Huggins parameters are calculated, because the v_2 values are unusually high. It is not clear whether this is a pecularity of the FC-2202 elastomer, of the solvent or both. Swelling of the same PPG elastomers in Freon 113 also yields very high v_2 values (Table 7). PPG itself and the chain extended (with HDI) but not crosslinked polymer are both soluble in Freon 113.

The swelling curve for TP-340 crosslinked FC-2202 does not coincide with that of the CTI crosslinked one; however, this difference disappears if the v_2 values are corrected for extractables.*

TABLE 7

SWELLING OF FC-2202 AND PPG BINDERS

v_2 values in different solvents

		Moles Crosslinker/g Binder			
		0.25×10^{-4}	0.5×10^{-4}	1.0×10^{-4}	1.5×10^{-4}
Binder	Solvent	v_2	v_2	v_2	v_2
CTI/HDI/FC-2202	Freon 113	0.14	0.23	0.36	0.41
CTI/HDI/PPG	Freon 113	0.23	0.31	0.35	0.42
CTI/HDI/PPG	Benzene	0.06	0.10	0.13	0.17

6. Physical Properties

Initial modulus, tensile and elongation at break were determined with all four binder series as listed in Table 8.

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* In order to obtain the v_2 value of the unplasticized (i.e., no extractables) elastomer (= $v_{2,u}$) one has to divide $v_{2,p}$ (v_2 value of the elastomer with plasticizer or extractables, which is otherwise designated as uncorrected v_2) by v_o, which is the elastomeric network volume fraction in the unswollen, original elastomer, still containing the extractables.(5)

In general, it can be said that the TP-340 crosslinked binders (FC-2202 and PPG) are quite similar, with the FC-2202 being somewhat superior at higher crosslink densities, whereas the CTI crosslinked FC-2202 is considerably softer than its PPG counterpart. Both PPG binders though are not too different. The explanation for the different properties of the CTI crosslinked FC-2202 binder may be found in its initial insolubility in FC-2202, so that chain extension is favored over crosslinking in the early stage of cure.

7. Plasticized FC-2202 Binder

For practical purposes the FC-2202 binders need some plasticizer as cosolvent for the curatives. Earlier screening showed that the FC-9 plasticizer and the phosphate $OP[-OCH_2-(CF_2)_4H]_3$ are best suited for this purpose. However, if used at a concentration of 30%, some plasticizer was exuded from the binder regardless of crosslinker, but at no time the binder appeared turbid, i.e., no phase separation occurred as was also shown with a plasticized binder containing FC-2202, HDI (NCO/OH = 1.0) and 30% plasticizer (FC-9) but no crosslinker. This binder never separated into two phases, but remained clear and homogeneous. However, exudation increased with increasing crosslinking. With a concentration series of FC-9 plasticizer in a CTI/HDI/FC-2202 binder it was found that very slight exudation still occurred at 25% but none at all at 20% plasticizer concentration. At the same time the moduli of these plasticized binders were determined (see Table 9).

TABLE 8

PHYSICAL PROPERTIES OF FC-2202 AND PPG BINDERS

Binder	Moles crosslinker per g binder	E_o	σ_m	ε_m
TP-340/HDI/PPG	0.25×10^{-4}	31	77	1185
TP-340/HDI/FC-2202*	0.5×10^{-4}	50	36	314
TP-340/HDI/PPG	0.5×10^{-4}	61	90	445
TP-340/HDI/FC-2202*	1.0×10^{-4}	84	67	159
TP-340/HDI/PPG	1.0×10^{-4}	104	71.5	140
TP 340/HDI/FC-2202*	1.5×10^{-4}	154	108	133
TP-340/HDI/PPG	1.5×10^{-4}	162	76	81
CTI/HDI/PPG	0.25×10^{-4}	21	34	770
CTI/HDI/FC-2202*	0.5×10^{-4}	10.5	35	863
CTI/HDI/PPG	0.5×10^{-4}	52	61	228
CTI/HDI/FC-2202*	1.0×10^{-4}	38	14	280
CTI/HDI/PPG	1.0×10^{-4}	82	52	99
CTI/HDI/FC-2202*	1.5×10^{-4}	50	17	231
CTI/HDI/PPG	1.5×10^{-4}	174	70	65

* Properties of the FC-2202 binders have been measured after extraction of solubles with Freon 113 and redrying.

TABLE 9

MODULI OF PLASTICIZED FC-2202 BINDERS

Binder: CTI/HDI/FC-2202/Plasticizer FC-9

The binder (without the plasticizer) contained always the same amount of crosslinker (0.5 x 10^{-4} moles/g binder)

% Plasticizer (FC-9)	E_o	E_{equib}
10	9.0	6.2
20	5.5	4.5
30	2.9	2.2

TABLE 10

CROSSLINK DENSITY SERIES WITH A PLASTICIZED (30% FC-9) FC-2202 BINDER

TP-340/HDI/FC-2202/FC-9 (30%)

XD, moles/g	E_o, psi	v_{2m}
5 x 10^{-5}	5	0.234
10 x 10^{-5}	46	0.359
15 x 10^{-5}	57	0.385

Similar binders with either CTI or TP-340 as crosslinker (XD = 5 x 10^{-5} moles/g) were prepared using phosphate plasticizer (30%, #2 of Table 4). The moduli measured for these binders are shown in Table 11:

TABLE 11

	Binder	XD, moles/g	E_o	E_{eq}	% Stress Decay at 20% Elongation
1.	CTI/HDI/FC-2202/ Phosphate Plast.	5×10^{-5}	7.0	2.3	20.8
2.	TP-340/HDI/FC-2202/ Phosphate Plast.	5×10^{-5}	5.3	1.6	30.4

Very slight exudation was still noticed with the phosphate plasticizer at 20% concentration. The phosphate plasticized binders were cured with dibutyltindiacetate as a catalyst, since FeAA, trifluoro- and hexafluoro-FeAA are deactivated by this plasticizer.

Two other fluorocarbon plasticizers (available through a fluorocarbon synthesis program) with a branched structure, were also exuded at 30% concentration.

After it was established that FC-9 will not be exuded at the 20% level two more crosslinker series were made with CTI and TP-340 as crosslinkers to determine the physical properties, particularly modulus, of the plasticized binders for selection as propellant binders. The test results are listed in Table 12 and graphically presented in Figure 10.

From these data a crosslinker concentration of 0.55×10^{-4} to 0.60×10^{-4} for CTI and 0.40×10^{-4} to 0.50×10^{-4} moles/g for TP-340 is required for a target modulus of about 10 psi.

In preparing these binders it was noticed that in presence of the cure catalyst (FeAA, conc. 8×10^{-8} M/g binder) the mixture became instantaneously homogeneous upon slight heating (especially the TP-340 system); also, the TP-340 crosslinked elastomers were all completely transparent, whereas a slight turbidity was noticed in the CTI binders, especially at higher crosslinker concentration.

Eventually a formulation was selected to study gel time as a function of FeAA/HAA concentration. It consisted of TP-340/HDI/FC-2202/FC-9 (20%), with a crosslinker concentration of 0.5×10^{-4} moles/g binder. A constant molar ratio of FeAA:HAA (1:1) was used throughout. The results are presented in Figure 11.

TABLE 12

PHYSICAL PROPERTIES OF FC-2202 BINDERS WITH DIFFERENT CROSSLINK DENSITIES AND 20% PLASTICIZER (FC-9)

Binder	Moles crosslinker per g binder	E_o	$E_{eq.}$	% Stress Decay	σ_m	ε_m
CTI/HDI/FC-2202/ 20% FC-9	0.35×10^{-4}	1.6	0.5	29.5	--	--
	0.50×10^{-4}	6.9	4.8	12.2	--	--
	0.65×10^{-4}	16.8	14.3	3.7	--	--
	0.80×10^{-4}	29.7	28.0	1.9	--	--
TP-340/HDI/ FC-2202/20% FC-9	0.35×10^{-4}	1.4	0.9	25.9	7.2	976
	0.50×10^{-4}	18.8	16.5	2.5	27.3	384
	0.65×10^{-4}	22.0	20.7	1.9	32.6	347

C. TASK III: PROPELLANT STUDIES

1. 75 vol.% Solids Loading Checkpoint

For the 75 vol. % solids loading checkpoint both TP-340 and CTI crosslinked FC-2202 polymers, plasticized with 20 wt.% FC-9, were used as binders. Both binders were made with 0.5 x 10^{-4} moles crosslinker/g binder. The NCO/OH ratio was raised to 1.03. The AP blend selected consisted of 40 parts MA and 30 parts each of SS and +48 AP. With a calculated binder density of 1.65, the propellant contained 78.2 wt.% total AP, corresponding to 75 vol.%.

It was found that the FeAA/HAA concentration had to be adjusted, due to the incorporation of AP, and an FeAA concentration of 0.005 wt.% in propellant and an HAA concentration of 0.002 wt.% were eventually selected.

To obtain reliable Rotovisco data, a minimum of 50g propellant was required. Since other propellants have been measured with at least 100g, and also because the spindle used had to be modified, a test propellant was made to correlate both readings; this propellant consisted of a PPG/TP-340/HDI propellant with 75 vol.% of AP (same blend as used for FC-2202 propellant); 0.3% of a wetting agent was added for better processing. The correlation factor found was close to unity. After the viscosity measurements with the Rotovisco were made, the FC-2202 propellants were cured and minibars were cut to determine physical properties. It was, however, noticed that these samples cured somewhat softer than samples which were retained from the propellant batch and cured separately.

The mix procedure used with these propellants was as follows: all binder ingredients (except isocyanate, FeAA and HAA) were stirred so that a homogeneous solution resulted. AP was mixed in under vacuum successively, i.e., first MA, then SS and finally +48. The temperature was maintained at 135°F, but at the end of the mix cycle it was dropped to 110°F. Then the isocyanate was added and mixed in for 3 min. at ambient pressure. After this the FeAA was added (solution in Freon 113), and finally the HAA (solution in Freon 113), both mixed in under vacuum. The propellant was then cast.

Propellant #1:	FC-2202/TP-340/FC-9/HDI Binder
Propellant #2:	FC-2202/TP-340/FC-9/HDI binder, but with 0.12% TEPAN (bonding agent)
Propellant #3:	FC-2202/CTI/FC-9/HDI Binder with 0.12% TEPAN (bonding agent)

Propellants #1 and 2 were both fluid, castable propellants, whereas #3, though a coherent propellant, was much thicker, and was not submitted for Rotovisco viscosity measurements.

Viscosity data from propellants #1 and 2 as obtained by Rotovisco measurements as function of time are shown in Figure 12 for shear stresses of 5000 and 30,000 dynes/cm^2. Taking 25 kpoise at 30,000 dynes/cm^2 and 50 kpoise at 5000 dynes/cm^2 as the limiting viscosity for potlife, it is seen that propellant #1 had a potlife between 6 and 7 hrs. Propellant #2, however, showed a very rapid viscosity buildup and correspondingly short potlife. With all three propellants cure was satisfactory and physical properties data have been obtained, which are presented in Table 13.

TABLE 13

PHYSICAL PROPERTIES OF FC-2202 PROPELLANTS WITH 75 VOL.% SOLIDS

				Properties at 77°F					
				Average of 3 Minibars			Optimal Properties		
No.	wt. % AP	Crosslinker	Additive	σ_m	ε_m	E_o	σ_m	ε_m	E_o
1	78.2	TP-340	--	39.5	36.1	139	41.1	37.3	144
2	78.2	TP-340	TEPAN	43.8	34.5	186	40.4	36.1	166
3	78.2	CTI	TEPAN	81.6	30.6	436	92.7	32.2	401

These properties (low tensile) indicated that further adjustments were needed, particulary with the NCO/OH ratio.

The TEPAN bonding agent also was not very effective in this propellant. CTI was no longer used in the following propellants, because of the high propellant viscosity.

2. Higher Solids Propellants

Notwithstanding the need for further adjustments, propellants were now made with 82% solids, using the same oxidizer blend as before (MA:SS:+48 = 40:30:30) and binder as for propellant #1 (NCO/OH = 1.03).

Two batches were made, one was subjected to Rotovisco viscosity testing, the other was left undisturbed to find out quantitatively which effect this would have on the properties of the cured propellant.

The physical properties in this case were not different from the other propellant, in fact they showed that reproducibility was rather good.

TABLE 14

EFFECT OF ROTOVISCO TEST ON PHYSICAL PROPERTIES OF FC-2202 PROPELLANTS WITH 82% SOLIDS

No.			σ_m	ε_m	E_o
4a	Propellant used for Rotovisco measurements	Average of 3 minibars:	74.1	22.8	411
		Optimal Sample:	72.1	23.9	385
4b	Propellant not subjected to Rotovisco	Average of 3 minibars:	72	22.0	427
		Optimal Sample:	71	23.2	400

Again the rather low tensile values suggested that either an adjustment in the NCO/OH ratio, crosslink density or both had to be made.

With both propellants it was noticed that the exposed surface was somewhat harder than the interior, which is indicative of isocyanate excess. This was corrected in the following propellants, where the NCO/OH was reduced from 1.03 to 1.00. At the same time the crosslink density was increased from 5×10^{-5} to 6.5×10^{-5} moles crosslinker/g binder.

The following physical properties data have been obtained.

TABLE 15

EFFECT OF NCO/OH RATIO AND CROSSLINK DENSITY ON PHYSICAL PROPERTIES OF FC-2202 PROPELLANTS WITH 82% SOLIDS

			Physical Properties					
			Avg of 5 Minibars			Optimal Properties		
No.	NCO/OH	XD moles/g	σ_m	ε_m	E_o	σ_m	ε_m'	E_o
4b	1.03	5×10^{-5}	72	22	427	71	23.2	400
5	1.00	5×10^{-5}	93.1	17.9	686	95.4	18.5	698
6	1.00	6.5×10^{-5}	158.8	10.3	1936	161	12.2	1826

These data show that the NCO/OH ratio of 1.00 is the optimal one not only for gumstock but also for propellants, i.e., incorporation of AP causes only negligible, if any, side reactions, which consume isocyanate. The much higher than proportional increase of modulus with higher crosslink density was unexpected, but can probably be explained by assuming that TP-340 crosslinker is preferentially adsorbed on AP leaving the binder partially depleted of crosslinker. Propellant 4a could be processed without difficulty, but viscosity is far above the specified limits as seen in Figure 13.

Two apparent approaches to reduce the viscosity are the use of wetting or bonding agents and/or the use of oxidizer blends with better packing. The first approach is more desirable since it leaves more freedom to tailor ballistic properties through choice of a suitable oxidizer blend. For this reason the effect of wetting or bonding agents on processing, end of mix viscosity and viscosity build-up were explored as well as effects on cure and physical properties, and interference of wetting agents and bonding agents.

3. Evaluation of Wetting Agents

From earlier tests with wetting agents and UFAP/FC-2202 slurries three additives with outstanding performance were found (FC-190, FC-194 and FC-199), from which FC-194 was selected as the most effective one.

As test vehicle the following propellant was used:

TP-340	0.273%	XD = 5 x 10^{-5} moles triol/g binder	
FC-9	3.552%	NCO/OH Ratio = 1.03	
FC-2202	12.854%		
HDI	1.312%	+48 AP	24.6%
FeAA	0.005%	SS AP	24.6%
HAA	0.004%	MA AP	32.8%
Binder:	18.000%	Oxidizer	82.0%

With above propellant wetting agent FC-194 was employed at a concentration of 0.5%. The weight of the additive was taken off the FC-9 plasticizer.

In Figure 14 the Rotovisco viscosity data as function of time are shown for shear stresses of 5000 and 30,000 dynes/cm^2. Comparing the data with those for the propellant without wetting agent (Figure 13 and Table 16 below) shows that indeed a twenty fold reduction of viscosity is possible through wetting agents.

TABLE 16

PROPELLANT VISCOSITY AT 110°F (Kpoise)

	1 hr. after catalyst addition		6 hrs. after catalyst addition	
Additive	at 5 Kdynes/cm^2	30 Kdynes/cm^2	5 Kdynes/cm^2	30 Kdynes/cm^2
none	350	75	--	--
0.5% FC-194	15	4.2	44	5.4

Though the propellant cured to a point where it was solid, no full cure was obtained. Under pressure it crumbled and did not show rubbery properties. Even a binder made with the same concentration of FC-194 and a higher concentration of catalyst (no HAA) cured softer than a binder without the wetting agent. Similar problems had been encountered earlier with wetting agent FC-190. Another propellant made with FC-199 also did not fully cure.

To pinpoint the source of trouble, the effect of all three wetting agents on the isocyanate and the cure catalyst was investigated. A possible reaction of isocyanate in presence of above compounds could have been homopolymerization. This was checked, but such a reaction was not found, On addition of above wetting agents to a solution of FeAA neither a fading of the color nor a discoloration was seen; heating and evaporation of solvent produced very minor color changes. When solutions of FeAA in FC-2202 containing some MA AP were heated for 1 day at 60°C in presence of these wetting agents, some fading of the FeAA color was observed.

To find out whether other cure catalysts were more compatible, another batch of above propellant with 0.5% FC-194 was made. The batch was broken up in 5g samples and 2mg of the respective catalyst, mulled with 50 mg FC-9, was mixed in (amounts to 0.04% catalyst concentration).

The following catalysts were used:

1. Ferric acetylacetonate
2. Ferric phenylacetylacetonate
3. Ferric di-phenylacetylacetonate
4. Ferric oxinate (complex with 8-hydroxy-quinoline)
5. Ferric dehydracetate
6. Manganic diphenylacetylacetonate
7. Manganic oxinate
8. Manganic dehydracetate
9. Dibutyltindiacetate
10. Dibutyltindilaurate

The most complete cure was obtained with dibutyltindiacetate, next best was dibutyltindilaurate and then ferric acetylacetonate (FeAA); with the latter cure was marginal. All other catalysts failed to cure; in many cases very low catalyst solubility was certainly at least a contributing factor.

Based on these results the same propellant was made again, but with dibutyl-tindiacetate (0.05%) instead of FeAA/HAA. The propellant thickened up rapidly after catalyst addition and cured (3 days at 135°F). From mechanical properties data (see below), however, it is obvious that a full cure was not obtained:

Physical Properties at 77°F	σ_m	ε_m	E_o
Average of 5 minibars	22.4	23.3	188
Optimal Sample	21.9	30.9	202

Shore A Hardness: 18

This was also true for the same propellant with 0.5% FC-199 wetting agent and dibutyltindiacetate as cure catalyst.

It was also tried to reduce the concentration of wetting agent (FC-204) from 0.5% to 0.3% with FeAA/HAA as catalyst. At this wetting agent concentration the propellant was not as fluid as with 0.5%. In spite of the reduced concentration, the propellant did not fully cure.

The interference with the cure catalyst may be due to the particular structure, which all three wetting agents have in common. Presence of impurities does not seem to be the problem, because efforts have been made to purify these additives.

The fact that viscosity was building up rather normally and that a certain state of cure was reached may indicate that through some side reaction(s) chain termination occurred to a small extent, but the relatively soft binder selected (low crosslink density) is more sensitive toward such changes, i.e., a higher crosslinker concentration could have been a sufficient and effective remedy.

Even without wetting agent the introduction of AP tends to reduce the crosslink density of the binder, i.e., a binder, which was in contact with AP, which was subsequently centrifuged off, was softer than a control.

One contributing factor may be the selective adsorption of crosslinker (TP-340) on the oxidizer; the steep increase of propellant tensile and modulus with relatively small increases in crosslink density of the propellant binder also points to this possibility.

Using a propellant with 82% AP (MA:SS:+48 = 40:30:30) the binder was adjusted to a crosslink density of 6.5×10^{-5} moles crosslinker/g binder (NCO/OH = 1.00) which was shown to produce a propellant with a very high modulus (No. 6, Table 15). When 0.5% wetting agent FC-194 was incorporated, however, also this propellant failed to cure.

No further attempts were made then to achieve propellant cures in presence of any of the most effective wetting agents (FC-190, 194 and 199) which are fluorocarbon derivatives. Instead, a series of other wetting agents was investigated which, though possibly not quite as effective, might not interfere with the cure.

A rapid screening of wetting agents available from another program was initially made with a pastelike mixture of UFAP (3μ) and FC-2202 (1:1 b.w.) using 1% wetting agent, but a wetting agent selected on this basis gave no satisfactory result when mixed in a real propellant. It was soon found out that the presence of plasticizer changed the order of effectiveness of wetting agents, which were then tested in a propellant mix which contained all ingredients but the crosslinker (TP-340), HDI and FeAA/HAA.

Presence of TP-340 did not change this order significantly. Based on these tests diethanolamide of oleic acid ("DEO") emerged as the most suitable wetting agent. When used in a real propellant, it was effective as a wetting agent up to the point when FeAA/HAA was added to the propellant mixture, which contained already the HDI. From here the propellant became more viscous than one without wetting agent and had to be spatula cast. The physical properties of this propellant were the following:

	σ_m	ε_m	E_o
Average of 5 minibars	89.8	17.7	635
Optimal Properties	91.5	18.9	640

Still another problem is the compatibility with bonding agents. Two propellants (82% solids) were made, one with TP-340 and the other with CTI as crosslinker, both containing wetting agent (FC-194) and bonding agent (TEPAN) at the same time. It turned out that simultaneous application of TEPAN and FC-194 not only wipes out the wetting effect completely, but in fact renders the mixture dryer than with TEPAN alone. At no point did the mixture consolidate enough to become castable.

Further tests with wetting agents were then discontinued and other approaches to low propellant viscosities taken.

4. Bonding Agents

The use of bonding agents in propellants is not only attractive because of the improved physical properties, which can be obtained, but also because of the low end of mix viscosities, which are often observed with such additives. It is not until the addition of cure catalyst that a remarkable wetting effect is found, in fact, before addition of catalyst the propellant mixture appears even drier. Only by partial reaction with curatives these highly polar compounds, which are well adsorbed (even chemisorbed) onto the AP, may be converted to "wetting agents".

The first bonding agent used with FC-2202 propellant was TEPAN. Though it worked well in other fluorocarbon propellants, it did not improve FC-2202 propellant properties to any large extent nor did it show improved processing, in fact end-of-mix propellant viscosity was somewhat higher than with a control. To test other bonding agents, a propellant was selected with 82% AP (MA:SS:+48 = 40:30:30) and a FC-2202 binder with TP-340 as crosslinker, HDI as curative, FC-9 plasticizer as solubilizing aid (20% of binder) and FeAA/HAA as catalyst system (0.005 and 0.004%, respectively); NCO/OH was 1.00 and XD = 5 x 10^{-5} moles crosslinker/g binder, based on TP-340 concentration. Rotovisco data on these propellants have been obtained (Figures 15 and 16) as well as physical properties. The physical properties of the respective propellants are shown in Table 17.

TABLE 17

PHYSICAL PROPERTIES OF FC-2202 PROPELLANTS WITH BONDING AGENTS

Prop. No.	Bonding Agent	Concentration (Binder %)	Physical Properties					
			Avg of 5 Minibars			Optimal Properties		
			σ_m	ε_m	E_o	σ_m	ε_m	E_o
	None	--	93.1	17.9	686	95.4	18.5	698
(7)	C-1	1.5	64	20	482	60	22	420
(8)	FC-156	0.2	159.3	16.3	1314	163.8	17.5	1297
(9)	FC-122	0.2	144.6	14.6	1244	146.9	15.2	1186
(10)	FC-201	0.2	136.2	19.1	965	138.4	20.0	907
(11)	FC-202	0.2	137.9	19.7	1020	131.1	20.4	988

From the data in Table 17 it is seen that C-1 is not a good bonding agent in this type of propellant as was also true for TEPAN. However, the other compounds proved to be good bonding agents in this system. In particular, #10 and #11 surpass the control in elongation, but also show improved tensile strength. This makes it possible to lower crosslink density for better elongation without substantially sacrificing tensile strength.

Considering both improvement of physical properties and propellant viscosity, bonding agent FC-156 (No. 8) is probably the best choice. From Figures 15 and 16 it is seen that end-of-mix viscosity is the lowest with FC-156 (about 1/10 of that of the control). Viscosity buildup with time is rapid though for FC-156 as well as FC-122. With FC-201 and FC-202 only 50% of the previous FeAA concentration was used, which is reflected in the slower viscosity buildup. No data were obtained for the C-1 propellant, which was nearly as viscous as the control. Concentration of bonding agent may also be critical. The relatively high concentration of TEPAN and C-1 used heretofore, which had been adopted from other propellant systems where this was the optimum, may not be appropriate for this system. It seemed therefore possible that TEPAN and C-1 would also do better at the lower concentration. This was checked with a propellant identical with the one for testing the other bonding agents, using 0.2% of the additive. It was found that again there was no effect on end of mix viscosity in contrast to FC-156 (Figures 17 and 18).

Physical properties of these propellants are tabulated below and compared with a control* and a propellant with 0.2% FC-156, but otherwise also the same composition.

TABLE 18

			Physical Properties					
	Bonding	Agent Conc.	Avg. of 5 minibars			Optimal Properties		
No.	Type	% of Binder	σ_m	ε_m	E_o	σ_m	ε_m	E_o
12	None	--	96.7	9.9	1184	109.8	11.1	1244
13	FC-156	0.2	125.6	12.1	1314	116.4	12.8	1186
14	TEPAN	0.2	156.2	11.6	1754	153.7	11.7	1616
15	C-1	0.2	157.1	12.6	1442	161	13.4	1395

There is some improvement of properties over the control with all of these bonding agents, but apparently at this low concentration the effect is not large.

With FC-156 a series was run to study the effect of concentration on end-of-mix viscosity and viscosity buildup. Catalyst concentration

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* A new lot of FC-9 plasticizer was used, and it was found that propellants cured somewhat harder, resulting in lower elongations as compared with previous propellants. The IR spectra of both lots of FC-9 are practically identical.

was reduced to 50% of the one used before; crosslinker concentration was also less.

The results are plotted in Figure 19. It seems that at 0.2% FC-156 an optimal concentration is reached as far as viscosity is concerned. Both viscosity at 5000 dynes/cm^2 and 30,000 dynes/cm^2 are well below the specified limits.

5. Adjustment of Propellant Properties in Presence of Bonding Agents

With bonding agents like FC-156 as necessary ingredients for low end-of-mix viscosities a propellant series was made with different crosslink densities of the binder to determine the trade-off of tensile strength for elongation. The propellants had the same composition as the one described before (Table 18, No. 13) except that the concentration of TP-340 was a variable here. As a bonding agent FC-156 was used at a concentration of 0.2% (binder). The results are listed in Table 19.

TABLE 19

EFFECT OF BINDER CROSSLINK DENSITY ON PROPELLANT PHYSICAL PROPERTIES

			Physical Properties					
			Avg. of 5 Minibars			Optimal Properties		
No.	XD (moles TP-340/g Binder)	Bonding Agent	σ_m	ε_m	E_o	σ_m	ε_m	E_o
13	5.0×10^{-5}	FC-156	125.6	12.1	1353	116.4	12.8	1186
16	4.5×10^{-5}	FC-156	140.7	11.9	1611	145.8	12.6	1593
17	4.0×10^{-5}	FC-156	109.5	13.6	1180	105.6	14.2	1151
18	3.5×10^{-5}	FC-156	80.2	20.2	674	77.4	22.4	581
19	3.0×10^{-5}	FC-156	53.7	26.2	390	49.2	30.5	302
20	4.0×10^{-5}	FC-201	104.4	17.1	842	114.8	18.5	881

It is seen that an elongation of better than 25% can be reached only at the expense of tensile strength. There is, of course, also the possibility to improve physical properties at somewhat higher crosslink density by using more favorable blends of oxidizer, as long as they are compatible with ballistic requirements.

Replacing FC-156 by FC-201 (same concentration) at a crosslink density of 4×10^{-5} moles TP-340/g binder resulted in a propellant with better physical properties (see Table 19, #6), but end-of-mix viscosity is far above acceptable levels (see Figures 17 and 18).

6. Particle Size Distribution of AP and Viscosity of FC-2202 Propellants

Another possibility to decrease propellant viscosity is through choice of proper blends of AP with different particle sizes, though the freedom of ballistic tailoring will be limited by this. Nevertheless, it would be worthwhile to know how much propellant viscosity could be reduced by optimal blends.

For this purpose propellants were made with different blends of AP (82%) and their processing characteristics determined as well as their physical properties. The binder for these propellants was the same as described before with XD = 5×10^{-5} moles crosslinker/g binder and NCO/OH = 1.00. The AP blend used so far (#1, MA:SS:+48 = 40:30:30) was compared with: #2) A blend based on Farris' calculations(6) to give maximum packing fraction.

(MA:SS:+48 = 17.5:36.5:52).

#3) A blend based on Farris' calculations(6) close to maximum packing fraction (more fines) (UFAP, 3μ:HS:UG = 35:45:20)

#4) A blend based on semiempirical calculations of Alley and Dykes(7) for maximum packing fraction of a MA, UG and +48 mixture. Table 20 below summarizes the results obtained.

TABLE 20

EFFECT OF AP BLEND ON PROCESSING AND PHYSICAL PROPERTIES OF FC-2202 PROPELLANTS

			Physical Properties					
			Avg of 5 Minibars			Optimal Properties		
Prop. No.	AP Blend #	Processing	σ_m	ε_m	E_o	σ_m	ε_m	E_o
5	1	Processable (see Figure 20)	93.1	17.9	686	95.4	18.5	698
21	2	Best processing (See Figure 20)	86.4	13.8	856	102.6	15.0	930
22	3	Batch never became fluid, spatula cast	hard and brittle					
23	4	Somewhat more viscous than # 5	116.2	9.7	1523	117.7	10.1	1467

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(6) R. J. Farris, Trans. Soc. Rheol. 12, 281 (1968).

(7) B. J. Alley and H.W.H. Dykes, 4th ICRPG Solid Propulsion Meeting, CPIA Publ. No. 188, Vol, II, p. 223, April 1969 (Confidential report.)

Viscosity buildup of propellants with Blend #1 and #2 are shown in Figure 20. It is quite evident that processing (or propellant viscosity, respectively) can be substantially improved by using proper blends, however, even with optimal compositions, viscosity is still above the specified limit and one has to rely on other means to reduce the viscosity further, as for example using bonding agents like FC-156.

7. Effect of Particle Size Distribution and Total Solids on Viscosity and Physical Properties of FC-2202 Propellants in Presence of Bonding Agents

With the vastly improved processability achieved through bonding agents like FC-156 it was now possible to explore not only wide variations in particle size distribution or even bimodal instead of trimodal blends, but also the limits of processability with total solids above 82%.

The effect on physical properties was evaluated as well.

Variations in solids are, of course, most important for the tailoring of ballistics, but these effects which have been also evaluated for the following propellants, will be discussed later under Ballistic Properties, although some of the blends were selected with ballistic applications in mind, especially those with higher percentages of small particle size AP.

To assess the effect of higher concentration of fine AP (MA) or the effect of using AP of still smaller particle size (3μ UFAP instead of MA) at constant total AP concentration (82%), propellants were made with a FC-2202/TP-340 (5×10^{-5} moles/g binder)/HDI/FC-9 (20%)/FC-156 (0.3%) binder. The solids composition and physical properties are summarized in Table 21 below:

TABLE 21

		Physical Properties					
		Avg. of 5 Minibars			Optimal Properties		
Prop. No.	Solids Composition (82% Total)	σ_m	ε_m	E_o	σ_m	ε_m	E_o
24	UG(RRD):HS:UFAP (3μ) 52:30.5:17.5	103	13.2	1442	101.2	14.0	1409
13	* +48:SS:MA 30:30:40	125.6	12.1	1353	116.4	12.8	1186
25	+48:SS:MA 20:20:60	200.6	6.4	4000	199.4	7.2	3646
26	(Bl-blend)SS:MA 50:50	197	7.4	2890	218.1	9.1	2837

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* 0.2% of FC-156 instead of 0.3%.

The physical properties of propellants 13, 24 and 25 with trimodal blends show that a blend which results in poor packing, such as #25 in contrast to #24,which is optimal packing according to Farris,(6) will produce high tensile and modulus along with low elongation. This is also reflected in the viscosities of the respective propellants with high packing solids giving lower viscosity. Propellant #24 was very fluid (Figures 21, 22) and had an excellent potlife. No viscosity increase was seen within the six and a half hour time period, where the viscosity was measured; yet the propellant cured well within one day. Other propellants with 82% and higher solids were made with a binder similar to the one mentioned before, but with a lower crosslink density (3.5×10^{-5} moles TP-340/g binder) and 0.25% (of binder) FC-156. The solids and the respective physical properties of such propellants are presented in Table 22.

Though the physical properties of propellants #27 and 18 (Table 22) are not too different, their end-of-mix viscosity is (Figures 23, 24). The viscosity for propellant #27 was exceptionally low; compared with No. 18, the initial viscosity is six times lower.

TABLE 22

Prop. No.	Solids, %	AP Composition	Physical Properties Avg. of 5 Minibars σ_m	 ε_m	 E_o	 Opt. Properties σ_m	 ε_m	 E_o
27	82	+48:SS:MA 52:30.5:17.5*	101	22.0	713	--	--	--
18	82	30:30:40	80.2	20.2	674	77.4	22.4	581
28	84	52:30.5:17.5*	69.1	18.9	523	74.1	20	558
29	84	As #27, but MS instead of SS MA	83.0	20.6	587	--	--	--
30	84	30:30:40	114.7	13.0	1215	101.2	13.6	984
31	86	52:30.5:17.5	89.1	15.5	878	93.3	16.1	935

The higher tensile and modulus and lower elongation values for propellants #30 and 31 are again reflected in their higher end-of-mix

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* Optimal according to R. J. Farris for 80% volume loading.

viscosity, as seen in Figures 21 and 22. Propellant #31 with 86 wt.% AP corresponds to an 83.7% volumetric loading. It should be pointed out that this propellant still consolidated well, flowed under gravity and leveled out under vibration. Well consolidated propellants with even higher solids are quite feasible.

According to Farris(6) lowest viscosity should be obtained, if particle sizes are spaced evenly as to their size ratio (a high ratio, e.g., 10:1, is preferred). Considering this it should be more advantageous to use MS grind (≃70μ) instead of SS grind (≈130μ) in a trimodal blend with MA AP as fine (7-9μ) and +48 (≈400μ) as coarse oxidizer.

A propellant (No. 29, Table 22) with this blend was made with 84% total solids. End-of-mix viscosity of the corresponding propellant was, however, higher than with SS AP as a trimodal blend component (see Figures 23 and 24). Physical properties are shown in Table 22 (No. 29). The gain in physical properties is small and hardly justifies the use of MS instead of SS AP, particularly in view of the higher end-of-mix viscosity.

Using Farris' optimal trimodal composition (fine:medium:coarse = 17.5:30.5:52) one propellant was made with mostly very fine oxidizer, (UFAP, coated, 0.6μ; MA;MS) and one with mostly coarse oxidizer (MS, UG RRD, +32). Since viscosities in both cases were high, no Rotovisco measurements were made. Both propellants, however, consolidated well, vibrated down and even seemed to flow under gravity.

Since the bimodal BI-blend (SS:MA = 50:50, Propellant No. 26, Table 21) neither produced a low propellant viscosity nor good physical properties, another bimodal blend was evaluated, corresponding to an optimal blend for minimum viscosity according to Farris(6) (CD-blend, SS:MA = 70:30). The binder used for these propellants was the same as for the previous propellants (Table 22).

Both 82% and 84% total solids were incorporated. The resulting end-of-mix viscosities and viscosity build-up are shown in Figures 23 and 24. For 82% total solids, viscosities are well below the specified limits in contrast to the BI-blend, but at 84% total solids they exceed these limits. Physical properties of the respective propellants are found in Table 23. Again on the 82% level physical properties requirements are met. With some lower crosslink density these requirements probably could be met for the 84% solids propellant, but its end-of-mix viscosity is clearly unacceptable.

TABLE 23

Prop. No.	Solids (CD Blend)	Physical Properties (Average of 5 Minibars) σ_m	ε_m	E_o
32	82%	108.7	31.9	674
33	82%	123.8	25.5	1044*
34	84%	122.6	20.6	1012

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* This propellant is the same as No. 32, except that a new lot of FC-9 plasticizer was used. The IR spectra of the new and the previous lot are practically identical.

All these results show clearly the superiority of Farris' optimal compositions for bimodal and trimodal blends, which, in combination with bonding agents like FC-156 made it possible to meet viscosity specifications up to 84% solids.

Before any integrated improvement (propellant viscosity and physical properties) could be attempted, the ballistic properties connected with various oxidizer blends had to be evaluated first.

8. Effect of Oxidizer Loadings and Blends on Propellant Ballistic Properties

The first burning rates and pressure exponents have been measured with epoxy-coated regular Crawford Bomb strands (1/4" x 1/4" x 3") and similarly coated ministrands (0.1" x 0.2" x 1.0"), which showed a reasonably good correlation (Figure 25). The data obtained this way are listed in Table 24:

TABLE 24

Prop. No.	% Solids	Solids Composition	r_{200}, ips	n
13	82	+48:SS:MA = 30:30:40	0.090	0.70
24	82	UG(RRD):MS:UFAP(3μ) = 52:30.5:17.5	0.090	0.60
25	82	+48:SS:MA = 20:20:60	0.088	0.55
26	82	SS:MA = 50:50 (Bl-blend)	0.099	0.63
28	84	+48:SS:MA = 52:30.5:17.5	0.097	0.72
30	84	+48:SS:MA = 30:30:40	0.089	0.64
31	86	+48:SS:MA = 52:30.5:17.5	0.086	0.72

Based on these data it was then tried to increase the pressure exponent through several approaches:

1. By decreasing the C-H content of the binder by decreasing the amount of plasticizer.
2. By varying total solids and particle size of AP, and
3. By ballistic additives.

In the first case a propellant with 82% solids (40:30:30 = MA:SS:+48) was made whose binder contained but 10% of FC-9 plasticizer instead of the usual 20% (Propellant 1A). In the second case total solids and particle size of AP were varied as shown in Table 25.

TABLE 25

OXIDIZER BLENDS USED IN PROPELLANTS FOR INVESTIGATING BALLISTIC PROPERTIES

Propellant	Total AP, %	Blend
2A	84	Farris Optimal Trimodal, MA:SS:+48 = 17.5:30.5:52
2B	86	Farris Optimal Trimodal, MA:SS:+48 = 17.5:30.5:52
2C	88	Farris Optimal Trimodal, MA:SS:+48 = 17.5:30.5:52
2D	82	Farris Optimal Bimodal, MA:SS=30:70
2E	84	Farris Optimal Bimodal, MA:SS = 30:70
2F	82	Farris Optimal Trimodal, UFAP (coated, 0.6μ):MA:MS = 17.5:30.5:52
2G	82	Farris Optimal Trimodal, MS:UG (RRD): +32 = 17.5:30.5:52
2H	82	Farris Optimal Trimodal, MA:SS:+48 = 17.5:30.5:52
3A	82	as 2H + 0.5% BRA-101
3B	82	as 2H + 0.5% Silon S
3C	82	as 2H + 0.5% P-33
3D	82	as 2H + 0.5% ATMP

In propellants 2A-C the effect of increasing solids was to be investigated, and in propellants 2F and G the effect of shifting the particle size distribution to either very fine or very coarse oxidizer.

For the third approach a base propellant was used with 82% AP (trimodal Farris, MA, SS, +48) and 0.5% of a ballistic additive. The additives tested comprise BRA-101, Silon S, P-33 carbon black and ammonium tetra-metaphosphate (ATMP) in propellants 3-A, B, C and D.

When P_{DL} tests were run with propellants #2A and B (unrestricted) it was found that #2A would extinguish at 230 psig and #2B at 250 psig, at a depressurization rate of 7 psi/sec. However, when burning rates were determined with 1/4 in. diameter solid strands, restricted with an epoxide resin, burning was sustained at 100 psia and below.

Since the propellant is well overoxidized, it was suspected that the restriction serves as fuel. This was confirmed in several ways. When solid strands of propellant 3B, coated with an epoxide resin, were burned at 200 psia and extinguished by depressurization, it was found that the strands burned much faster near the restriction as seen in Figure 26a). In a propellant without any ballistic additive, but otherwise the same as 3B (2H, Table25) the effect was not as strong, but nonetheless noticeable.

Replacing the epoxide coating by a more inert restriction (Viton A) prevented the propellant from burning down the sides of the strand and resulted in even burning (see Figure 26b) except that with most propellants burning was not sustained below 400 psia, in some cases not even at 1000 psia, possibly because of heat losses. (See Table 26)

The only propellant, which burned down to 200 psia (not at 165 psia) was #2G with a high percentage of coarse AP, whereas its counterpart (#2F, high percentage of fine AP) would not burn even at 1000 psia.

Propellants with additives (3A, B, C and D; intermediate particle size blend) differed in the lowest pressure, where burning was sustained. No. 3C would not burn even at 1000 psia, though it contained carbon black (P-33, 0.5%) as an opacifier and fuel.

With some variations, however, even propellant 2F burned at 200 psia with Viton-A restriction (see Table 26). When the restriction thickness was increased (5 coatings with Viton A), this propellant burned evenly at 200 psia, but the amount of accumulated, melted coating raises some doubts as to the validity of the data obtained. One coating with a Viton A solution containing K-titanate and TiO_2 on top of a single coating with Viton A also sustained burning at 200 psia, as did an epoxide resin or tape on top of a single Viton A coating.

In general it seems that slopes are higher with the Viton A than with the epoxy restriction (see Table 27), and burning rates at 200 psia are lower than 0.10 ips. In case of an additive (BRA-101, propellant #3A), the slope changed only from 0.80 to 0.86, but the burning rate was considerably higher. Propellants #3B and D also had high slopes, but extrapolated burning rates at 200 psia are well below 0.10 ips (see Table 27).

TABLE 26

EFFECT OF RESTRICTION ON PROPELLANT BURNING

	Epoxy Restriction			Viton A Restriction		
Propellant # [a]	No. of Coats	Regression Uniformity	Min. Combustion Pressure,psia	No. of Coats	Regression Uniformity	Min. Combustion Pressure, psia
2A	2	--	≤100[c]	--	--	--
2B	2	--	≤100[c]	1	Uniform	≤500[e]
2B				d	Uniform, level burnout surface	≤200[c]
2C	2	--	≤100[c]	--	--	--
2D	b	--	≤60[c]	--	--	--
2E	b	--	≤50[c]	--	--	--
2F	2	--	≤100[c]	2	Uniform	≥1000[h]
2F				5	Uniform	≤200[c]
2F				f	Uniform	≤200[c]
2F				g	Uniform	≤200[c]
2G	2	--	≤100[c]	2	Uniform	≤200[i]
2H	2	Non-uniform Not as bad as 3B	≤200[c]	f	--	≤200[c]
3A	2	--	≤100[c]	1	Uniform	≤500[j]
3A				5	--	≤400[c]
3B	2	Non-Uniform See Fig.26a	100[c]	2	Uniform	≤400[k]
3C	--	--	--	2	Uniform	>1000[h]
3D	--	--	--	2	Uniform	≤300[l]

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a For propellant identification, see Table 25.
b Special, thick restriction with carbon black as filler.
c Not tested at lower pressures
d One coat with Viton A, 2 coats with a mixture of Viton A (70%) and filler (30%). The filler was a 50:50 mixture of K-titanate and TiO_2
e Did not burn at 400 psia
f One coat Viton A, one coat epoxy resin
g One coat Viton A, then wrapped with cloth tape.
h Not tested at higher pressures
i Did not burn at 165 psia
j Did not burn at 400 psia
k Did not burn at 300 psia
l Did not burn at 200 psia and 1000 psia

TABLE 27

PRELIMINARY BURNING RATES AT 200 PSIA AND PRESSURE EXPONENTS FROM SOLID PROPELLANT STRANDS WITH EPOXY OR VITON A RESTRICTIONS

Propellant # [a]	Epoxy Restriction			Viton A Restriction		
	No. of Coats	r_{200}, ips	n	No. of Coats	r_{200}, ips	n
2A	2	0.086[c]	0.60	--	--	--
2B	--	--	--	1	0.086[e]	0.50
2B				d	0.067	--
2C	2	0.110[c]	0.60	--	--	--
2D	b	0.099	0.60	--	--	--
2E	b	0.103	0.64	--	--	--
2F	2	0.080	0.66	--	--	--
2G	2	0.074	0.66	2	0.052	1.00
2H	--	--	--	f	0.079	--
3A	2	0.086	0.80	5	0.126[e]	0.86
3B	--	--	--	2	0.043[e]	1.00
3D	--	--	--	2	0.055[e]	1.00

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[a] For propellant identification see Table 25.

[b] Special, thick restriction with carbon black as filler.

[c] Interpolated values

[d] One coat with Viton A, 2 coats with a mixture of Viton A (70%) and filler (30%). The filler was a 50:50 mixture of K-titanate and TiO_2.

[e] Extrapolated value

[f] One coat Viton A, one coat epoxy resin.

Propellant 1A (10% plasticizer only) showed a slope of 0.68 and r_{200} = 0.090 ips, which is essentially not different from similar propellants with 20% FC-9 plasticizer (epoxy-coated burning rate strands).

As seen from Table 27 (epoxy restriction) propellants 2A, C (increasing solids, 84 and 88%) had about the same slope but r_{200} was higher with #2C. From propellant #2B only a burning rate at 100 psia was available, which was about the same as for #2A at this pressure. Propellants #2D and 2E (82 and 84% CD blend) also had similar slopes and burning rates, which was true as well for propellants #2F and 2G (fine vs. coarse AP). With 0.5% BRA-101 as a ballistic additive (#3A) a propellant was obtained with n = 0.80 and r_{200} = 0.086 (Propellants #3B-D were not tested with epoxide resin restriction).

Since the Viton-A epoxide resin combination (one coat of each, the Viton A restriction first) looked most satisfactory, most of the foregoing propellants were made over again, using this restriction throughout.

In some cases, where the results seemed to be inconsistent with 1/4" diameter strands, the burning rate tests were repeated with 1/2" diameter strands. The results are presented in Table 28. All strands have a diameter of 1/4", if not stated otherwise.

In spite of the improved coating the data still seem to be somewhat irregular. With Farris optimal trimodal blends (MA/SS/+48, propellants 2H-1 and 2H-2) the slope seems to decrease with the strand diameter, which is not the case with CD blend (propellants 2D-1 and 2D-2). It is felt at this point that reliable slopes and burning rates of this type of propellant can be obtained only from motor firings. The apparent trend of decreasing slope with decreasing overall particle size (Nos. 1, 2, 6, 8) tends to support this view.

TABLE 28

No.***	% Solids	AP Blend	r_{200}, ips	n	Lower Burning Limit, psia Burning	No Burning	Remarks
2G	82	Farris,MS/UG/+32	0.075	1.00	150	--	
2H-1	82	Farris,MA/SS/+48	0.063	1.4	200	--	
2H-2	82	Farris,MA/SS/+48	0.077	0.98	200	==	1/2" strands
2A	84	Farris,MA/SS/+48	0.068	1.0	150	--	
2B	86	Farris,MA/SS/+48	--	--	--	500	
2D-1	82	Farris,MA/SS (CD)	0.070	0.80	150	--	
2D-2	82	Farris,MA/SS (CD)	0.082	0.80	150	--	1/2" strands
2F	82	Farris,UFAP/MA/MS	0.064	0.26	200	--	No burning was obtained at 500 psia.
3B	82	Farris,MA/SS/+48	0.055	1.05	500	300	* r_{200} extrapolated
3D	82	Farris,MA/SS/+48	0.072	0.64	500	300	** r_{200} extrapolated.
3C	82	Farris,MA/SS/+48	--	--	--	500	0.5% P-33
3A	82	Farris,MA/SS/+48	--	--	500	300	0.5% BRA-101

* 0.5% Silon 3

**0.5% ATMP

***For propellant identification see Table 25.

9. Adjustments of Propellant Composition for Optimum Viscosity and Physical Properties

Since both bimodal and trimodal oxidizer blends, optimized according to Farris,(5) emerged as the most suitable ones in respect to propellant viscosity and physical properties, further improvements in physical properties through adjustments of composition were sought with either blend.

So far, propellant elongations at maximum tensile (ε_m) just exceeded the required 25% (between 25 and 30% for bimodal Farris blend (CD blend), and barely to 25% for trimodal Farris blends at 82% total solids). It was felt that a better margin was needed for scale-up in order to meet this goal.

a. Bimodal Blends

The rather good physical properties obtained with CD-blend (ε_m better than 25%) suggested that minor adjustments in crosslink density of the propellant binder would be sufficient to improve properties enough to qualify the propellant for scale-up.

It was shown earlier how relatively small changes in crosslink density affected physical properties of an FC-2202 propellant containing 82% solids (MA:SS:+48 AP = 40:30:30) and a binder with 20% FC-9 plasticizer, TP-340 as a crosslinker, FC-156 as a bonding agent and processing aid, HDI as a curative and FeAA/HAA as the catalyst system. These results showed that the crosslink density should not be higher than 3.5×10^{-5} moles crosslinker/g binder for acceptable properties, in particular elongation (compare Table 19). This was found to hold true also for propellants with CD-blend AP (Table 29).

TABLE 29

EFFECT OF BINDER CROSSLINK DENSITY ON PROPELLANT PHYSICAL PROPERTIES (BINDER CONTAINING 20% FC-9 PLASTICIZER, 0.25% BONDING AGENT (FC-156), 2.5×10^{-3} % FeAA, 2.0×10^{-3} % HAA)

No.	% Solids (CD-Blend)	XD (moles TP-340/g Binder)	Physical Properties Average of 5 Minibars σ_m	ε_m	E_o
32	82	3.5×10^{-5}	108.7	31.9	674
35	82	4.0×10^{-5}	121.5	12.2	1291
34	84	3.5×10^{-5}	122.6	20.6	1012
36	84	4.0×10^{-5}	176.8	12.2	1977
33*	82	3.5×10^{-5}	123.8	25.5	1044
37*	82	3.25×10^{-5}	144.5	26.3	937
37-R*	82**	3.25×10^{-5}	99.2	29.2	563
38*	82% CA-blend	3.25×10^{-5}	75.5	15.2	723

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* A new lot of FC-9 plasticizer was used. The IR spectra of the new and the previous lot were practically identical.

** No. 37-R is a repeat of No. 37.

At a crosslink density of 3.25×10^{-5} moles TP-340/g binder, quite acceptable physical properties are obtained. Together with satisfactory castability and potlife as well as ballistics this would make it an attractive candidate for scale-up. However, when repeated, the viscosity build-up was faster than before (Figures 27a,b) so that the minimum potlife of 6 hours was not obtained at 110°F using the self-imposed stringent processing criteria established for this program. Further decrease of catalyst concentration for adjustment of potlife is not desirable because cure reproducibility would decrease. However, the formulation would probably meet all requirements if the propellant draw-off temperature is reduced slightly to 105 or 100°F.

By replacing the CD-blend with a CA-blend (30:70 = MA:UG) castability and potlife could be vastly improved (Figure 27a, b) but physical properties became quite inadequate, as seen from Table 29.

b. Trimodal Blends

With Farris optimal trimodal blend (MA, SS, +48) castability was excellent, and the potlife minimum of 6 hours well exceeded, but physical properties (elongation) of the propellant were somewhat short of the minimum requirements. Some change in the particle sizes of the Farris optimal trimodal composition could correct this shortcoming, though end-of-mix viscosity would be increased. To investigate whether this trade-off would be acceptable, a series of propellants were made, which differed only in the particle sizes used to make the trimodal blend. Binder ingredients were the same as for the propellants with bimodal AP blends, except that the crosslink density was slightly higher (3.3×10^{-5} moles/g binder). The blends and the physical properties of the respective propellants are shown in Table 30, and the viscosity/time curves in Figures 28a, b.

TABLE 30

EFFECT OF TRIMODAL AP BLENDS ON PROPELLANT PROPERTIES

	Farris Optimal Composition					
No.	Fine 17.5	Med. 30.5	Coarse 52	σ_m	ϵ_m	E_o
39	MA	SS	UG	89.2	28.9	672
40	MA	MS	UG	90.8	25.3	580
41	MA	MS	+48	98.6	24.3	618
42	MA	SS	+48	101.0	22.0	713

If propellant physical properties and end-of-mix viscosity are compared, it is readily seen that the increase in elongation parallels the viscosity increase and not one of these propellants meets the physical properties and viscosity requirements simultaneously.

To meet the viscosity requirements the MA/SS/+48 blend had to be used, but further improvements in propellant physical properties could be sought only by changes in the binder composition other than crosslink density.

c. Binder Composition

(1) Reduction in Plasticizer Concentration

To evaluate how a decrease in plasticizer concentration would affect propellant physical properties, propellants with compositions as shown in Table 31 were made.

TABLE 31

EFFECT OF PLASTICIZER CONCENTRATION ON PROPELLANT PHYSICAL PROPERTIES (82% Solids (MA:SS:+48 = 40:30:30))

		XD	Physical Properties (Average of 5 Minibars)		
No.	FC-9 Conc., %	moles TP-340 per g binder	σ_m	ε_m	E_o
18	20	3.5×10^{-5}	80.2	20.2	674
43	10	4.0×10^{-5}	167	16.8	1346
44	0	3.5×10^{-5}	72.3	25.7	407

The results do not show a significant improvement of propellant physical properties even at 0% plasticizer. The lower tensile strength and modulus indicate that the propellant may not have cured completely, though it was kept at 135°F for two weeks. The longer cure time and the higher end-of-mix viscosity of propellants with less or no plasticizer (Propellant #44 was spatula cast; the amount of catalyst was twice as high as in #18) are definitely disadvantages, which are not compensated by better propellant properties.

(2) Use of HDI/TDI Mixtures

Since it has been shown that good physical properties can be obtained in highly aluminized FC-2202 propellants with an 1:1 (molar ratio) mixture of HDI and TDI,(8) this mixture of curatives was also tested in our propellants to assess its merits and trade-offs.

The first propellant composition was as follows: 82% solids (MA:SS:+48 = 40:30:30), binder with 20% FC-9, TP-340 (4×10^{-5} moles/g binder), 0.25% FC-156, HDI and FeAA/HAA. End-of-mix viscosity (Figure 29) was, however, higher than with an all HDI equivalent propellant (twice as high at 30 Kdynes/cm^2 and nearly eight times higher at 5 Kdynes/cm^2). Also, cure time is noticeably longer which agrees with the results obtained from rate studies (see Table 2). Compared with an equivalent HDI propellant the physical properties are better (see Table 32) at this crosslink density.

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(8) Hercules Final Report AFRPL-TR-70-128, October 1970.

TABLE 32

EFFECT OF CURATIVE ON PROPELLANT PHYSICAL PROPERTIES

		Average of 5 Minibars		
No.	Curative	σ_m	ε_m	E_o
45	HDI/TDI = 1:1 molar ratio	170.1	18.3	1384
17	All HDI	109.6	13.6	1180

With Farris optimal bimodal and trimodal blends and with a lower crosslink density it could be expected that all specifications would be met. The physical properties of such propellants (Table 33) are indeed outstanding, but as seen from Figure 30a, b, the end-of-mix viscosity with the trimodal blend barely meets the specifications and with the bimodal blend by far exceeds the specified limits.

TABLE 33

PHYSICAL PROPERTIES OF 82% SOLIDS FC-2202 PROPELLANTS WITH A 50:50 EQ. MIXTURE OF HDI AND TDI AS A CURATIVE

$XD = 3.5 \times 10^{-5}$ moles TP-340/g binder. 20%
FC-9 plasticizer, 0.25% FC-156 bonding agent,
5×10^{-3} % FeAA, 4×10^{-3} % HAA. *

No.	AP-Blend	σ_m	ε_m	E_o
46	MA:SS = 30:70	150.5	33.2	812
47	MA:SS:+48 = 17.5: 30.5:52	105.8	30.7	591

* FeAA and HAA concentration is in % of total propellant.

Since the physical properties looked so attractive, investigations were continued with higher HDI:TDI ratios to see whether end-of-mix viscosities could be reduced to a satisfactory level without sacrificing the good physical properties. This series was made with 82% Farris optimal trimodal blend (as in Table 33) and the same binder as before, but variable (increasing) HDI/TDI ratios. It became immediately clear that even reducing the TDI only from 50 to 40 eq. % brought about a sizable drop in the end-of-mix viscosity, further decreasing with decreasing TDI concentration (Figure 31). Another series was made with a slightly lower crosslink density (3.3×10^{-5} instead of 3.5×10^{-5} moles crosslinker/g binder), and the same catalyst level and mix procedure was used throughout. In this case the initial viscosities were all about equal (starting from HDI:TDI = 60:40 up to all HDI), and well below the specified limit. Potlife for the propellant with an 80:20 HDI/TDI mixture was about 10 hrs. (Figure 32).

For each crosslink density and a propellant with a 60:40 HDI/TDI mixture the catalyst concentration was determined, which would ensure a satisfactory potlife, but at the same time also a good cure. The corresponding propellant viscosity vs. time curves are found in Figures 33 and 34. In both cases an FeAA concentration of 4×10^{-3} % together with an HAA concentration of 3.2×10^{-3} % seems to be the best one for this propellant.

The physical properties of different propellants made with HDI/TDI mixtures are listed in Table 34 (except those for 50:50 HDI/TDI mixtures, which are found in Table 33). It is obvious that with as little as 20 eq. % TDI, the properties, particularly elongation, are substantially improved over an all HDI, but otherwise identical propellant (#42 of Table 30), whereas end-of-mix viscosity and potlife are not adversely affected.

TABLE 34

PHYSICAL PROPERTIES OF 82% SOLIDS FC-2202 PROPELLANTS MADE WITH MIXTURES OF HDI AND TDI. Solids: Farris Optimal Trimodal Blend (MA:SS:+48 = 17.5:30.5:52). Binder: 20% FC-9 Plasticizer, 0.25% FC-156 bonding agent, TP-340, FeAA, HAA.

No.	XD, moles Crosslinker/g binder	FeAA/HAA Conc. % X 10^3 *	HDI:TDI eq. ratio	Properties σ_m	ε_m	E_o
48	3.3×10^{-5}	5.0/4.0	60:40	101.5	31.9	500
49	3.3×10^{-5}	4.0/3.2	60:40	79.5	30.1	428
50	3.3×10^{-5}	3.0/2.0	60:40	81.5	28.2	448
51	3.3×10^{-5}	3.0/2.0	80:20	96.7	31.1	458
52	3.5×10^{-5}	5.0/4.0	60:40	116.8	31.1	560
53	3.5×10^{-5}	3.0/2.0	80:20	77.1	30.5	391

* Propellant percent.

From the combined data, propellant #51 of Table 34 emerges as the best candidate for scale-up of 82% solids propellants with Farris' optimal trimodal blend.

Judging by this improvement through HDI/TDI mixtures it seemed to be possible now to make FC-2202 propellants, which meet viscosity, potlife and physical properties specifications even with 82% bimodal Farris blends (CA blend) or 84% trimodal Farris blends (MA, SS, +48). Such propellants were also made, using the following binder for both: 20% FC-9 plasticizer, 0.25% FC-156, TP-340 as a crosslinker (XD = 3.3×10^{-5} moles/g binder), a 60:40 eq. mixture of HDI and TDI, 4×10^{-3} % FeAA and 3.2×10^{-3} % HAA. The viscosity/time curve for the first propellant is shown in Figure 27 (to compare with an all HDI propellant with the same AP blend), and for the second propellant in Figure 35, where it is compared with an all HDI, but otherwise identical propellant.

With 82% CA blend, the viscosity of the HDI/TDI propellant is somewhat higher than with the all HDI propellant, but well within specifications. With 84% Farris trimodal blend, HDI/TDI and all HDI propellant show about identical viscosity/time curves, but a somewhat better potlife with the HDI/TDI mixture, both meeting specifications. Physical properties, though, seem to be inadequate (Table 35). Judging from the low tensile strengths it appears that both propellants did not attain full cure within one week at 135°F.

TABLE 35

PHYSICAL PROPERTIES OF FC-2202 PROPELLANTS, CURED WITH A 60:40 eq. MIXTURE OF HDI AND TDI

Prop. No.	Total Solids	Blend	Properties σ_m	ε_m	E_o
54	82%	MA:UG = 30:70 (CA-blend)	67.6	24.2	500
55	84%	MA:SS:+48 (Farris optimal)	82.2	21.2	675

D. TASK IV: DEMONSTRATION PHASE: SELECTION AND SCALE UP OF CANDIDATE PROPELLANT

1. Selection of Candidate Propellant

Selection of the propellant for the demonstration phase was based on the formulation studies discussed before. The final choice was between a propellant with 82% CD-blend AP and all HDI as curative (Propellant No. 37, Table 29) and one with 82% trimodal AP (Farris optimal) and a mixture of HDI/TDI (80:20) as curative (Propellant No. 51, Table 34). To allow a comfortable margin for scaling-up effects in respect to processing and physical properties, propellant No. 51 was chosen as the candidate, although the cure characteristics of propellants with HDI/TDI mixtures as curative had not been as thoroughly studied as propellants with all HDI as curative.

2. 1-lb Pilot Batch for Scale-up

Before scaling up to full size (1 quart $\approx$ 1800 g) batches, a 1 lb (400 g) pilot batch was made to learn about scale up effects and take corrective measures for the larger batches, if necessary.

The binder composition was as follows:

	Binder		AP	
Components	% of Binder	% of Propellant	Components	% of Propellant
FC-156	0.250	0.045	MA	14.35
TP-340	1.000	0.180	SS	25.00
FC-9	20.000	3.600	+48, RRD	42.65
FC-2202	71.561	12.881		82.00
HDI	5.712	1.028		
TDI	1.477	0.266		
		18.000		
FeAA*	--	0.0040		
HAA *	--	0.0027		

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* On top of 100%.

To ensure a safe cure the catalyst concentration was raised, since there was ample potlife with propellant No. 51 (see Figure 32).

The propellant was mixed the following way:

FC-156, TP-340, FC-9 and FC-2202 were well stirred until a clear solution resulted. This premix was then cast into the mixer bowl and the beaker wiped clean with several portions of MA AP; these and the remainder of the MA AP were added to the premix. Mix temperature was 135°F. Then:

2 mins. mixing, no vacuum,

5 mins. mixing, vacuum, scrapedown.

All of SS AP added, 5 mins. vacuum mixing,scrapedown.

All of +48 AP added, 10 mins. vacuum mixing,scrapedown.

10 mins. vacuum mixing,scrapedown.

10 mins. vacuum mixing,scrapedown.

During the last 10 mins. the temperature was lowered to 110°F.

HDI/TDI mixture added, 5 mins. vacuum mixing (high shear), scrapedown.

At that point the propellant was pasty. Now half of the FeAA was added (as a solution in Freon 113),

5 mins. vacuum mixing (high shear),scrapedown. Propellant was less pasty.

Remainder of FeAA and HAA (also in Freon 113 solution) added, 10 mins. vacuum mixing (high shear), scrapedown. Propellant was soupy.

5 mins. vacuum mixing (high shear), cast.

In contrast to propellant No. 51 (Table 34 and Figures 32a, b) the viscosity build-up was very slow. Nine hours after catalyst addition time the viscosity at 5 Kdynes/cm^2 and 30 Kdynes/cm^2 was still very low (6.1 and 5.4 Kp respectively). Also, cure at 135°F was slower, and the propellant took 11 days to full cure.

The propellant physical properties (obtained from regular size Instron bars), however, matched those from propellant No. 51:

		Physical Properties		
Propellant No.	Batch Size	σ_m	ε_m	E_o
51	50g	96.7	31.1	458 (avg. of 5)
51-400	400g	98.3	32.5	558 (avg. of 4)

3. Full Size 1 qt. Propellant Batches

This result was encouraging enough to proceed to the three full-size 1800g batches. Only the FeAA and HAA level was adjusted to ensure a faster viscosity build-up (4.5×10^{-3} % FeAA and 3.0×10^{-3} % HAA).

The mix procedure for the three 1800g batches was nearly the same as for the 400g batch, except that after addition of all oxidizer and before addition of the HDI/TDI mixture the propellant was mixed for 3 x 15 mins. instead of 3 x 10 mins. After the addition of the second half of the FeAA and the HAA the propellant was mixed for 5 mins. and changed from pasty to very fluid within this time. It was mixed for another 10 mins and cast. Part of the propellant was cast for Instron bars, the remainder was used for double-plate tensile and peel specimens.

The viscosity build-up for these propellants is shown in Figures 36a, b. Measured at 5 Kdynes/cm^2, the potlife is about 12-1/4 hrs. and at 30 Kdynes/cm^2 about 10-1/4 hrs, taking 50 and 25 Kp respectively as a criterion. Although batch 51-1800-1 was only measured up to 8 hrs, the data are close enough to the other curves to extrapolate potlife. Spread in potlife is then 1-1/4 to 1-1/2 hrs. (see Figures 36a, b).

Propellant 51-1800-1 cured well within 11 days at 135°F and reached a Shore A hardness of 65; the other two propellants reached only a Shore A hardness of 57 by that time, but were also taken out then.

Physical properties were measured with standard size Instron bars and represent an average of six bars each. They are shown in Table 36.

TABLE 36

PHYSICAL PROPERTIES OF THREE IDENTICAL 1800g BATCHES OF FC-2202 PROPELLANT

Propellant No.	Physical Properties		
	σ_m	ε_m	E_o
51-1800-1	120.2	35.8%	877
51-1800-2	80.4	42.4%	501
51-1800-3	73.7	35.8%	596

Elongations are well within the specification (>25%).

Coefficients of variation (deviation from the mean value in terms of standard deviation/mean) are: for σ_m, 0.276 (27.6%); for ε_m, 0.0995 (9.95%) for E_o, 0.297 (29.7%). By comparison, these values from 5000 production batches of ANB-3066 propellant are: σ_m, ± 6.5%; ε_m ± 8.2%; E_o, ± 10.0%.

The total spread (comprising 99.74% of all propellants) for these properties, however, would be three times these values, i.e., ±20%, ±25% and ±30% respectively. The properties of above propellants are close to or would fall within such spread (± 25.5%, ± 8.7% and ± 28.6%, calculated as the maximum spread from the mean value of above data).

The difference in properties of propellant No. 51-1800-1 on one hand and 51-1800-2 and 3 on the other is hard to explain. Propellants No. 2 and 3 were both made two weeks later than No. 1. A fresh batch of MA oxidizer was used (the same for all propellants). Though all ingredients were properly stored, minute amounts of moisture could have been picked up by the oxidizer. A. E. Oberth discussed this effect in one of his reports.(9) In case of above propellants, the theoretical binder crosslink density is 3.3×10^{-5} moles branchpoints (crosslinker)/g, which is $\approx 6 \times 10^{-4}$ moles branch points for 100 g propellant (18% binder). In order to reduce the crosslink density by ≈ 50% (i.e., reducing the modulus by 50%), half of this concentration of a chain terminator is required.

In case of moisture (one mole of water consumes two equivalents isocyanate), $1/2\ (18/2) \times 6 \times 10^{-4} = 0.0027$ g H_2O/100g propellant are required, if it reacts completely. This minute amount of water can be even found as surface moisture of oxidizer stored with bags of drying agents (usually surface moisture of unground AP is between 0.002 and 0.003%).

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(9) A. E. Oberth, "Ambient Temperature Binder Cure Catalysts for Hydroxy Terminated Systems", AFRPL-TR-70-95, Report 1486-01Q-2, p. 6.

The longer cure time, when HDI/TDI mixtures rather than all HDI were used, and the higher reactivity of TDI with moisture, would favor such a water reaction. Contributing to the high sensitivity problem is the low crosslink density required for adequate physical properties.

For greater reproducibility there should be no larger time lapse between batches, however, in this case, it was preferred to obtain cure and physical properties data from one batch first before proceeding to the next two batches to make sure that no adverse scaling up effects would be encountered, which still could have been corrected at that point.

Measured propellant density (1.886 g/ml) was found very close to the calculated density (1.883 g/ml), indicating that no substantial cure shrinkage occurred.

Burning rates of above three propellants were determined with 1/2" x 1/2" x 3" strands, restricted with one coat of Viton A first, then with a coat of epoxy resin. Burning rates at 200 psia were 0.076 ips and the slope was 1.00 (Figure 37). Because of the low burning rate, strands were wired at 0, 1 and 2" rather than at 0, 2 and 4" as conventional.

E. TASK V: PROPELLANT-LINER BOND

As an additional task, several liner formulations were investigated to see whether a good propellant-liner bond could be obtained.

The excess of propellant from batches No. 51-1800-1, 2 and 3, which was not needed for Instron bars, was used to cast standard peel and double plate tensile (DPT) specimens on different liners.

For these propellant-liner bond tests the following liners were made:

No. 1: Liner SD-746, an Aerojet polyether-polyurethane liner;

a. Without washcoat

b. With washcoat: Isonate 143L 9.85%
FeAA 0.15%

1,1,1-trichloro-ethane 90.00%

The other liners used FC-2202 binders of compositions shown below:

TABLE 37

Binder Components	Composition in wt.% of different FC-2202 Liners				
	No. 2 (unfilled)	Binder for Filled Liner	No. 3 Filler Sb_2O_3	No. 4 Filler Fe_2O_3	No.5 Filler P-33
TP-340 (XD = 4×10^{-5})	1.212	1.212	0.848	0.848	0.970
FC-9	20.000	20.000	14.000	14.000	16.000
FC-2202 (Lot 6)	72.400	71.610	50.127	50.127	57.288
HDI	6.388	6.928	4.850	4.850	5.542
FC-156	--	0.250	0.175	0.175	0.200
Filler	--		30.000	30.000	20.000
FeAA (on top of Formulation)	0.0028		0.004	0.005	0.0075

Liners with designation (a) had no washcoat whereas those with designation (b) have a washcoat. Results of tensile tests are given in Table 38.

TABLE 38

TENSILE DATA OF DPT AND PEEL SPECIMENS WITH DIFFERENT LINERS AND FC-2202 PROPELLANT*

Liner No.	1a	1b	2a	2b	3a	4a	4b	5a
DPT (psi)	51.7	58.5	17.8	19.7	--	73.4	92.4	--
Peel (psi)	2.2	3.1	10.3	9.9	5.7	12.6	13.3	9.1

* For specimens 1a, b propellant No. 51-1800-1, for 2a, b and 3a propellant No. 51-1800-2, and for 4a, b and 5a propellant No. 51-1800-3 was used.

By far the best liner-propellant bond was obtained with FC-2202 liner, filled with ferric oxide (4a, b).

Besides the fillers, which are mentioned in Table 37, it was also tried to incorporate titanium dioxide and potassium titanate into FC-2202 binders. In spite of thorough drying at elevated temperatures, these fillers caused a soft cure and were eliminated as candidates for liner components.

V. CONCLUSIONS AND RECOMMENDATIONS

Binder: The FC-2202 prepolymer, Lot 5, is well suited as a propellant binder, since it responds normally to reaction with isocyanates, to conventional cure catalysts and to changes in crosslinker concentration. Low molecular weight ether-triols, like TP-340, are the most suitable crosslinkers, because they are soluble in FC-2202 and give elastomers with satisfactory and reproducible physical properties. For complete solubility of the curative a fluorocarbon plasticizer is required as a cosolvent (20% for FC-9). HDI is most soluble in such a mixture; but HDI/TDI mixtures are tolerable, if the TDI concentration is not too high. In presence of cure catalyst at 60°C, HDI is immediately soluble, but a HDI/TDI mixture of 80:20 (eq. ratio) requires only about one minute to become soluble. FeAA/HAA is a good catalyst system for such binders, for the catalyst activity can be easily adjusted by both changes in the FeAA/HAA ratio and absolute concentration.

Propellants:

a. Processability: For propellants with 82% solids and higher, processing aids are absolutely necessary. Wetting agents were not suitable, because they yielded propellants with inferior physical properties or prevented propellant cure altogether. Certain types of bonding agents, like FC-156, however, are eminently suited. Not only did they make possible processing of 86% solids propellants, but also improved physical properties.

For lowest viscosities one should also use bi- or trimodal AP blends with optimal compositions as recommended by R. J. Farris.(6) An 86% solids (83.7 vol.%) propellant with a trimodal Farris blend was still castable; one propellant with 88% was no longer castable, but a castable 87% solids propellant is still feasible. No optimization was attempted, and adjustments in bonding agent concentration, etc., should still result in improvements.

b. Physical Properties: Though physical properties of propellants with CD-blend and all HDI were satisfactory, those with a trimodal blend were somewhat short in elongation. Substantial improvements could be achieved with HDI/TDI blends with TDI concentration as low as 20 eq.%, but at the expense of a longer cure time, which may result in larger variations of physical properties. Better reproducibility may be obtained with an all HDI/CD-blend propellant. Elongations were better than 25% with minibones from 50g batches, and may further improve with larger batches and when measured with full-size Instron bars, as was the case with scaled-up propellants with a trimodal blend and an HDI/TDI mixture (80:20). Optimized concentrations of bonding agent FC-156, or bonding agents FC-201 and FC-202 may help to obtain still better elongations with high tensile strengths.

Density measurements of the scaled-up, cured propellant indicated that there is only a minimal cure shrinkage, which may be attributed to the presence of the FC-9 plasticizer; if so, then the plasticizer is not only beneficial in making the curative compatible, but also in preventing serious cure-shrinkage.

c. Ballistics: Ballistic properties of the FC-2202 propellants seem to vary with the type of restriction used on burning rate strands and might not represent those found in a motor.

Data from 1/2" diameter burning rate strands, coated with Viton A and epoxy resin show a burning rate of 0.082 ips at 200 psia and n = 0.80 for an 82% CD-blend FC-2202 propellant and 0.076 ips and n = 1.00 for an 82% trimodal Farris blend. The results are in favor of the CD-blend. However, it is felt that reliable ballistic data for this type of propellant can be obtained only from motor firings. Therefore, the Farris trimodal blend was used for better processability.

d. Liners: It is possible to obtain a good liner-propellant bond with FC-2202 propellant. The best tensile strengths (73.4 psi without and 92.4 psi with washcoat in double plate tensile tests and 12.6 and 13.3 psi respectively in peel tests) were found with a liner consisting of TP-340/FC-156/FC-9/FC-2202/HDI/FeAA/HAA and containing 30% iron oxide.

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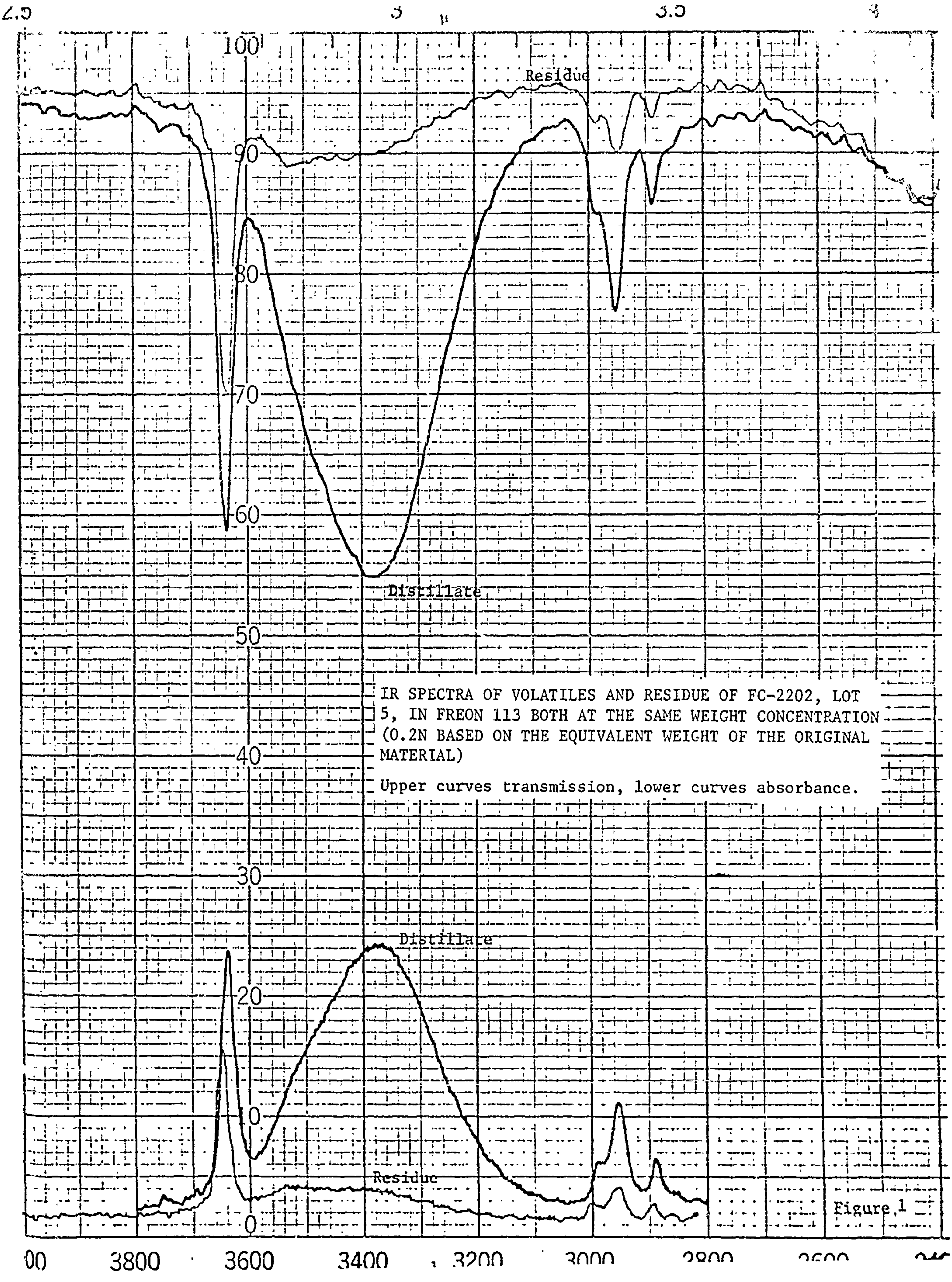
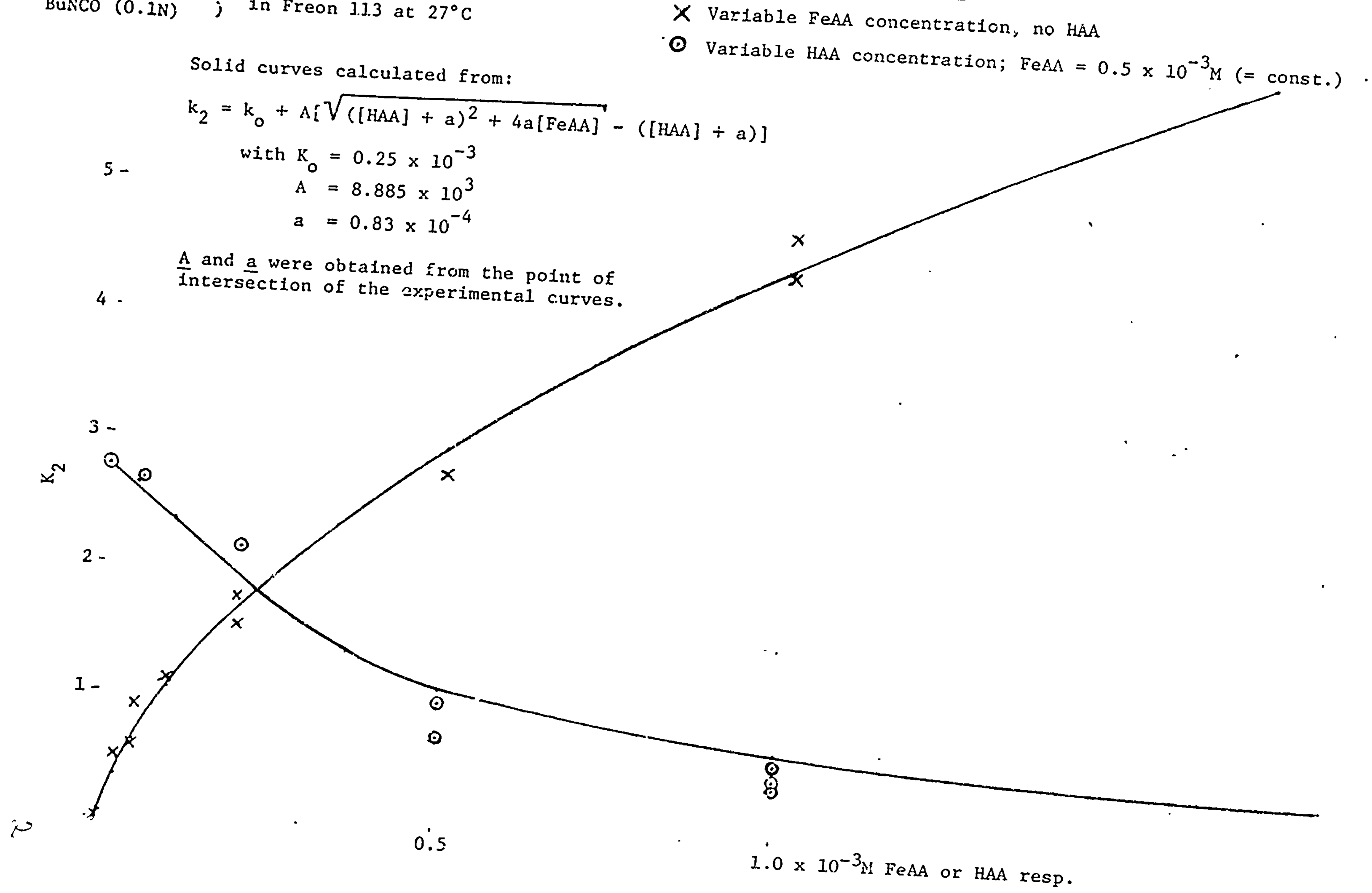


IR SPECTRA OF VOLATILES AND RESIDUE OF FC-2202, LOT 5, IN FREON 113 BOTH AT THE SAME WEIGHT CONCENTRATION (0.2N BASED ON THE EQUIVALENT WEIGHT OF THE ORIGINAL MATERIAL)

Upper curves transmission, lower curves absorbance.

Figure 1

THE FeAA/HAA SYSTEM WITH FC-2202/BUTYLISOCYANATE



FC-2202 (0.2N))
BuNCO (0.1N)) in Freon 113 at 27°C

× Variable FeAA concentration, no HAA

⊙ Variable HAA concentration; FeAA = 0.5×10^{-3}M (= const.)

Solid curves calculated from:

$$k_2 = k_o + A[\sqrt{([HAA] + a)^2 + 4a[FeAA]} - ([HAA] + a)]$$

with $K_o = 0.25 \times 10^{-3}$

$A = 8.885 \times 10^3$

$a = 0.83 \times 10^{-4}$

A and a were obtained from the point of intersection of the experimental curves.

STRESS DECAY AS FUNCTION OF CHAIN LENGTH BETWEEN CROSSLINKS
FOR FC-2202 AND PPG ELASTOMERS

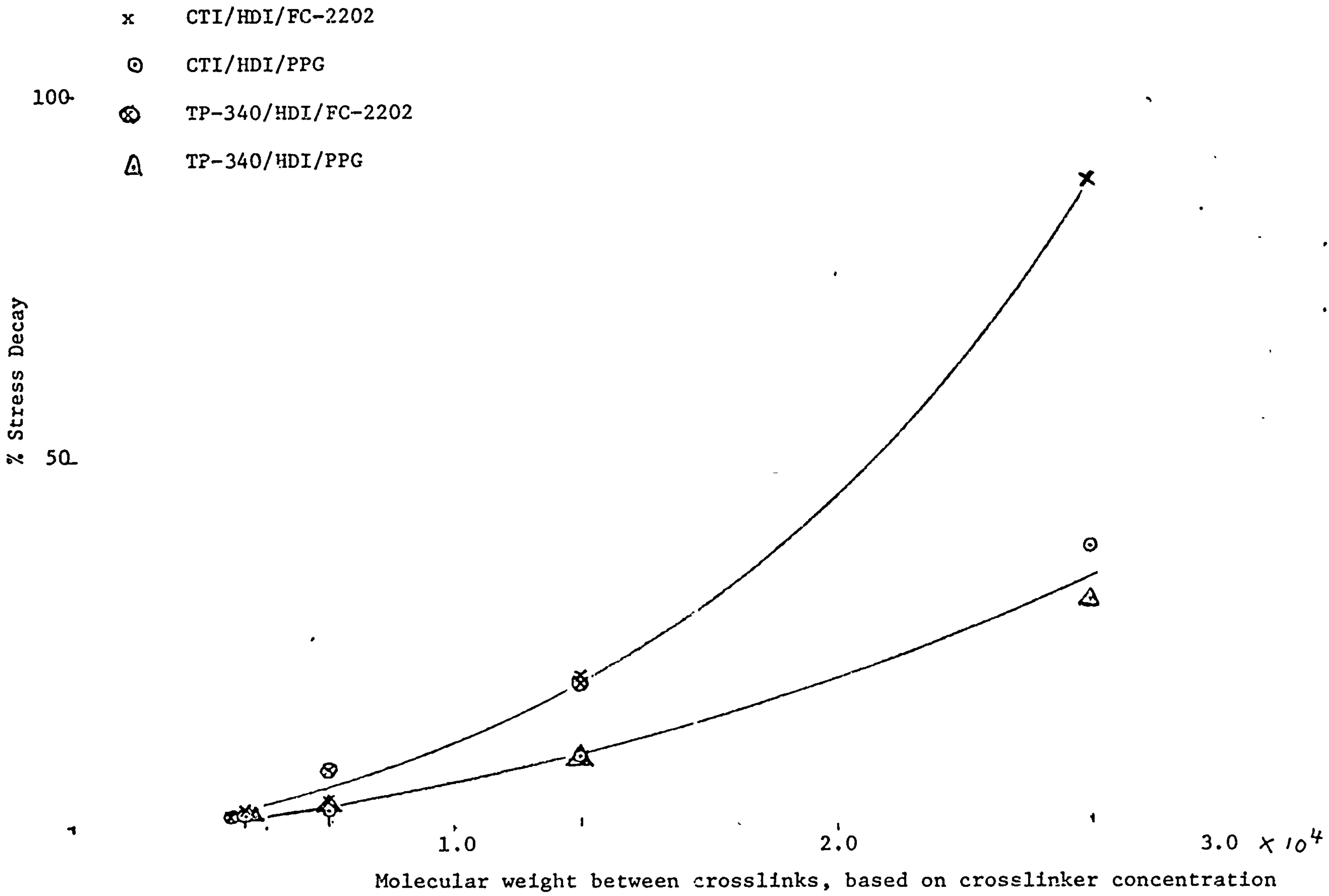


Figure 3

STRESS DECAY AS FUNCTION OF EQUILIBRIUM
MODULUS (CORRECTED FOR EXTRACTABLES)

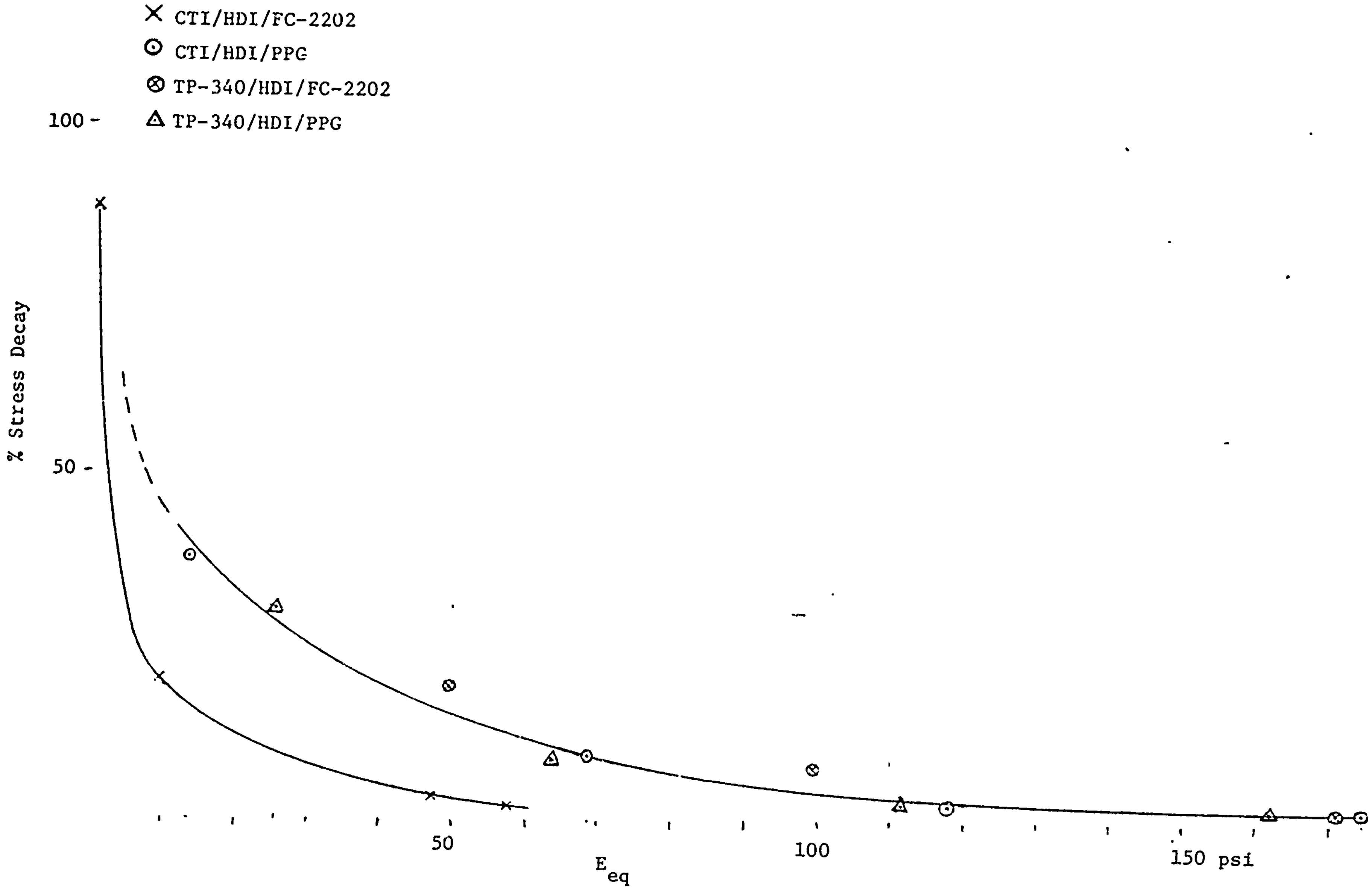


Figure 4

EQUILIBRIUM MODULUS OF FC-2202 AND PPG ELASTOMERS
AS A FUNCTION OF CROSSLINKER CONCENTRATION

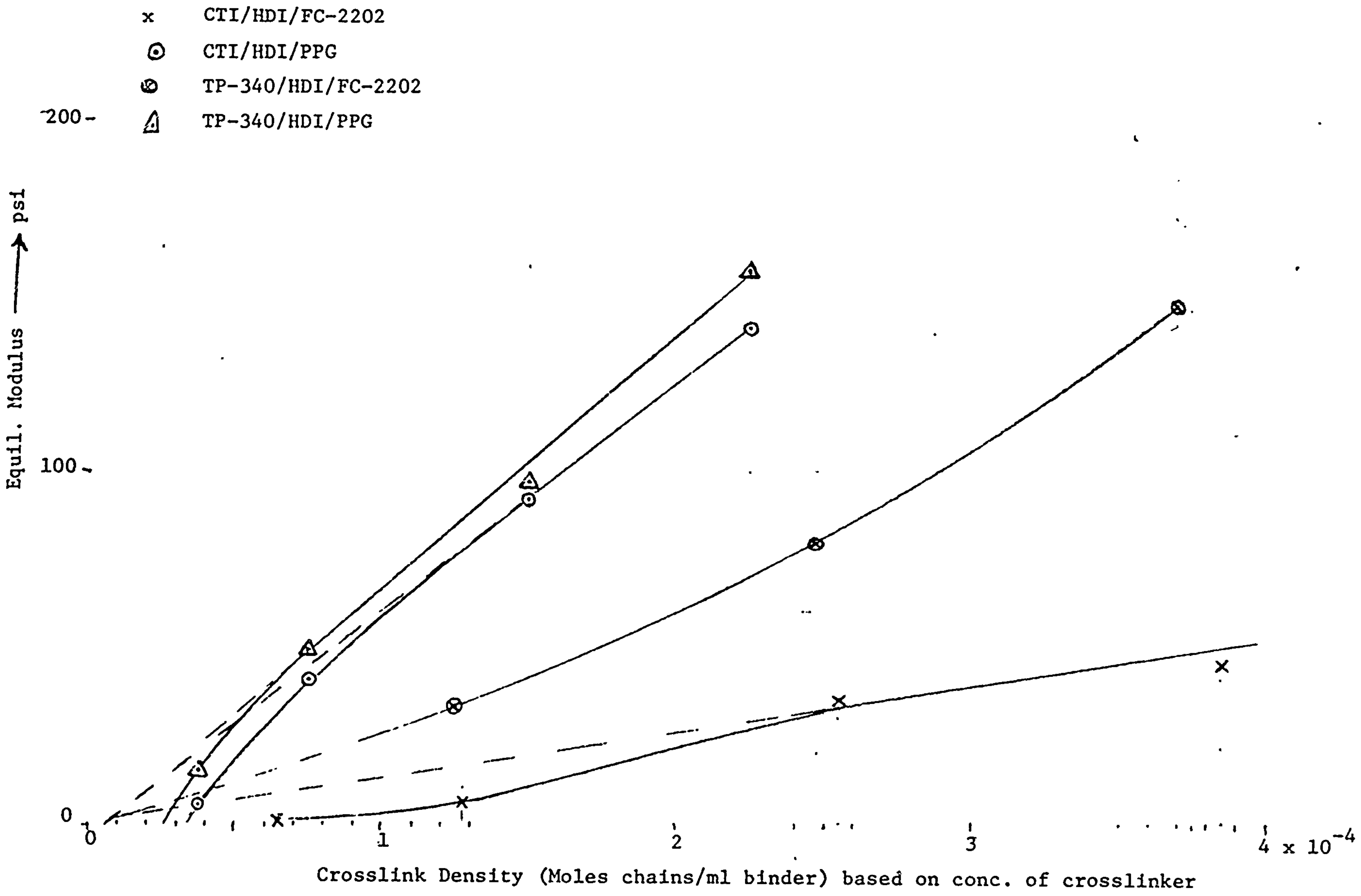


Figure 5

COMPARISON OF THEORETICAL CROSSLINK DENSITY (FROM CROSSLINKER CONCENTRATION) AND CROSSLINK DENSITY AS OBTAINED FROM EQUILIBRIUM MODULUS AND CORRECTED FOR EXTRACTABLES FOR FC-2202 AND PPG BINDER

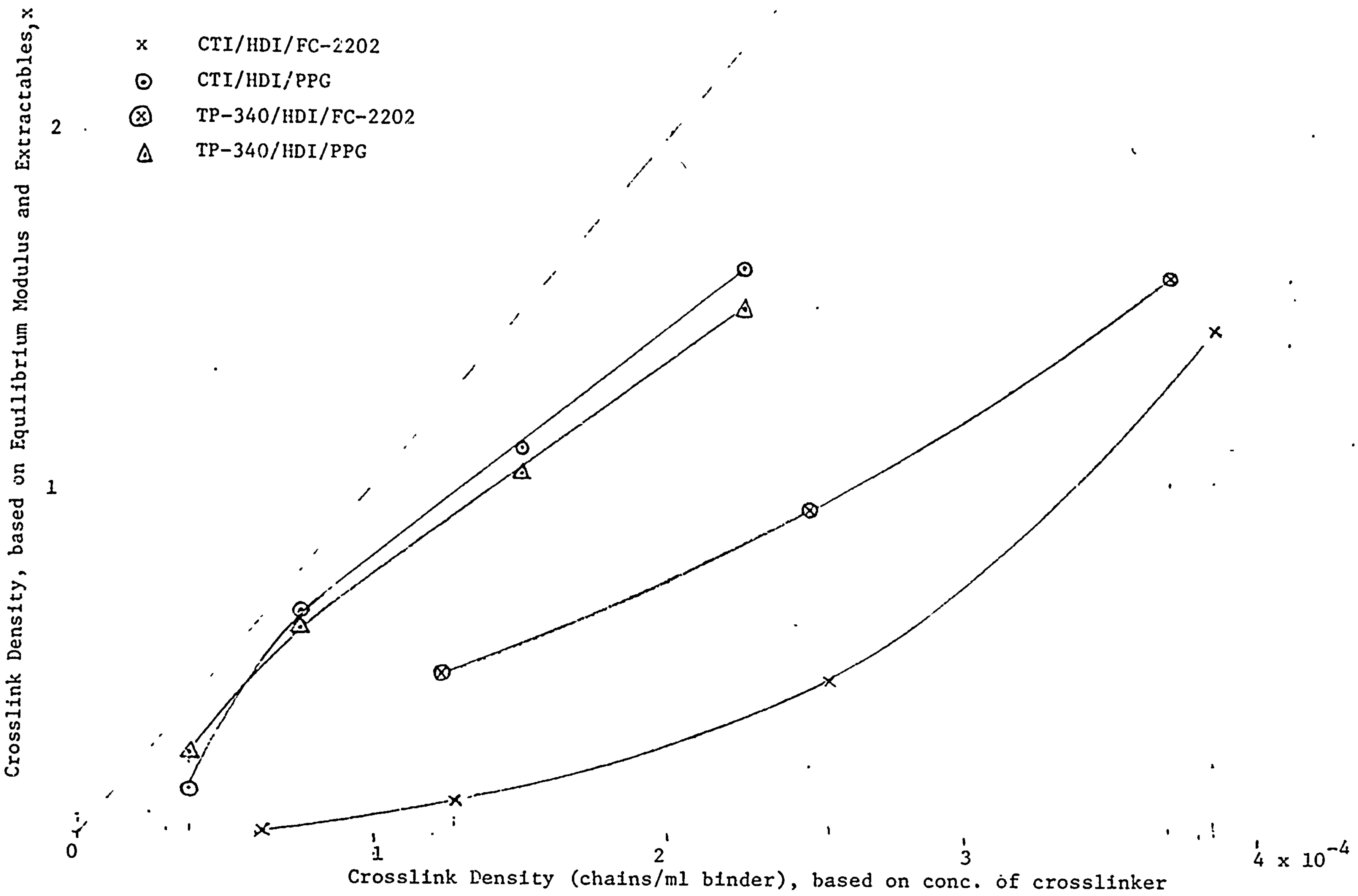


Figure 6

EXTRACTABLES AS FUNCTION OF CROSSLINK DENSITY FOR FC-2202
AND PPG ELASTOMERS

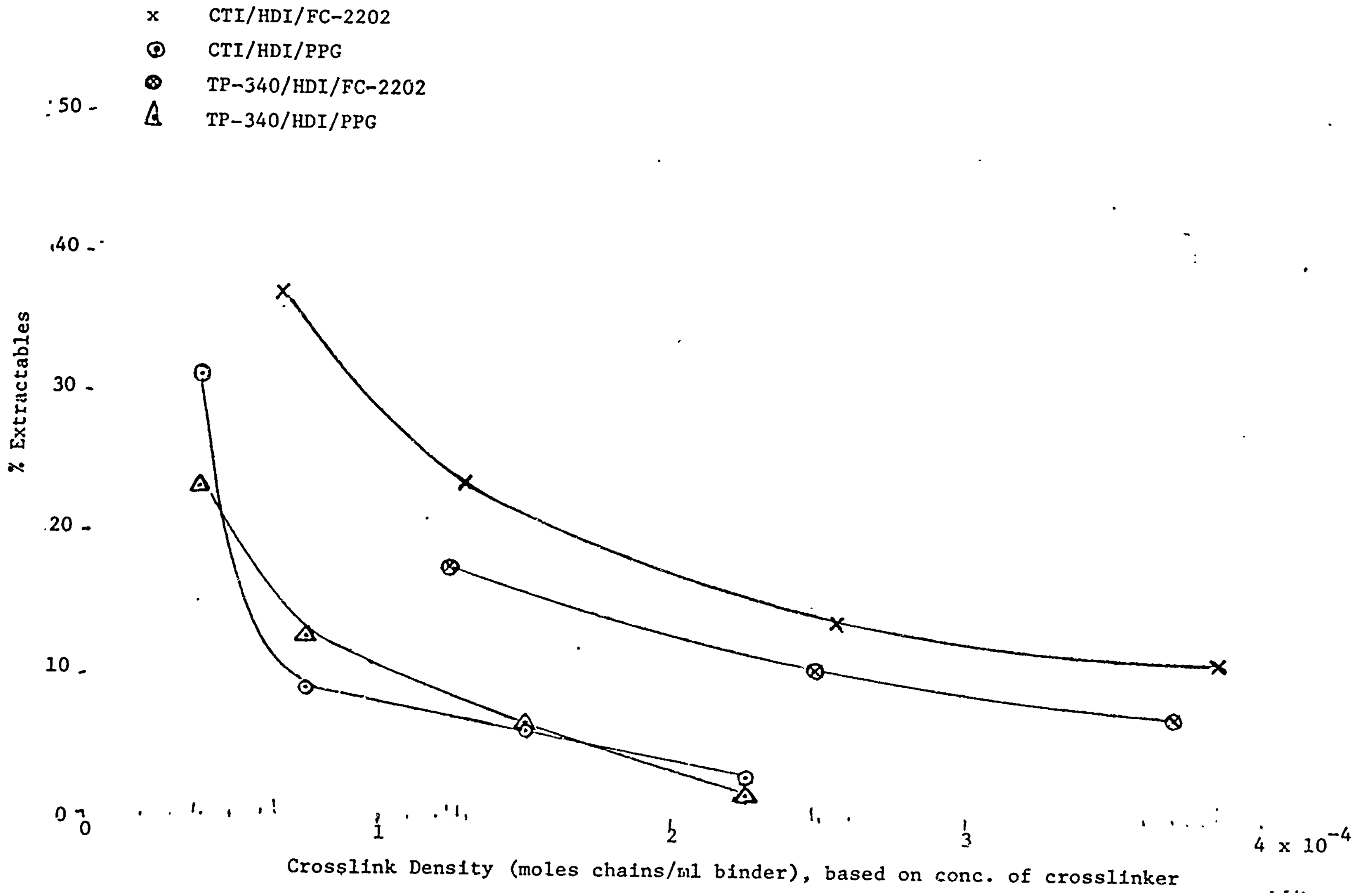


Figure 7

EXTRACTABLES AS FUNCTION OF EQUILIBRIUM MODULUS

(Corrected for Extractables)

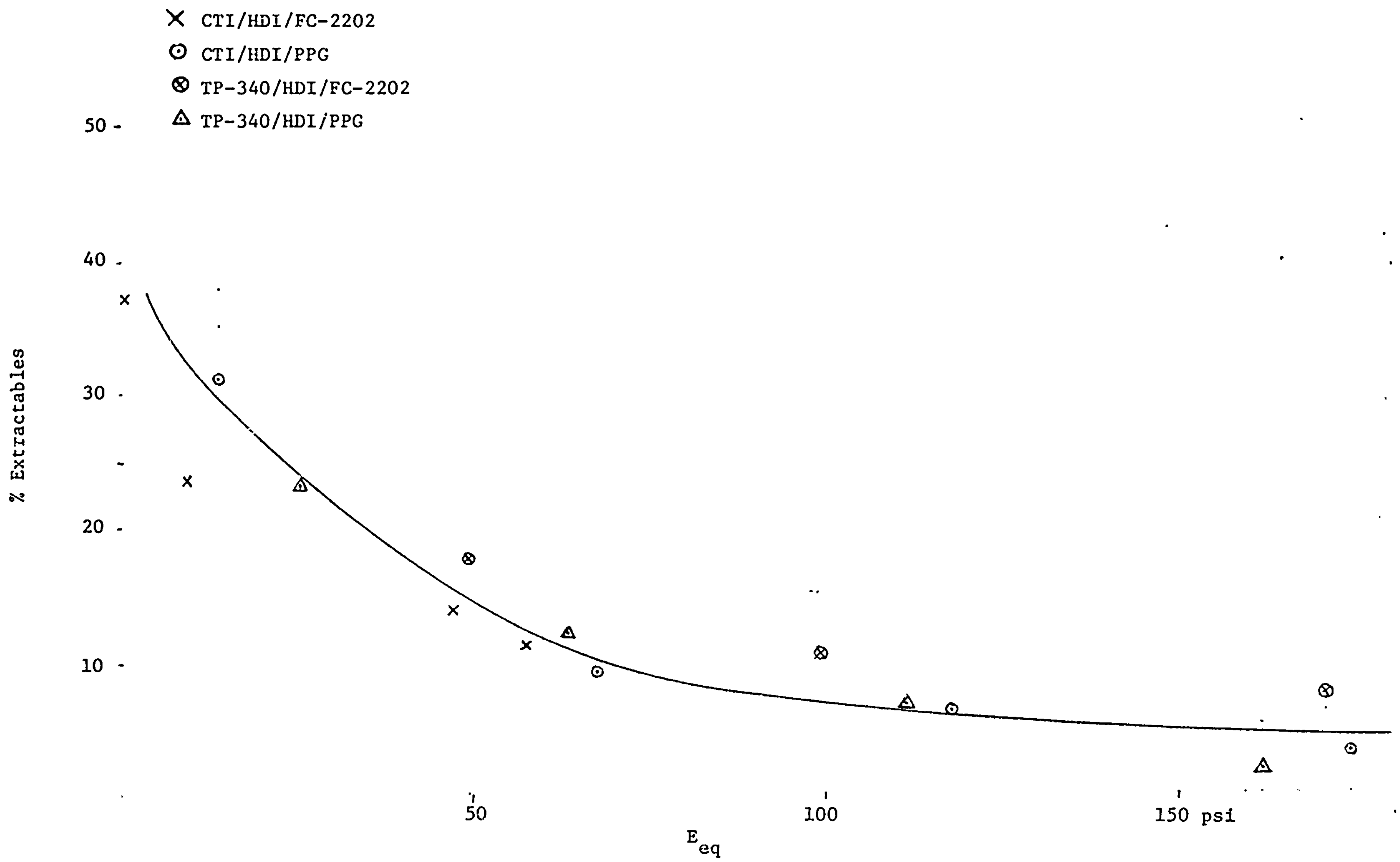


Figure 8

RUBBER FRACTION IN SWOLLEN RUBBER (v_2) FOR FC-2202 AND PPG ELASTOMERS, SWOLLEN IN FREON 113 AND BENZENE RESPECTIVELY, AS FUNCTION OF CROSSLINKER CONCENTRATION

Points in parentheses are corrected for extractables ($1 - v_o$)

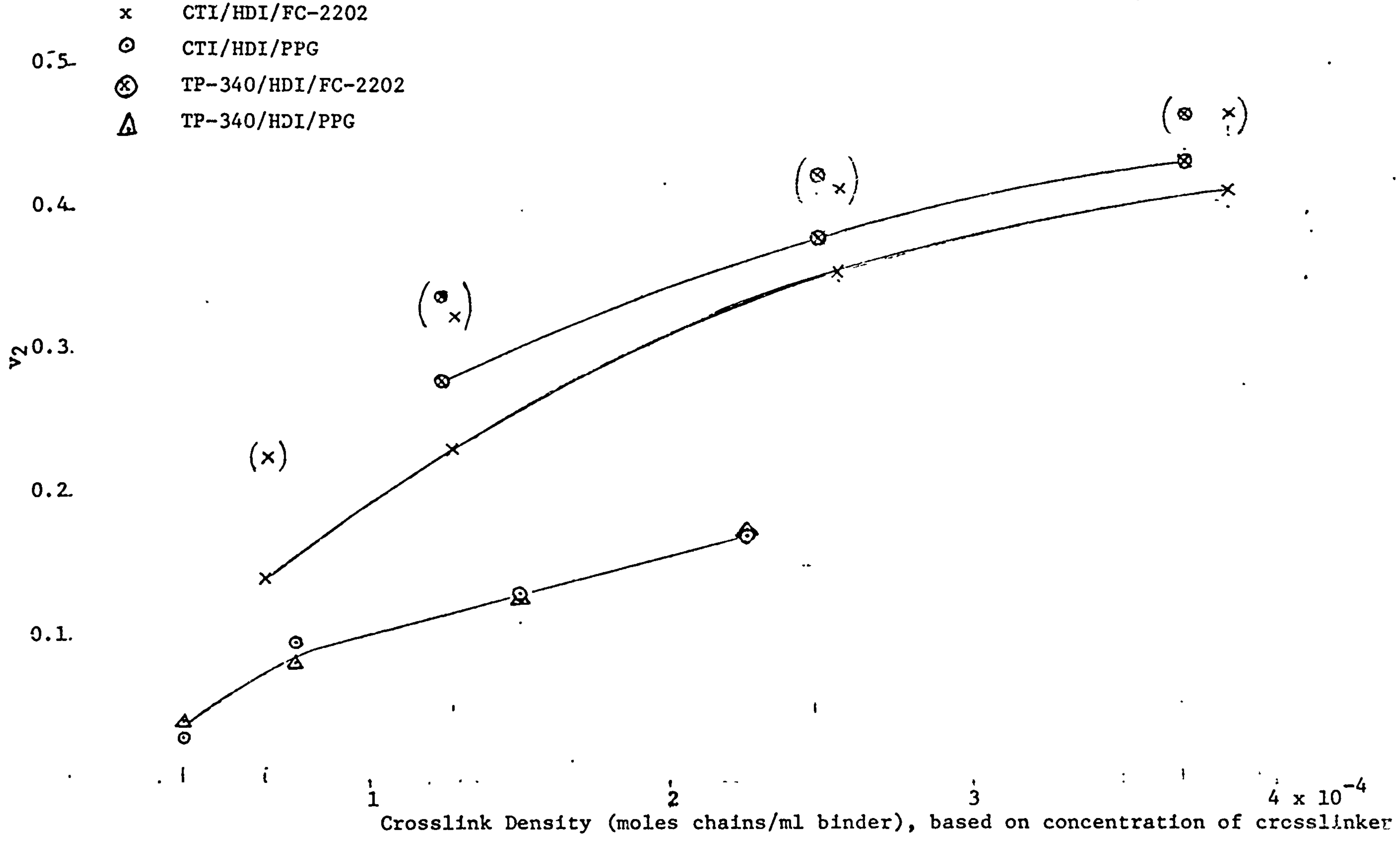


Figure 9

INITIAL MODULUS OF PLASTICIZED FC-2202 BINDERS AS FUNCTION OF CROSSLINKER CONCENTRATION

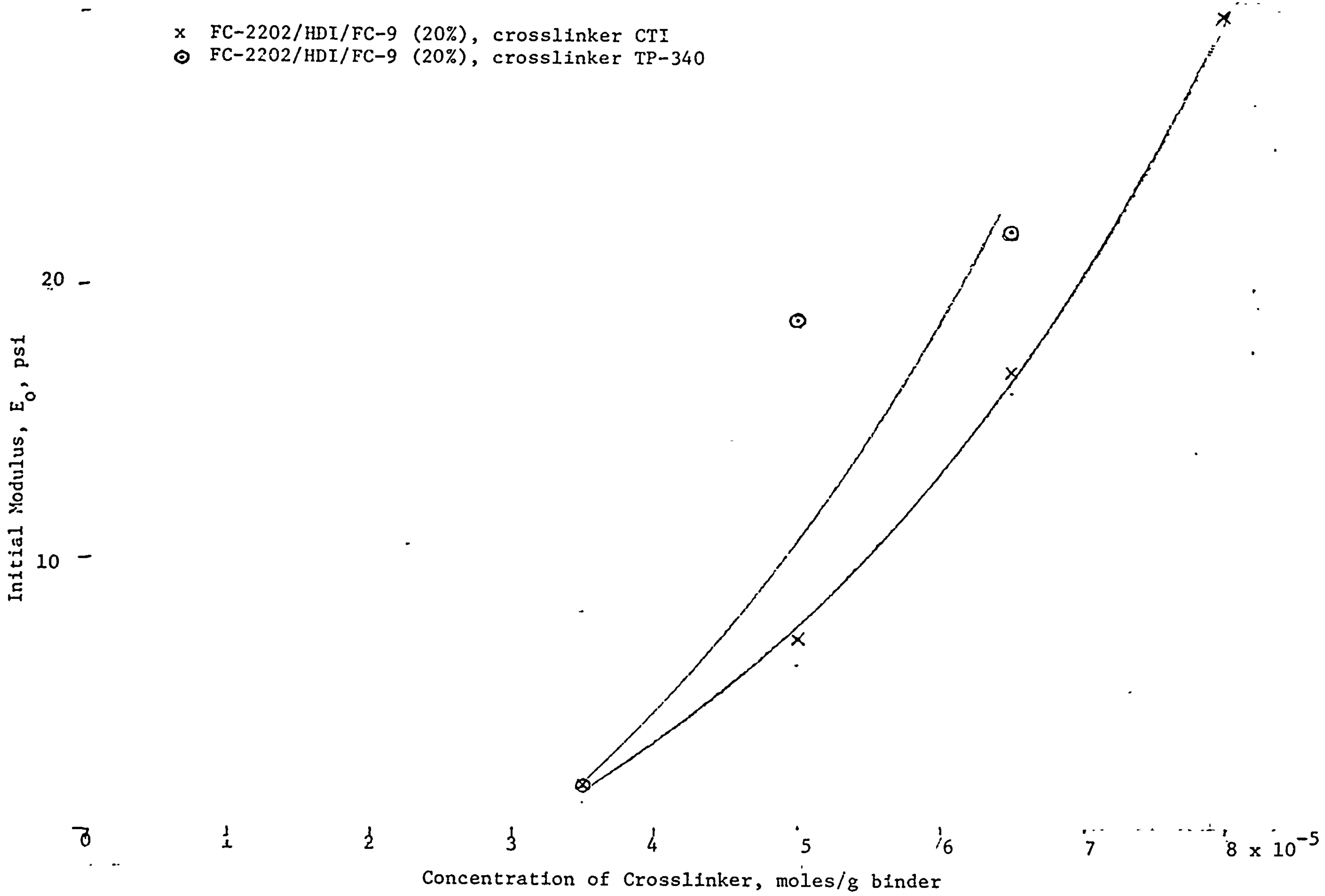
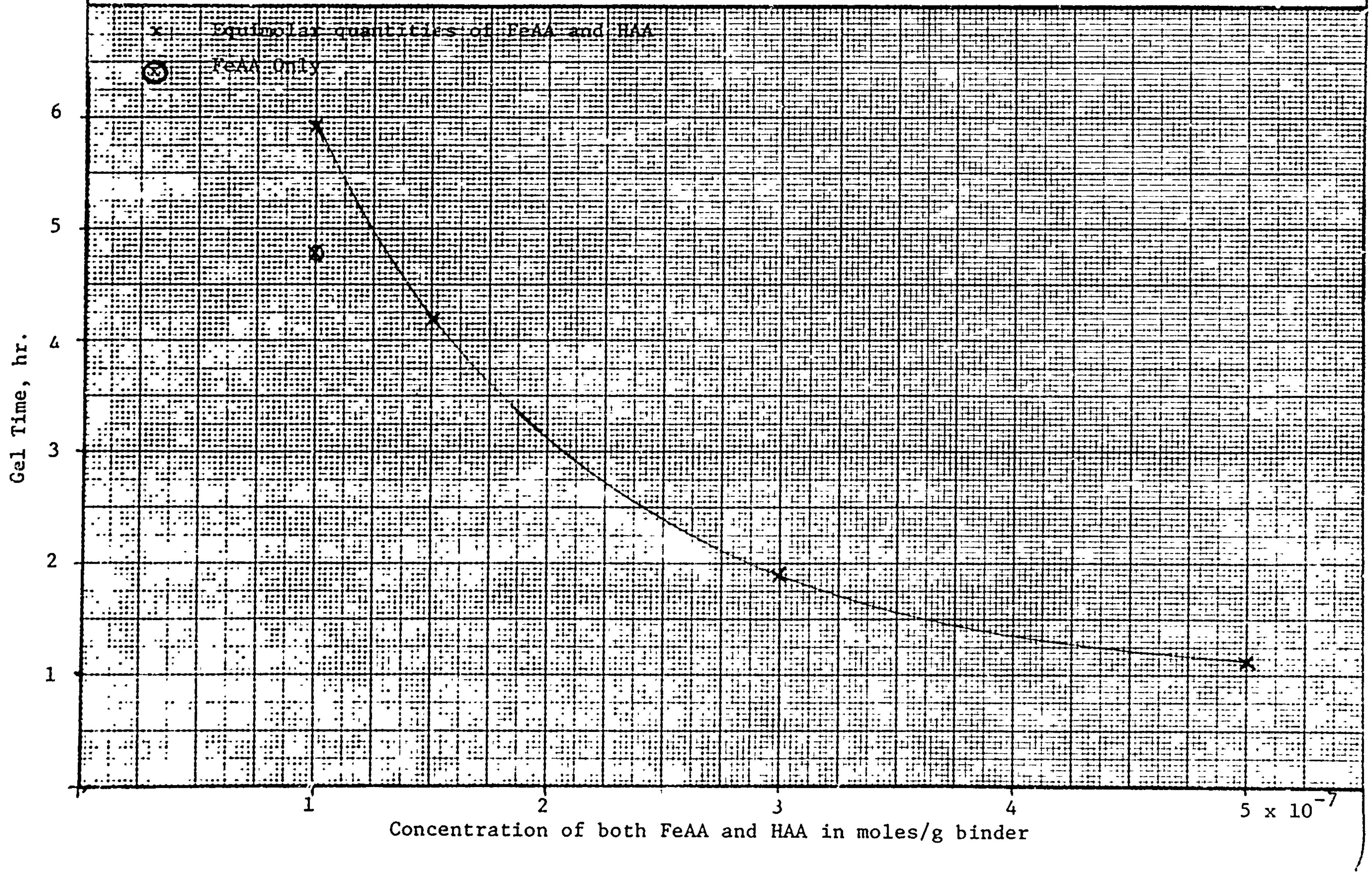


Figure 10

(title block)

GEL TIME OF A TP-340/HDI/FC-2202/FC-9 (20%)
BINDER AS A FUNCTION OF FeAA AND HAA CONCENTRATION



10 x 10 to the centimeter

Figure 11

VISCOSITY BUILDUP OF FC-2202 PROPELLANTS WITH 78.2 WT% AP
(75 vol. %) AT 110°F

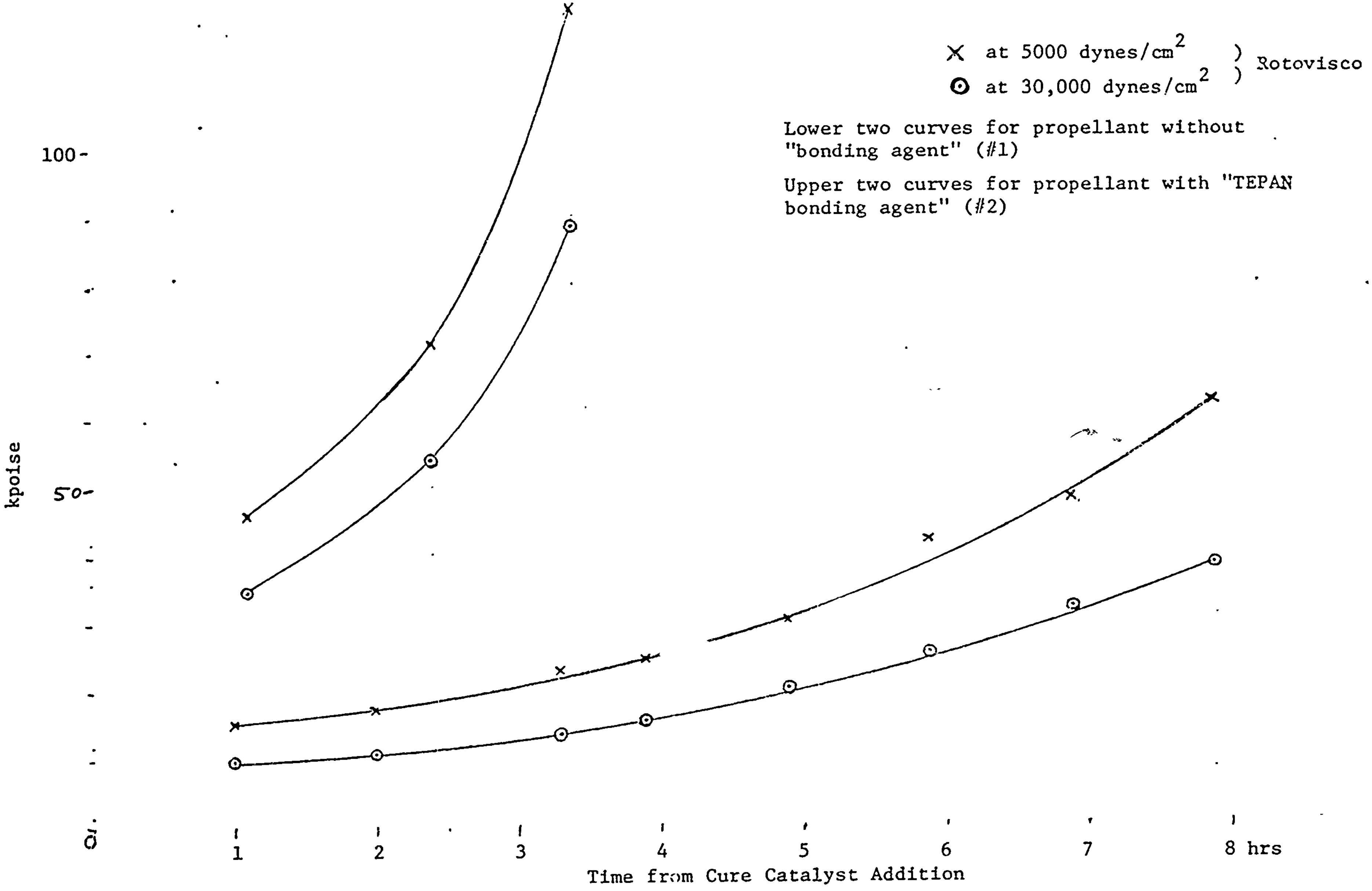


Figure 12

VISCOSITY BUILD-UP OF A FC-2202 PROPELLANT WITH
82 WT% AP AT 110°F

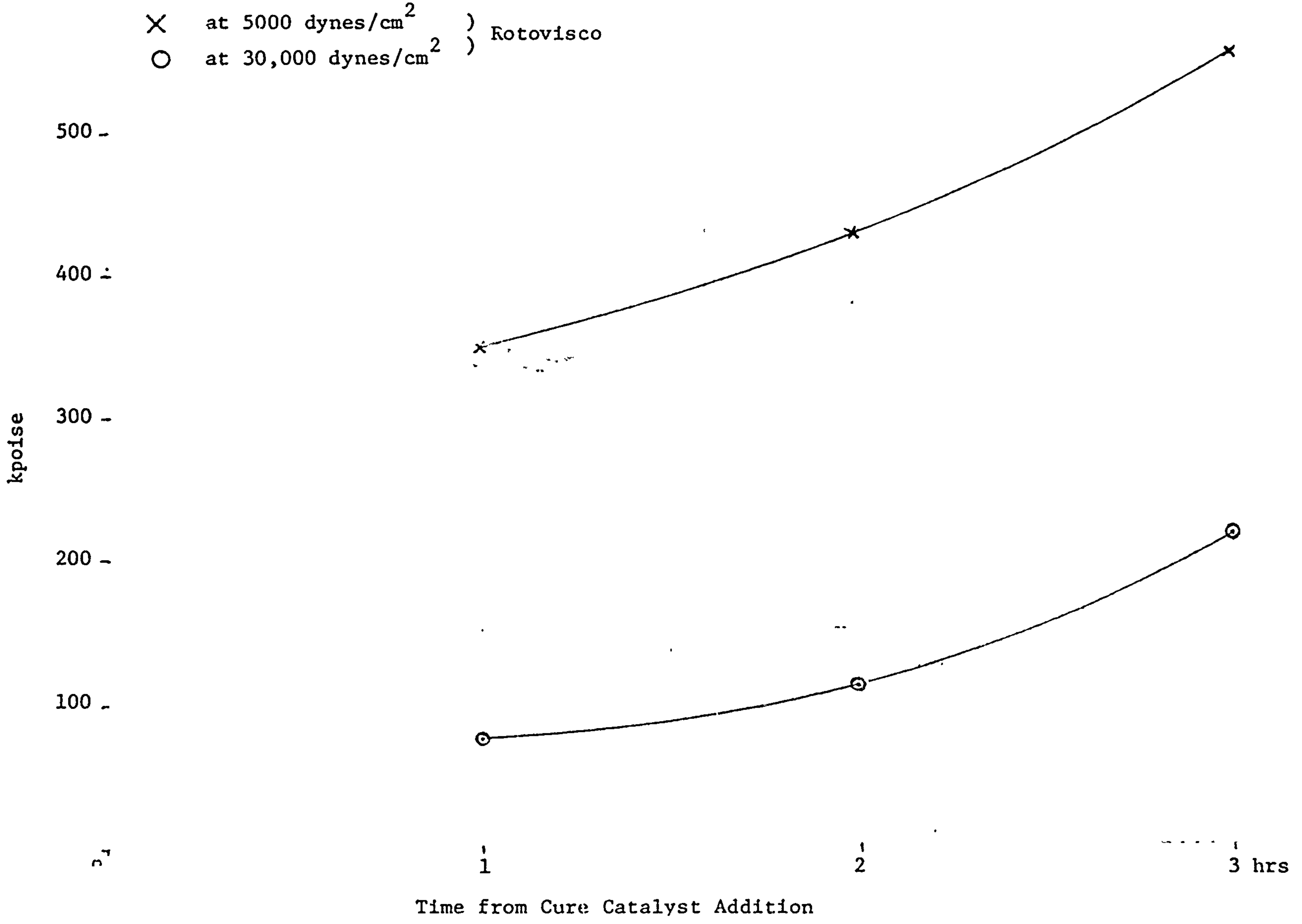


Figure 13

VISCOSITY BUILDUP OF A FC-2202 PROPELLANT
WITH 82 wt. % AF and 0.5% WETTING AGENT FC-194 AT 110°F

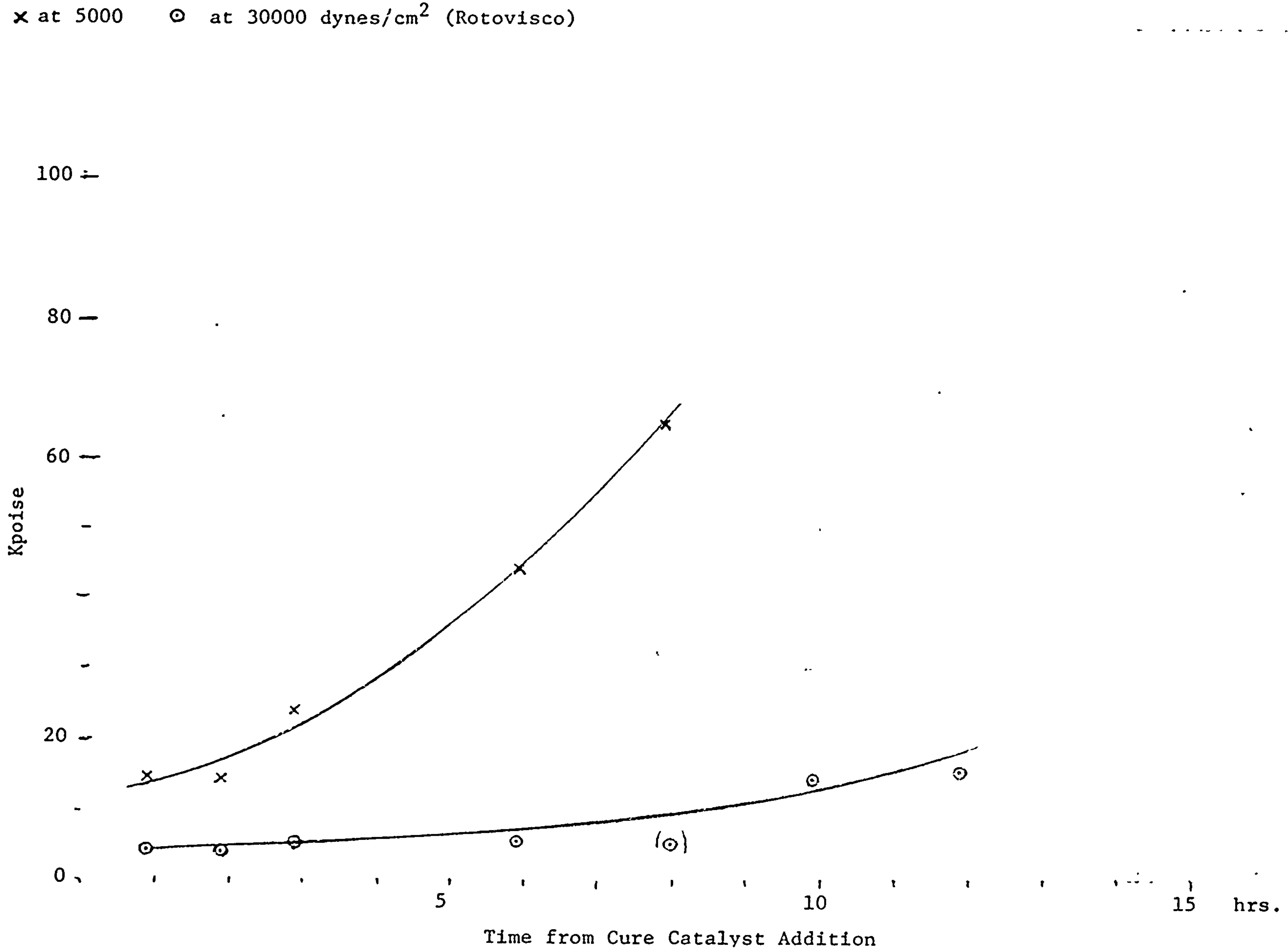
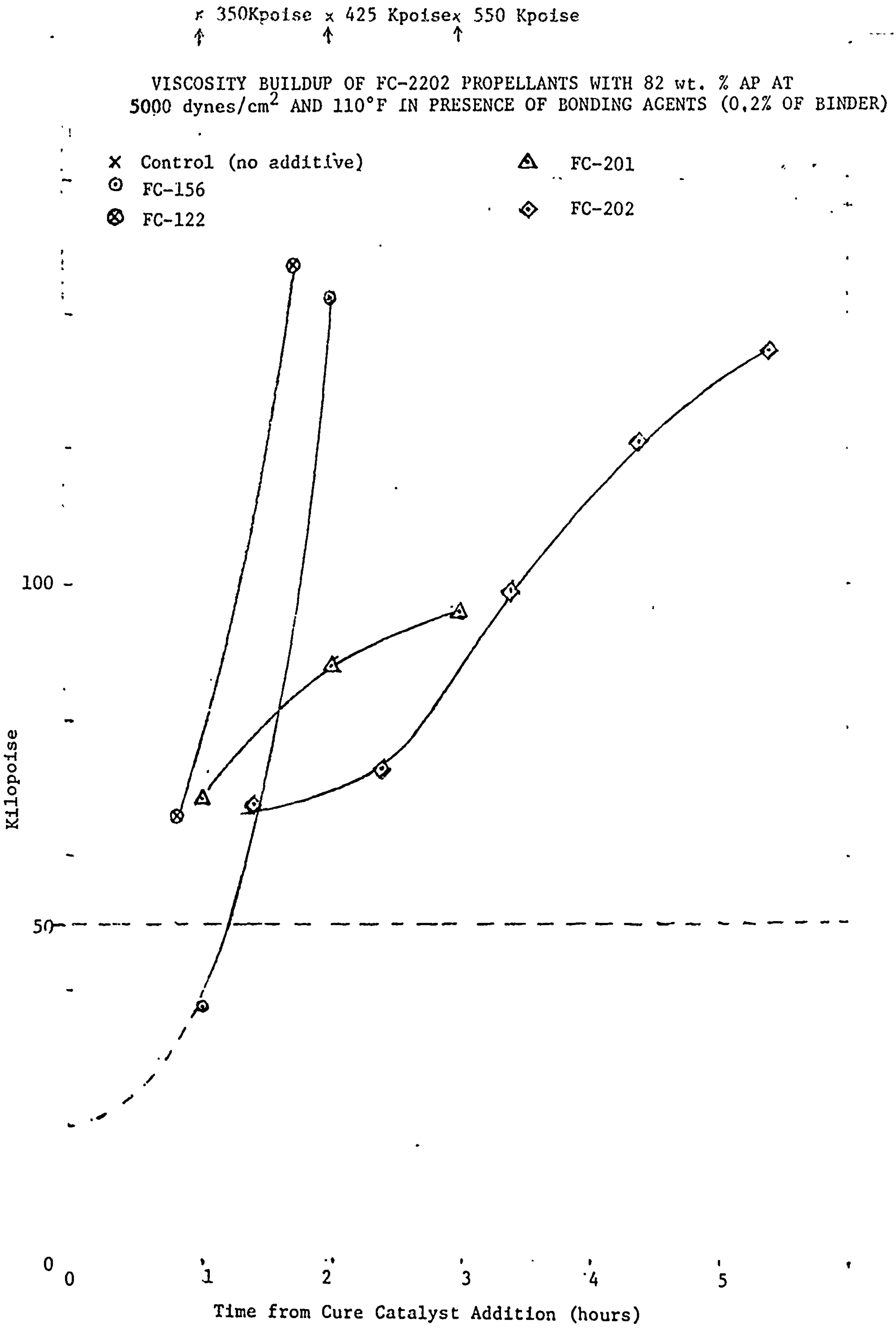


Figure 14



VISCOSITY BUILDUP OF FC-2202 PROPELLANTS WITH 82 wt. % AP AT 5000 dynes/cm^2 AND 110°F IN PRESENCE OF BONDING AGENTS (0.2% OF BINDER)

Figure 15

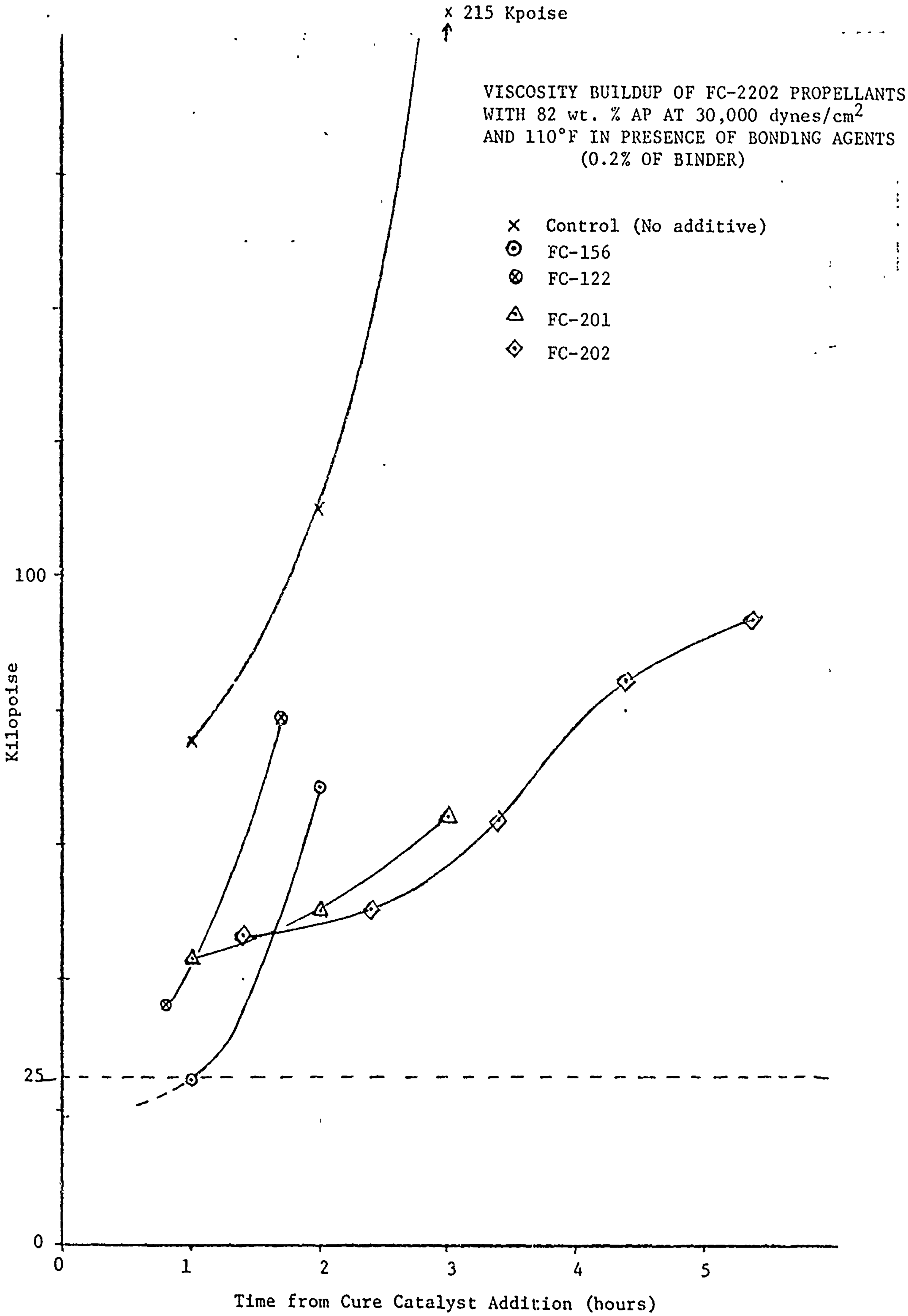
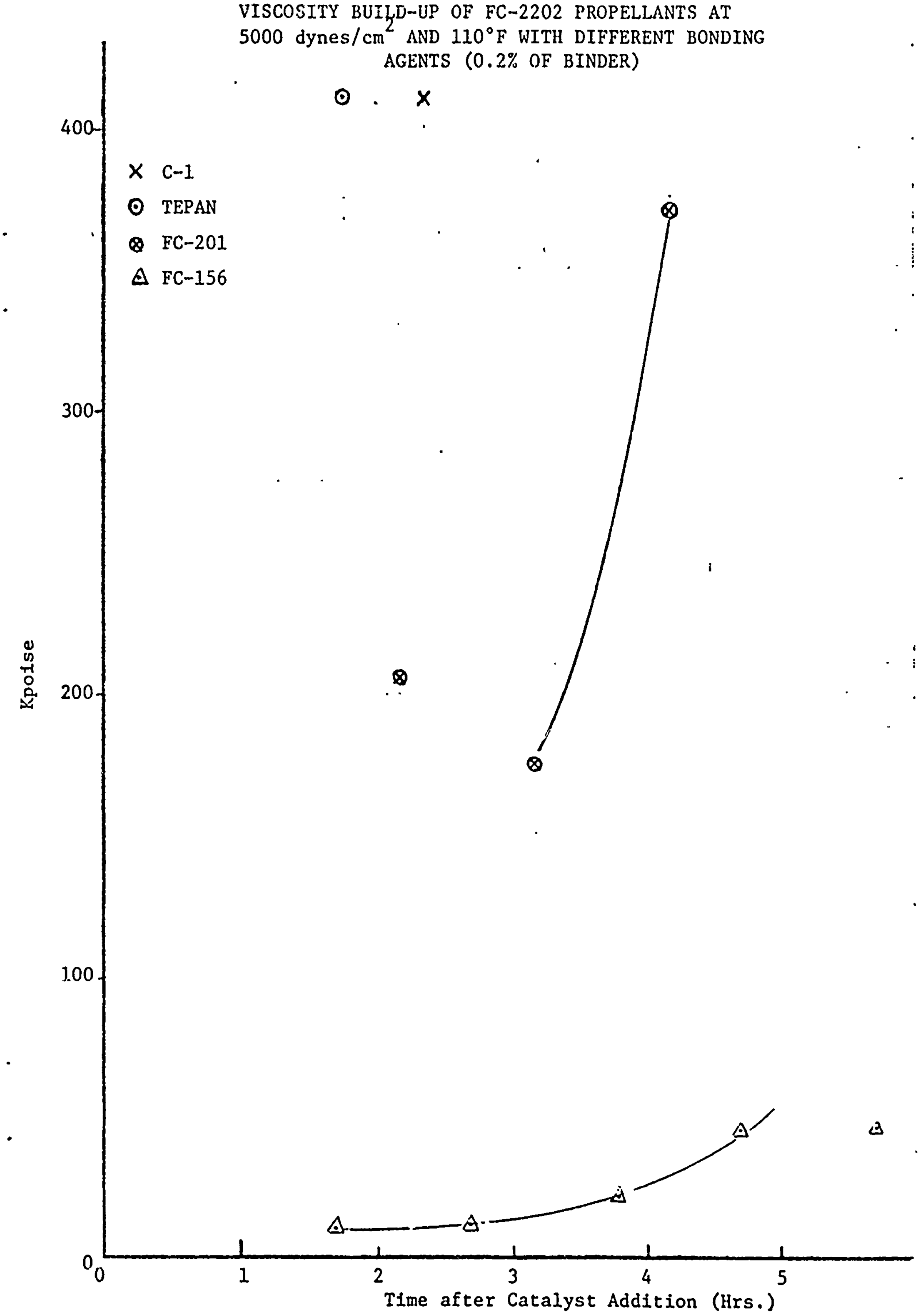

× 215 Kpoise
VISCOSITY BUILDUP OF FC-2202 PROPELLANTS WITH 82 wt. % AP AT 30,000 dynes/cm^2 AND 110°F IN PRESENCE OF BONDING AGENTS (0.2% OF BINDER)
× Control (No additive)
⊙ FC-156
⊗ FC-122
△ FC-201
◇ FC-202
Kilopoise
100
25
0
0
1
2
3
4
5
Time from Cure Catalyst Addition (hours)

Figure 16



VISCOSITY BUILD-UP OF FC-2202 PROPELLANTS AT 5000 dynes/cm^2 AND 110°F WITH DIFFERENT BONDING AGENTS (0.2% OF BINDER)

Figure 17

VISCOSITY BUILDUP OF FC-2202 PROPELLANTS AT
30000 dynes/cm^2 AND 110°F WITH DIFFERENT BONDING
AGENTS (0.2% OF BINDER)

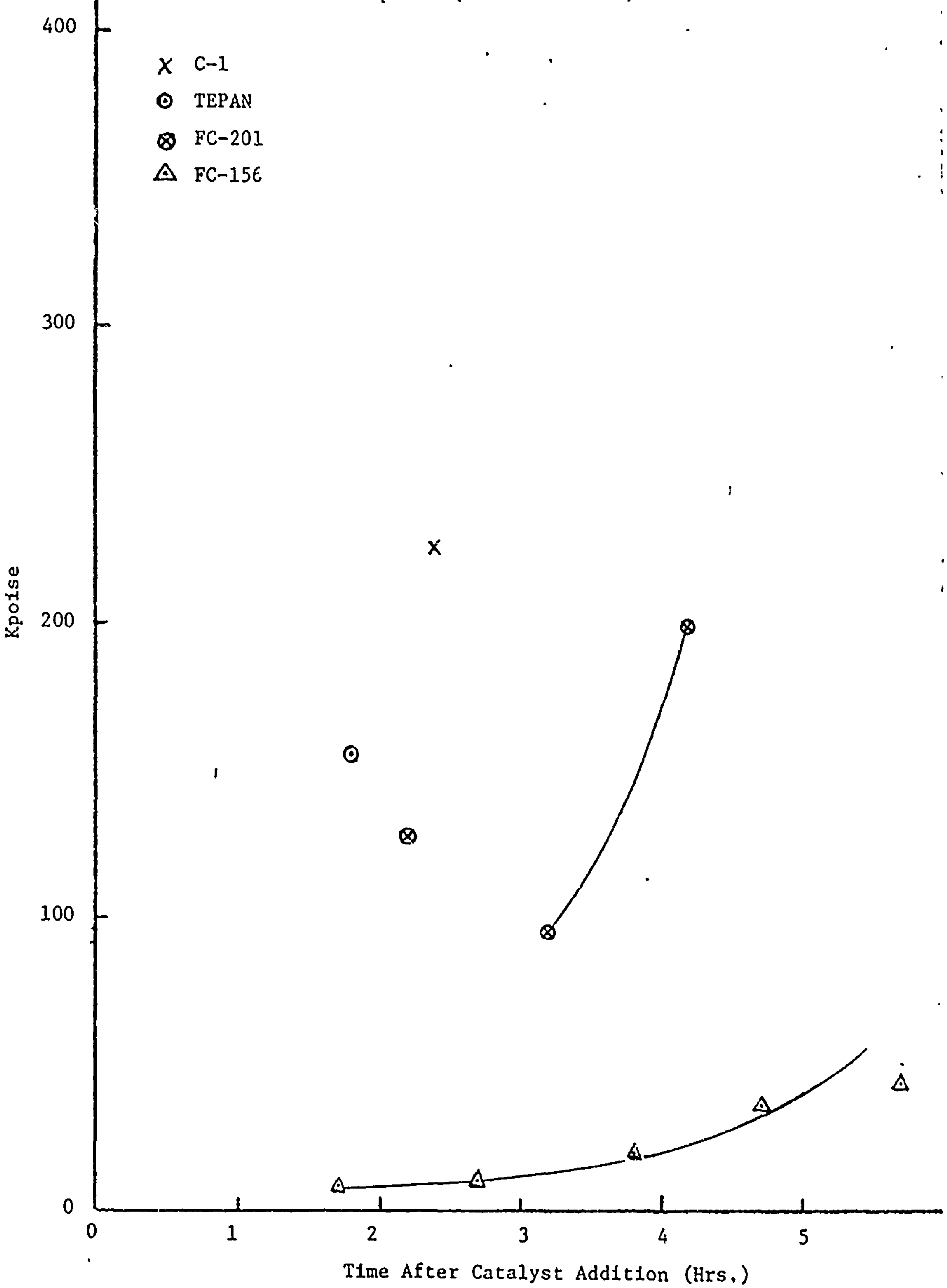
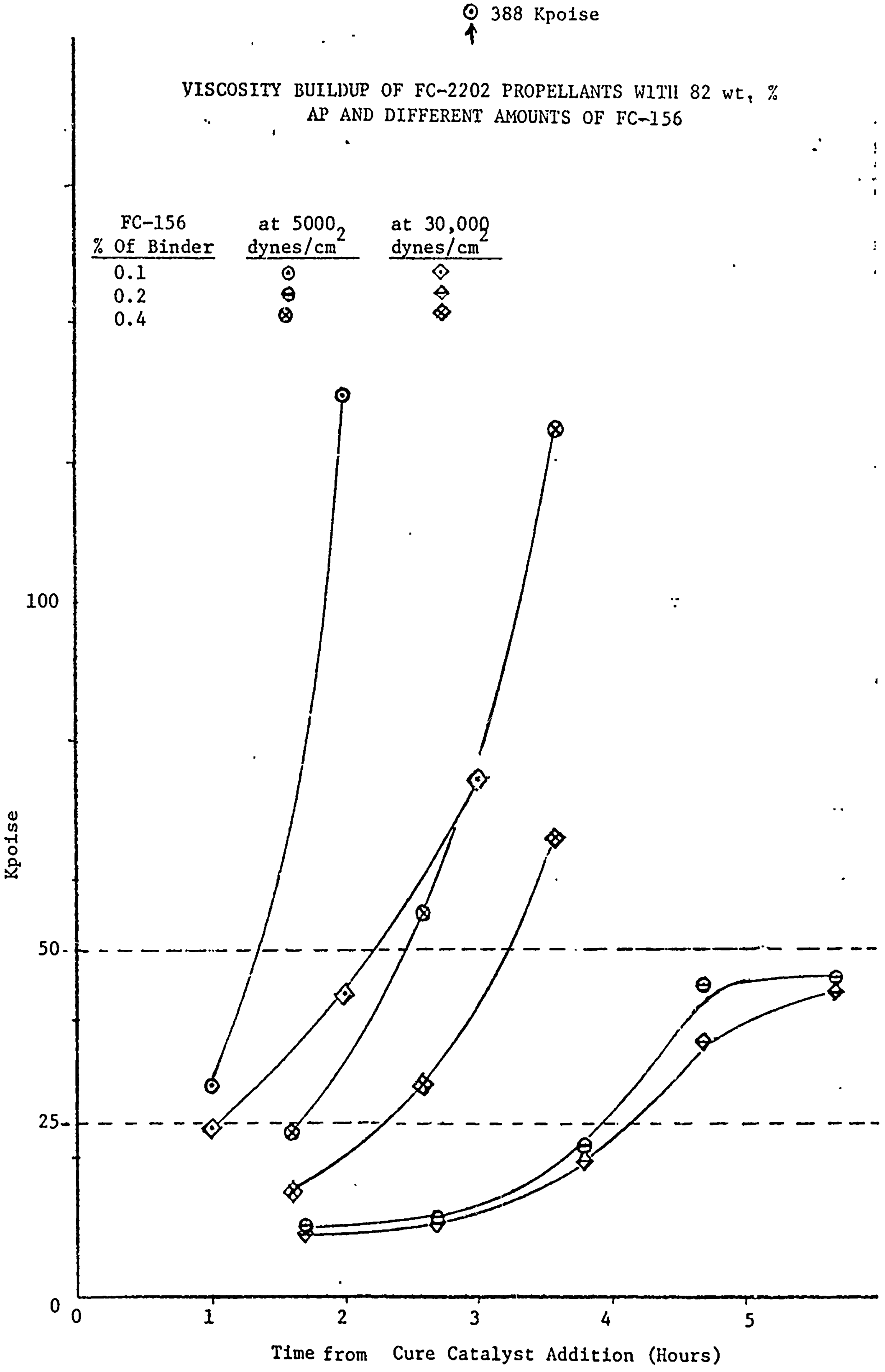
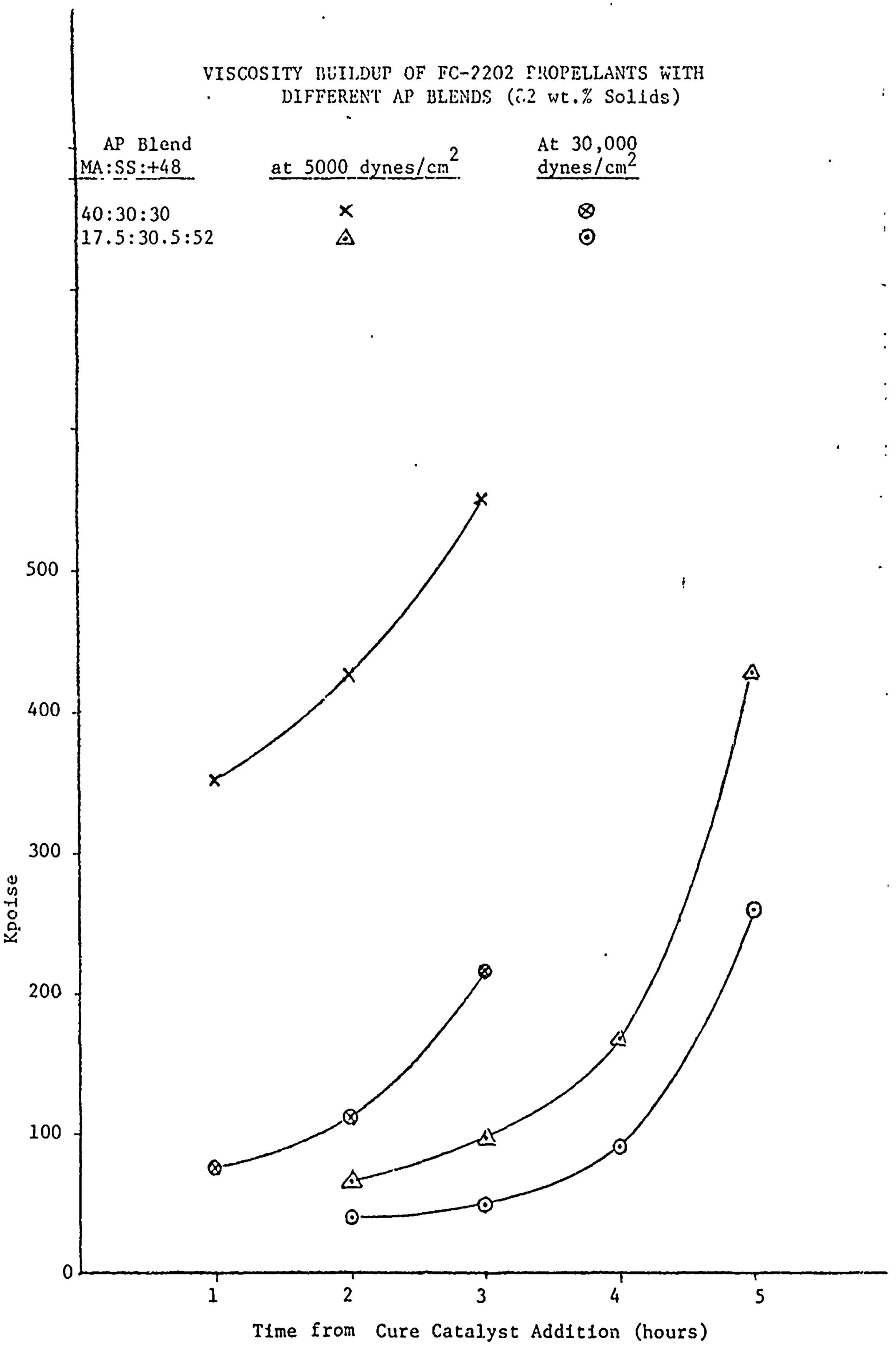


Figure 18



VISCOSITY BUILDUP OF FC-2202 PROPELLANTS WITH 82 wt, % AP AND DIFFERENT AMOUNTS OF FC-156

Figure 19



VISCOSITY BUILDUP OF FC-2202 PROPELLANTS WITH DIFFERENT AP BLENDS (82 wt.% Solids)

Figure 20

VISCOSITY BUILDUP OF FC-2202 PROPELLANTS WITH DIFFERENT SOLIDS AT 5000 dynes/cm² AND 110°F

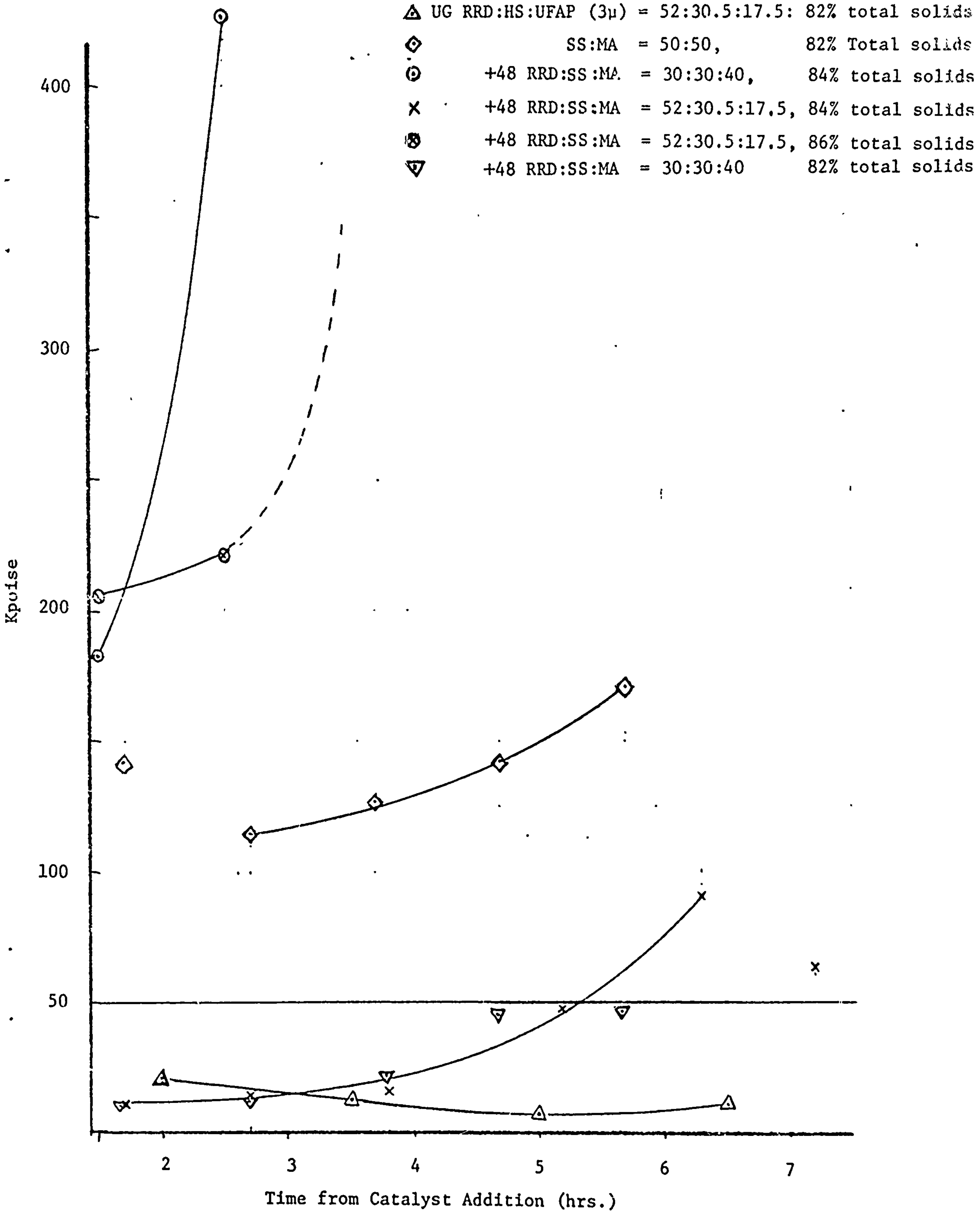
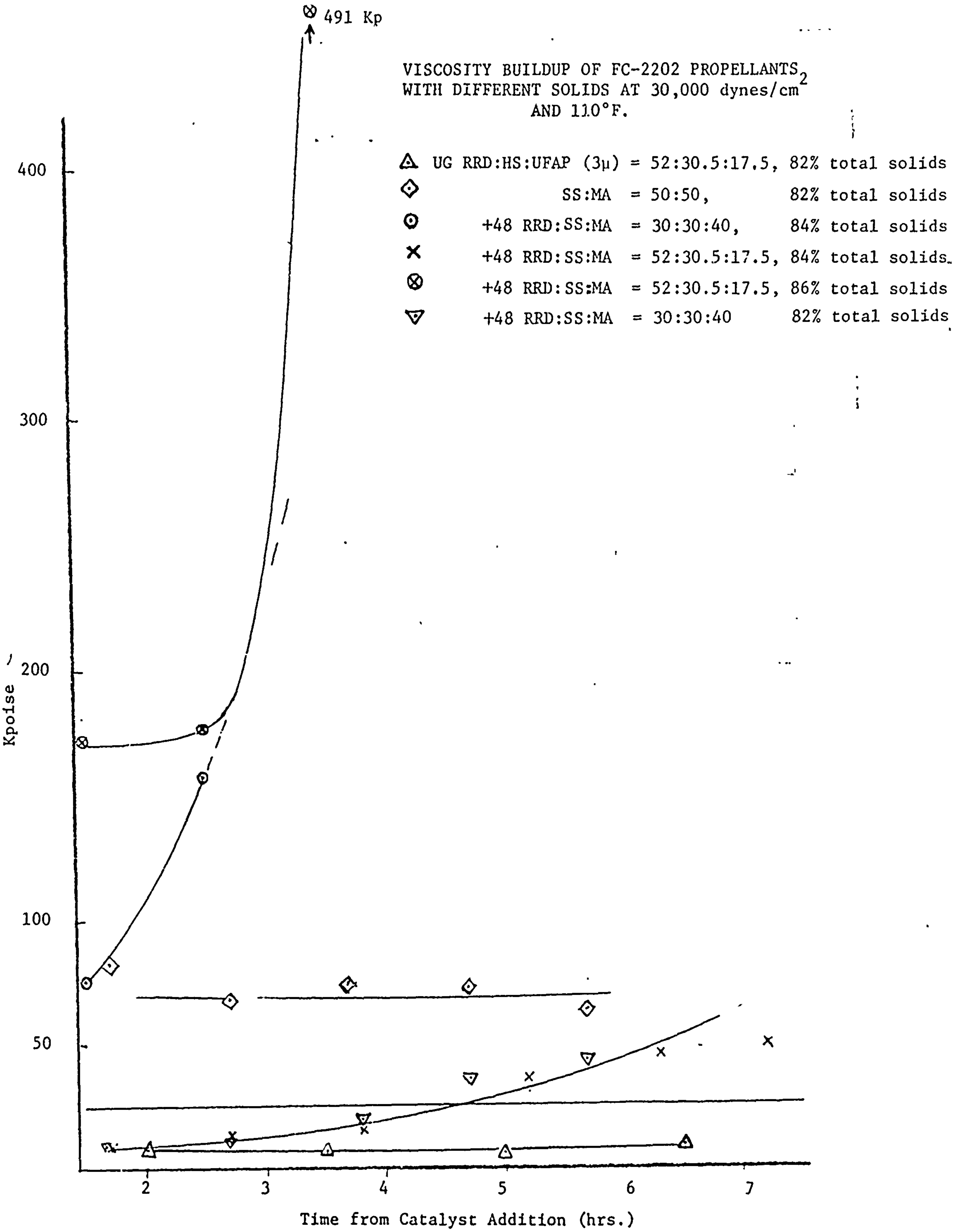
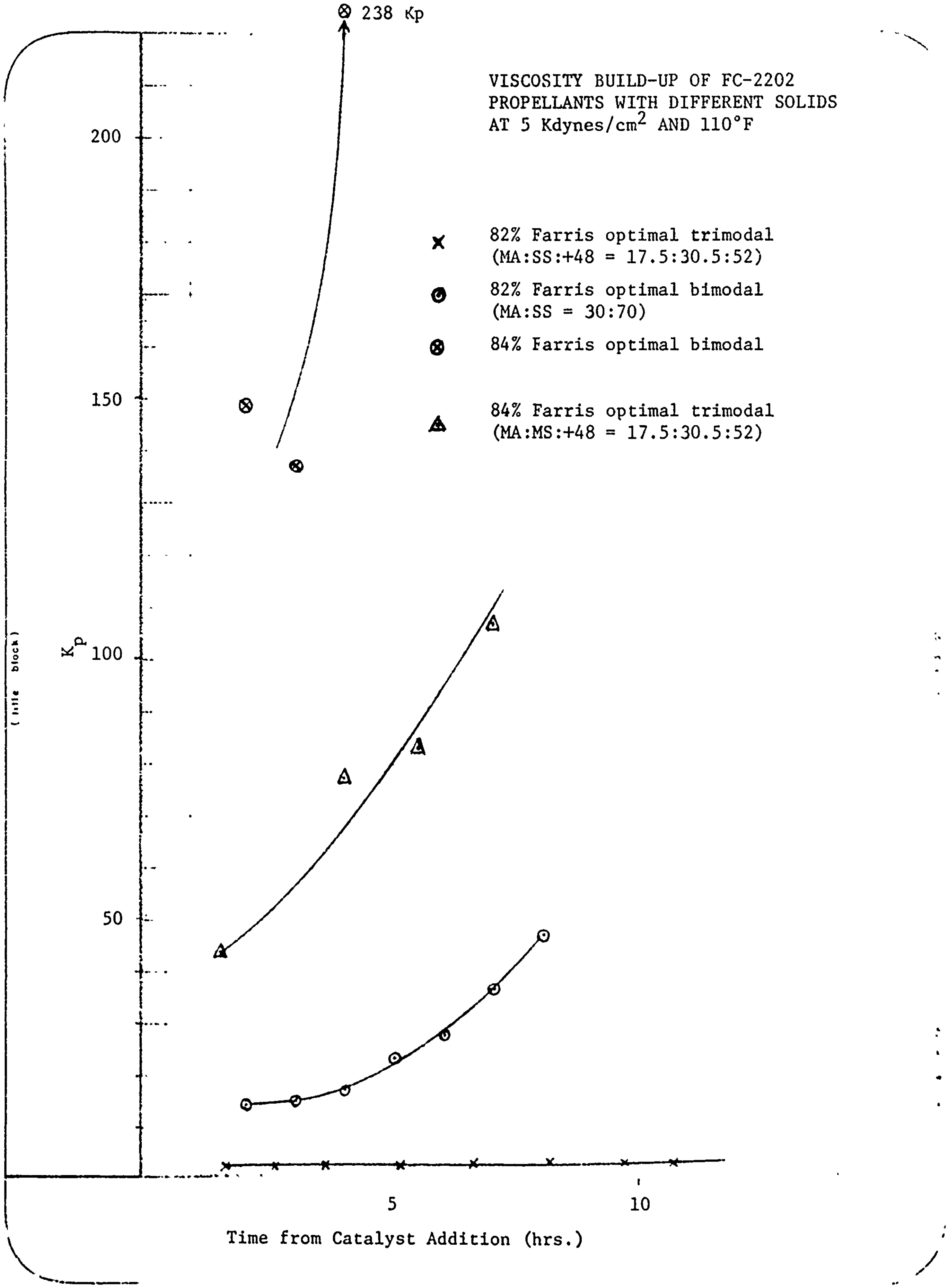


Figure 21



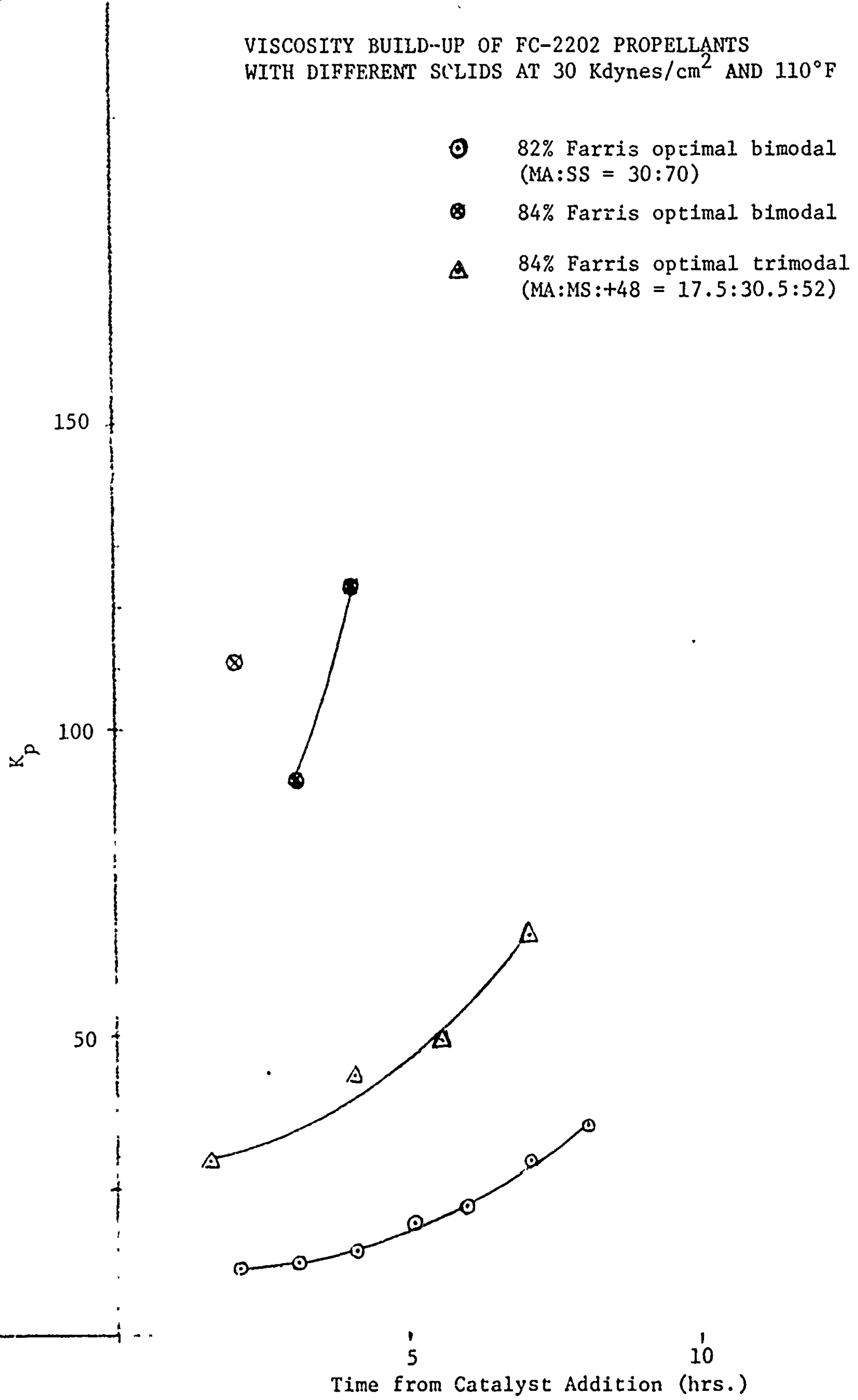
VISCOSITY BUILDUP OF FC-2202 PROPELLANTS WITH DIFFERENT SOLIDS AT 30,000 dynes/cm^2 AND 110°F.

Figure 22



VISCOSITY BUILD-UP OF FC-2202 PROPELLANTS WITH DIFFERENT SOLIDS AT 5 Kdynes/cm^2 AND 110°F

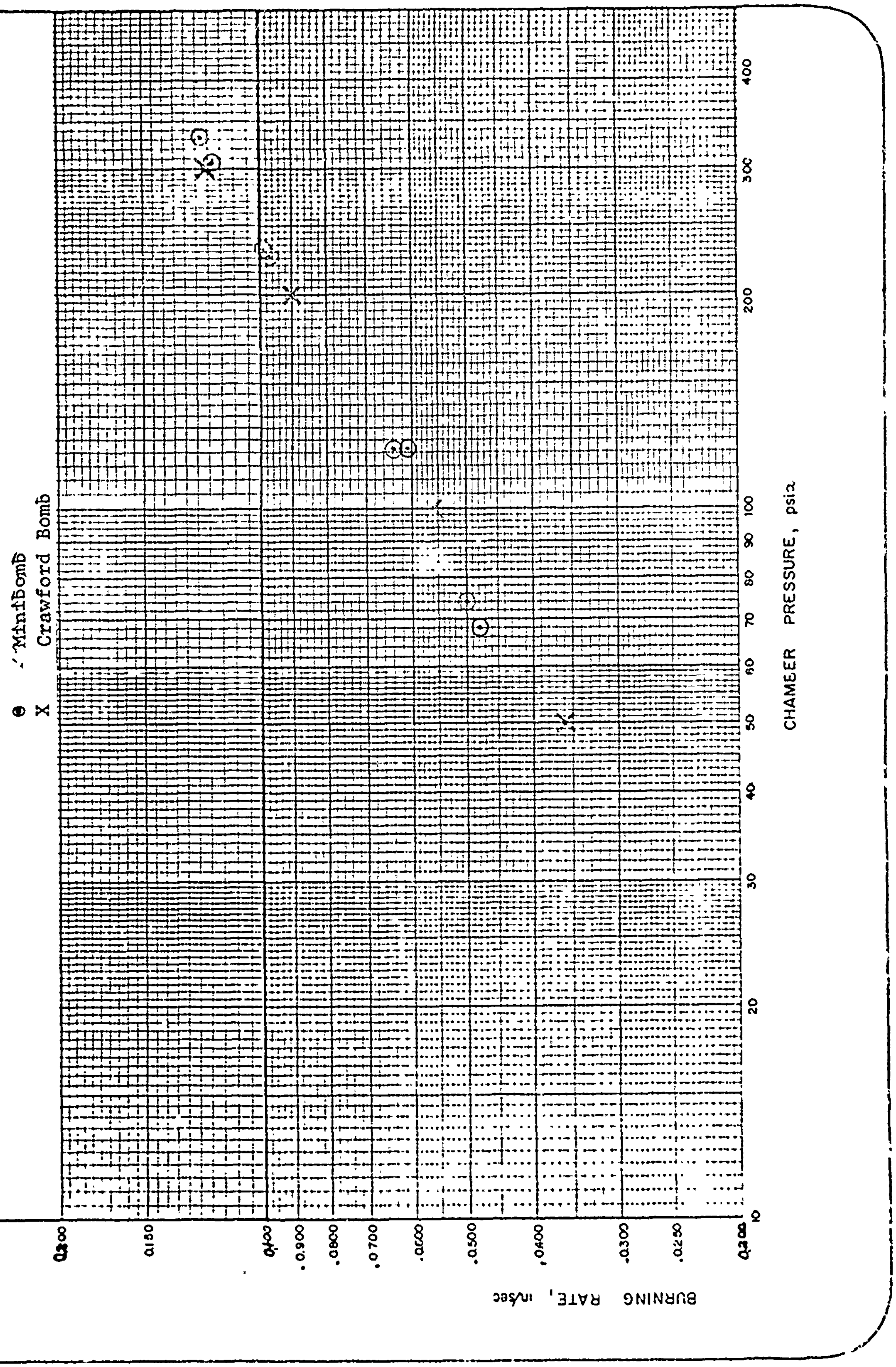
Figure 23



VISCOSITY BUILD-UP OF FC-2202 PROPELLANTS WITH DIFFERENT SOLIDS AT 30 Kdynes/cm^2 AND 110°F

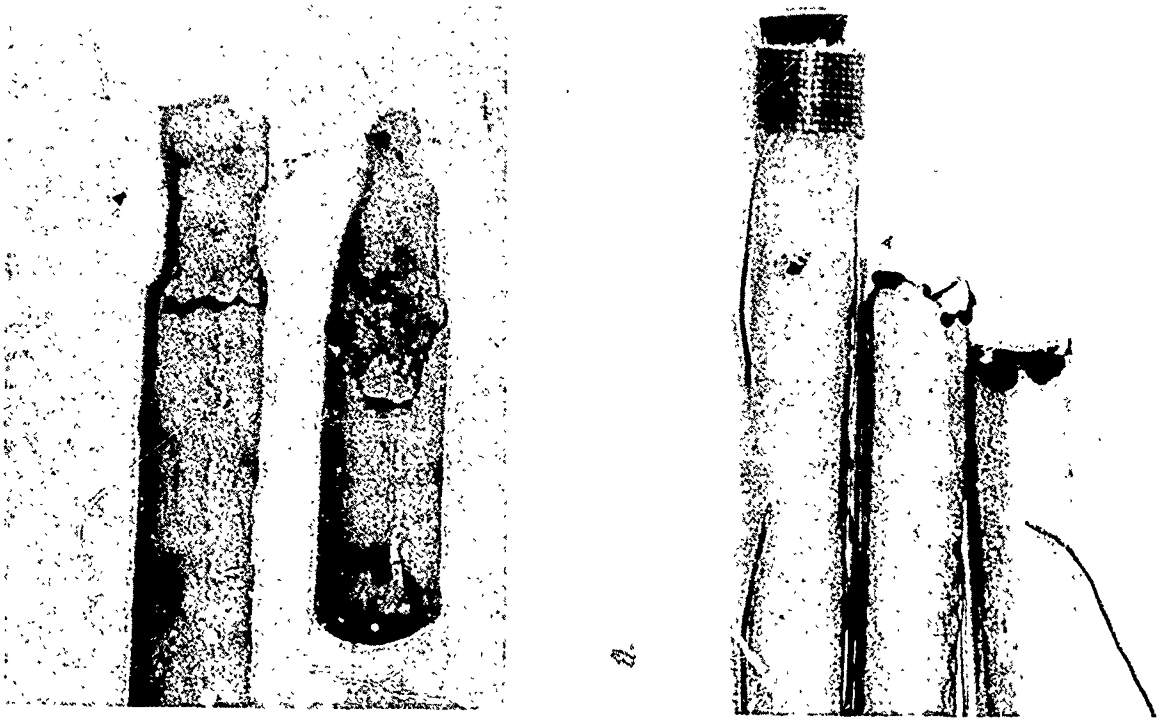
Figure 24

BURNING RATE OF A FC-2202 PROPELLANT WITH 82 wt. % AP (+48:SS:MA = 30:30;40)
(Propellant No. 13)



Figure

EFFECT OF RESTRICTION ON PROPELLANT SOLID STRAND BURNING



A.

B.

Extinguished Burning Rate Strands of FC-2202 Propellant

A. Propellant with a Genamide 2000/Epon 815 restriction. Burned at 200 psia, extinguished by depressurization.

B. Propellant with a Viton A restriction. Burned at 200 psia, stopped burning.

Figure 26

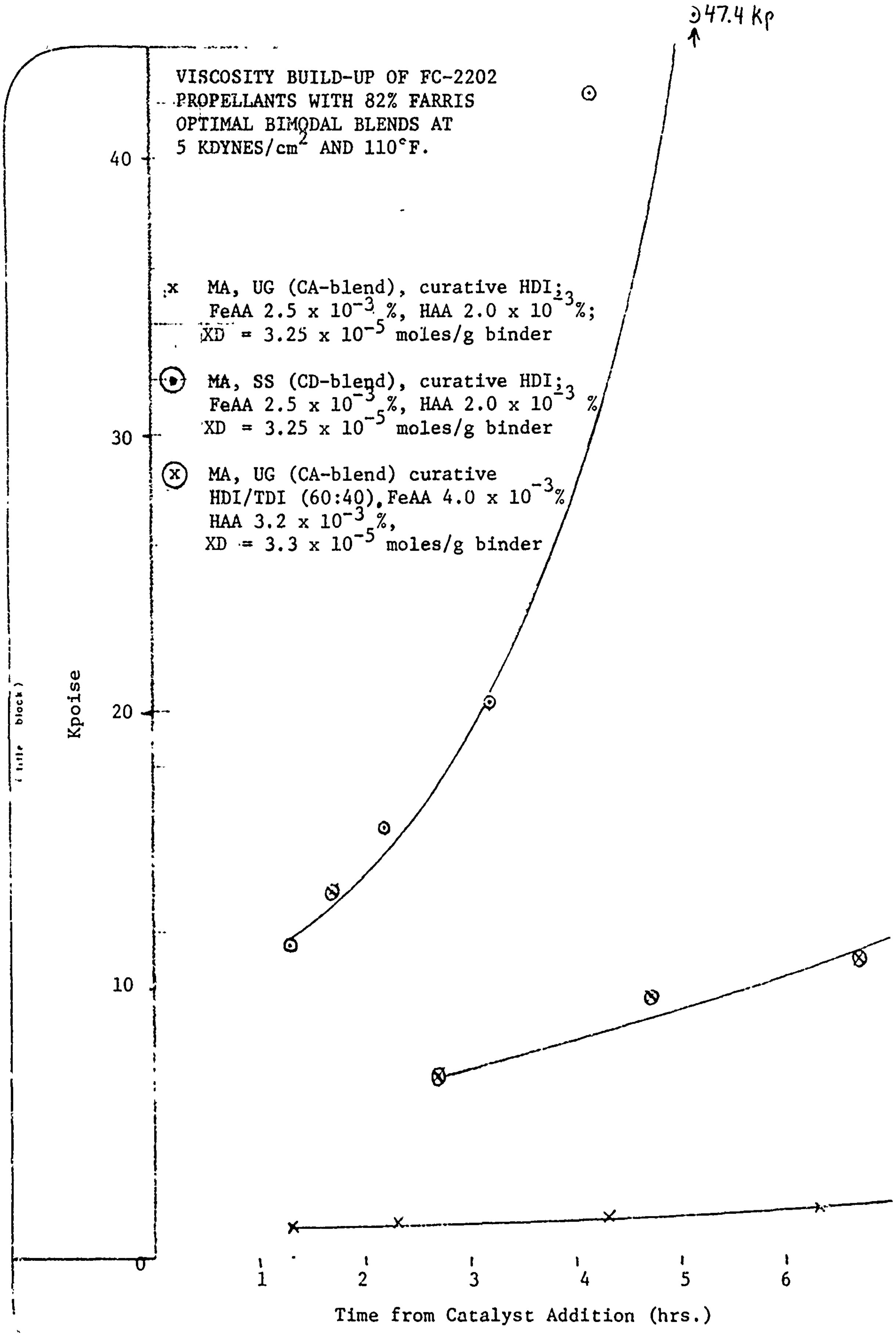

⊙47.4 Kp
VISCOSITY BUILD-UP OF FC-2202 PROPELLANTS WITH 82% FARRIS OPTIMAL BIMODAL BLENDS AT 5 KDYNES/cm^2 AND 110°F.
x MA, UG (CA-blend), curative HDI; FeAA 2.5 x 10^{-3} %, HAA 2.0 x 10^{-3} %; XD = 3.25 x 10^{-5} moles/g binder
⊙ MA, SS (CD-blend), curative HDI; FeAA 2.5 x 10^{-3} %, HAA 2.0 x 10^{-3} % XD = 3.25 x 10^{-5} moles/g binder
ⓧ MA, UG (CA-blend) curative HDI/TDI (60:40), FeAA 4.0 x 10^{-3} % HAA 3.2 x 10^{-3} %, XD = 3.3 x 10^{-5} moles/g binder
Kpoise
40
30
20
10
0
1
2
3
4
5
6
Time from Catalyst Addition (hrs.)

Figure 27a

VISCOSITY BUILD-UP OF FC-2202 PROPELLANTS WITH 82% FARRIS OPTIMAL BIMODAL BLENDS AT 30 Kdynes/cm^2 AND 110°F

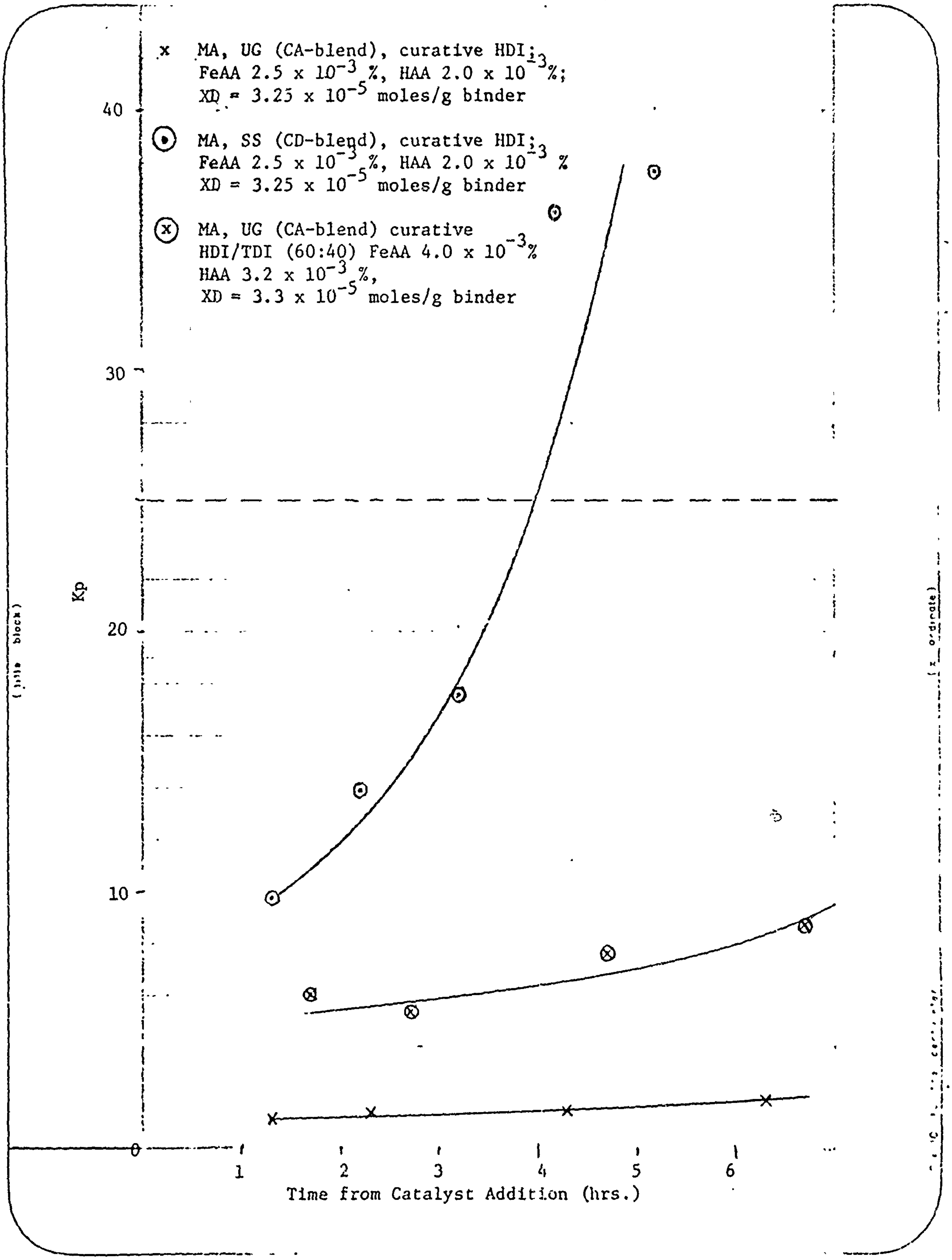


Figure 27b

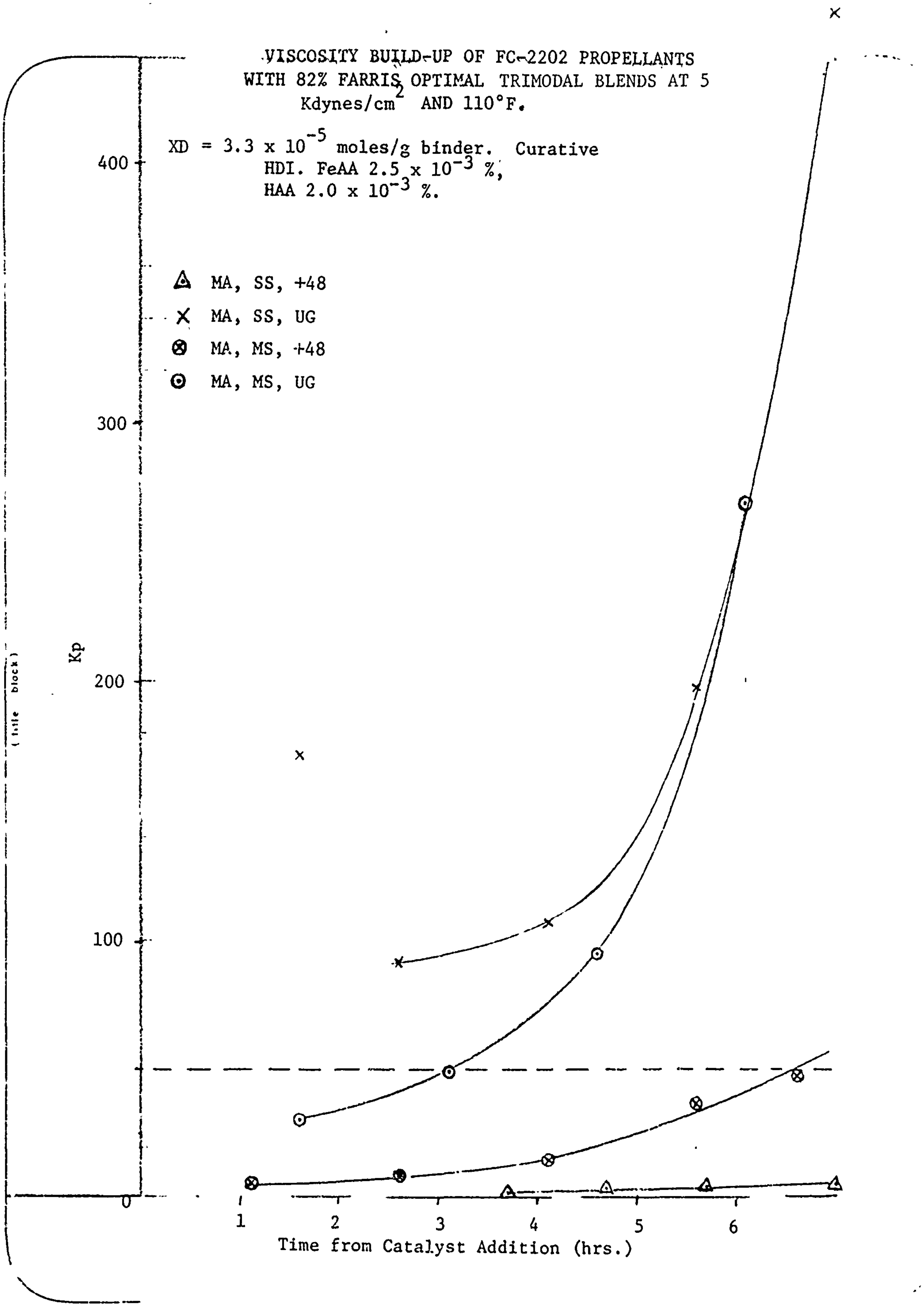

VISCOSITY BUILD-UP OF FC-2202 PROPELLANTS
WITH 82% FARRIS OPTIMAL TRIMODAL BLENDS AT 5
Kdynes/cm^2 AND 110°F.
XD = 3.3 x 10^{-5} moles/g binder. Curative
HDI. FeAA 2.5 x 10^{-3} %,
HAA 2.0 x 10^{-3} %.
△ MA, SS, +48
× MA, SS, UG
⊗ MA, MS, +48
⊙ MA, MS, UG
Kp
400
300
200
100
0
1
2
3
4
5
6
Time from Catalyst Addition (hrs.)
(Title block)

Figure 28a

VISCOSITY BUILD-UP OF FC-2202 PROPELLANTS WITH 82% FARRIS OPTIMAL TRIMODAL BLENDS AT 30 Kdynes/cm^2 AND 110°F.

XD = 3.3×10^{-5} moles/g binder. Curative HDI.
FeAA 2.5×10^{-3} %, HAA 2.0×10^{-3} %.

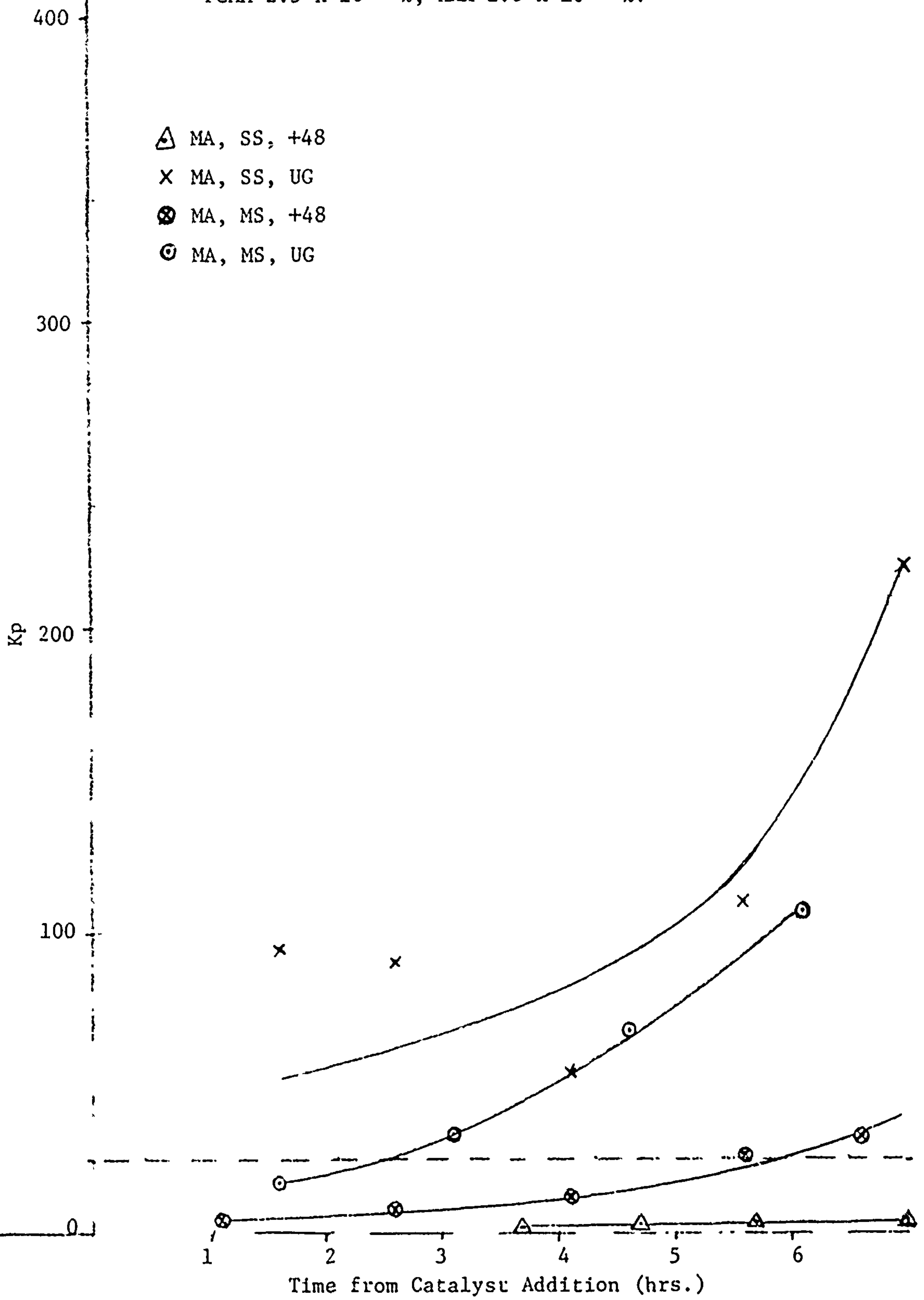
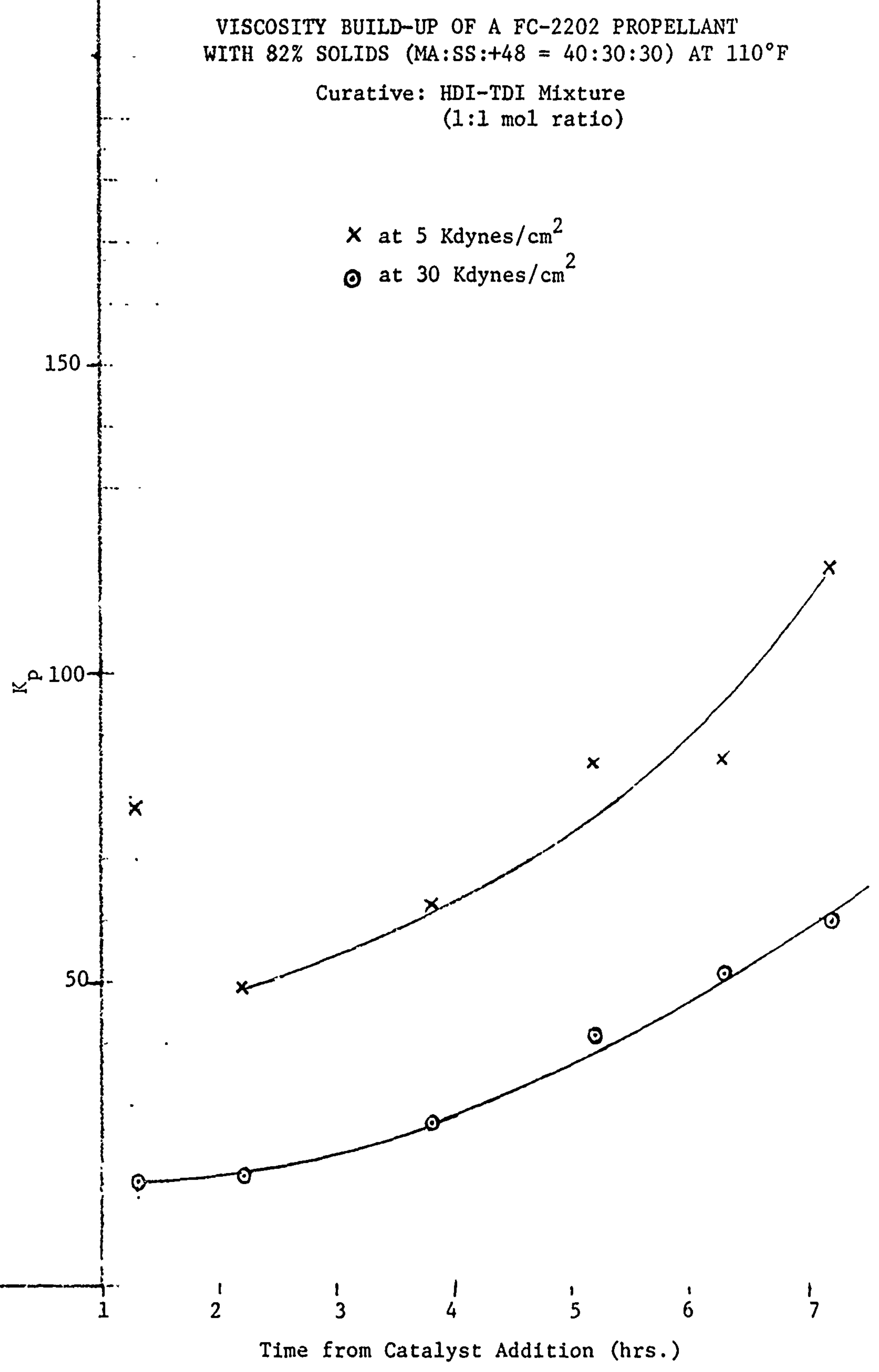


Figure 28b



VISCOSITY BUILD-UP OF A FC-2202 PROPELLANT WITH 82% SOLIDS (MA:SS:+48 = 40:30:30) AT 110°F

Curative: HDI-TDI Mixture (1:1 mol ratio)

Figure 29

VISCOSITY BUILD-UP OF FC-2202 PROPELLANTS WITH
82% SOLIDS (BIMODAL AND TRIMODAL FARRIS OPTIMAL BLENDS) USING
A 50/50 EQ. RATIO OF HDI AND TDI AT 5 Kdynes/cm^2 AND 110°F.
XD = 3.5 x 10^{-5} moles/g binder. 5 x 10^{-3}% FeAA,
4 x 10^{-3}% HAA.

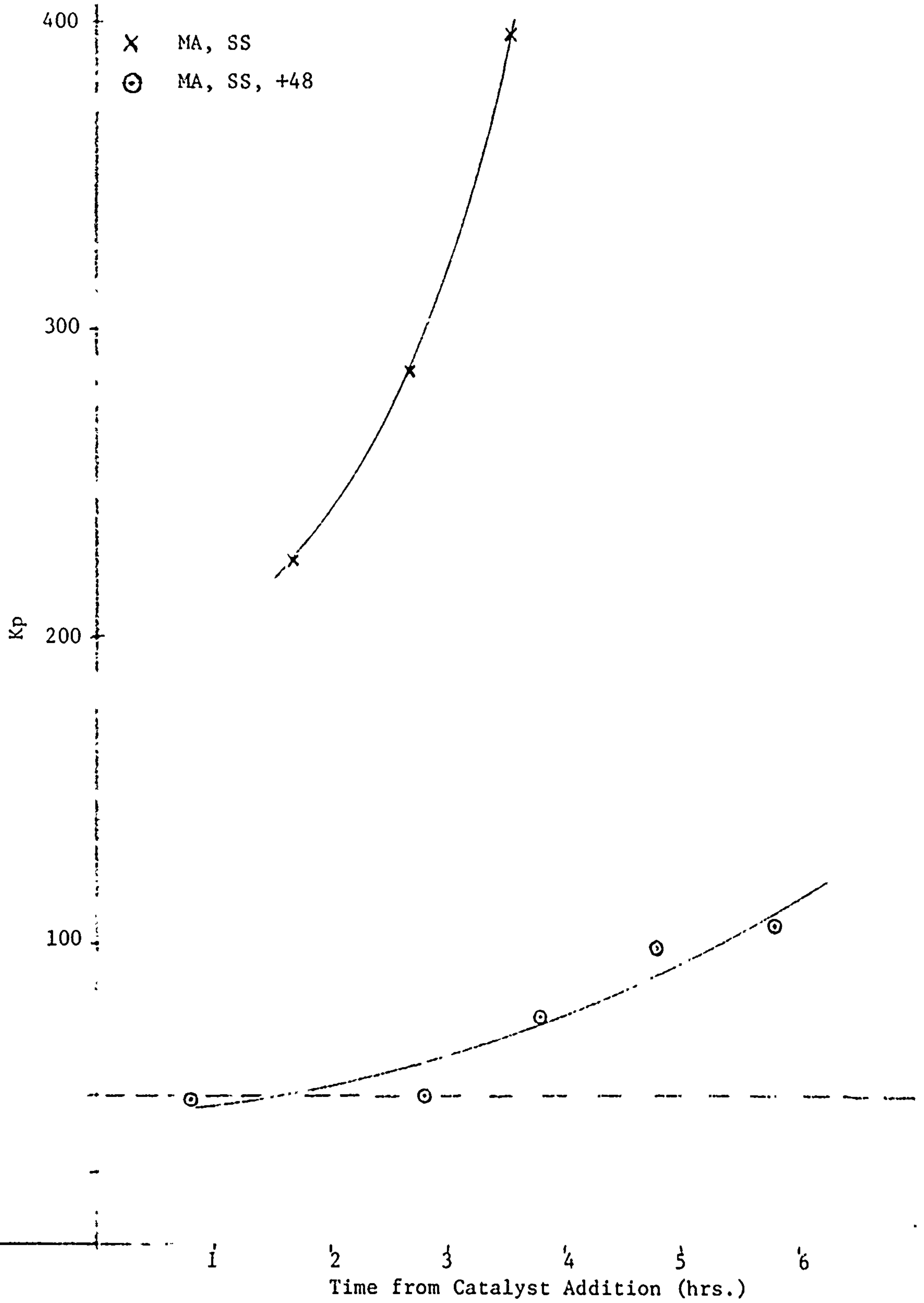
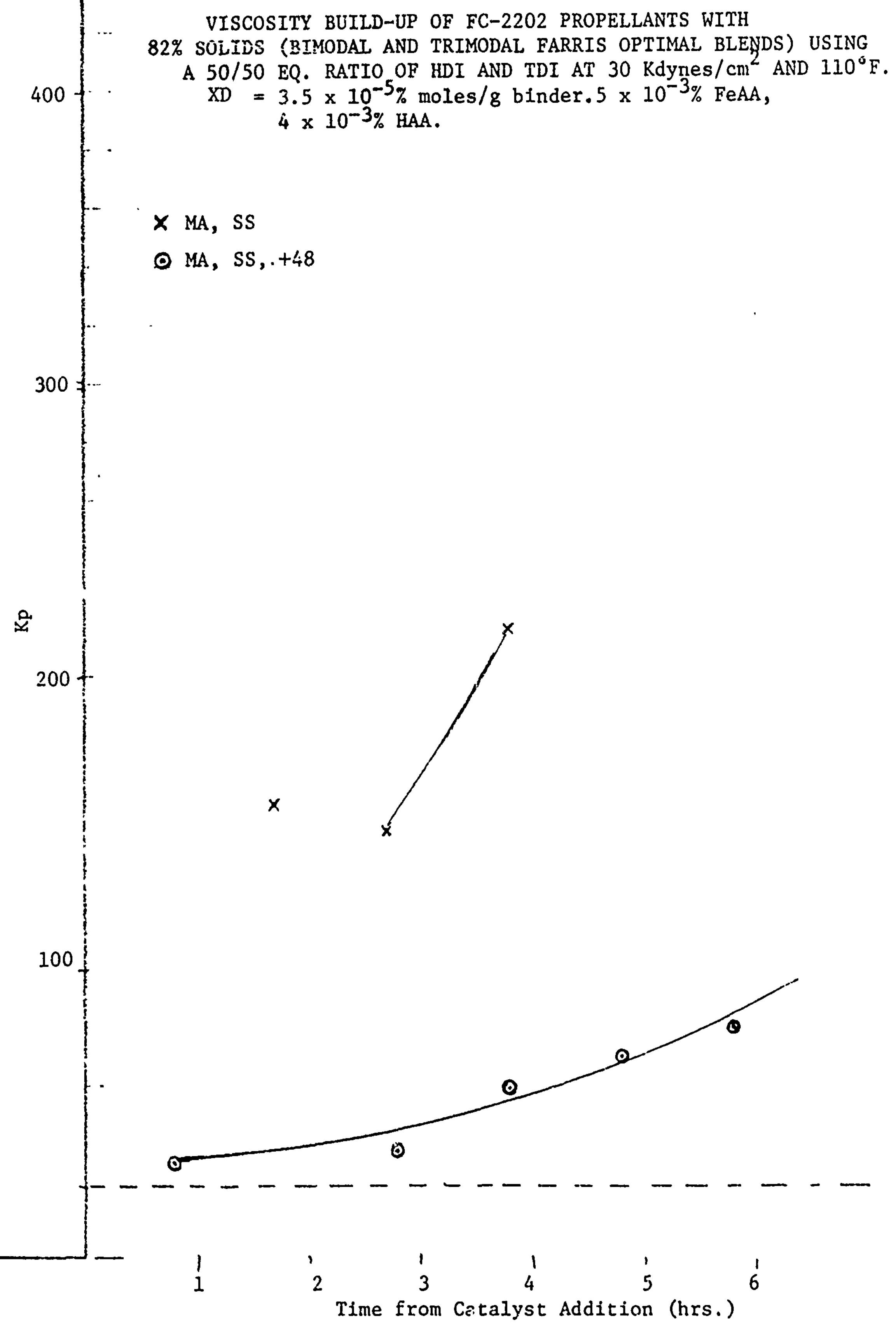


Figure 30 a



VISCOSITY BUILD-UP OF FC-2202 PROPELLANTS WITH 82% SOLIDS (BIMODAL AND TRIMODAL FARRIS OPTIMAL BLENDS) USING A 50/50 EQ. RATIO OF HDI AND TDI AT 30 Kdynes/cm^2 AND 110°F. XD = 3.5 x 10^{-5}% moles/g binder. 5 x 10^{-3}% FeAA, 4 x 10^{-3}% HAA.

Figure 30b

VISCOSITY BUILD-UP OF FC-2202 PROPELLANTS WITH 82% FARRIS OPTIMAL TRIMODAL BLEND (MA, SS, +48) AND CURATIVE MIXTURES WITH DIFFERENT HDI/TDI RATIOS AT 5 Kdynes/cm^2 AND 110°F.

XD = 3.5×10^{-5} moles/g binder

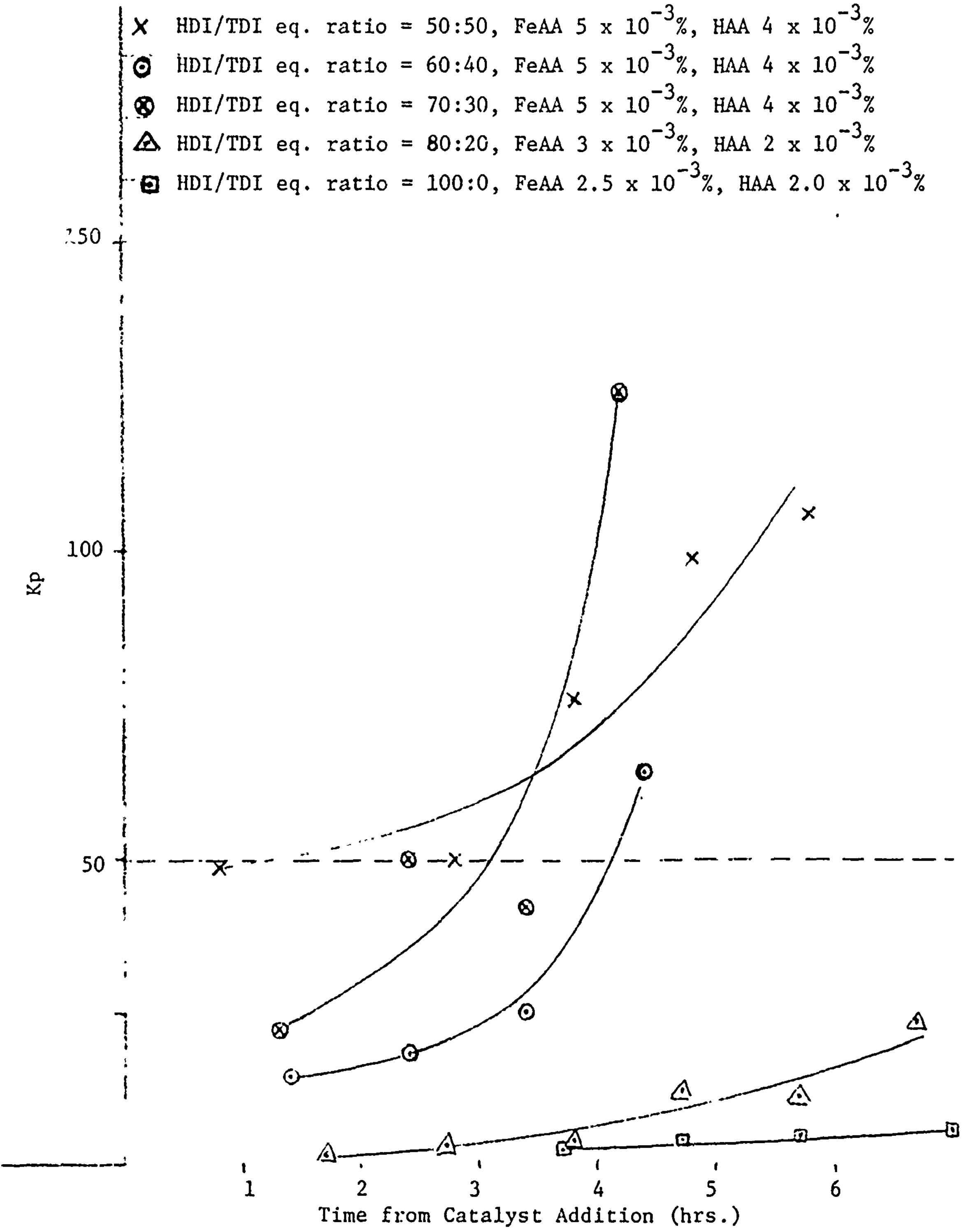


Figure 31a

VISCOSITY BUILD-UP OF FC-2202 PROPELLANTS WITH 82% FARRIS OPTIMAL TRIMODAL BLEND (MA, SS, +48) AND CURATIVE MIXTURES WITH DIFFERENT HDI/TDI RATIOS AT 30 Kdynes/cm^2 AND 110°F.

XD = 3.5×10^{-5} moles/g binder

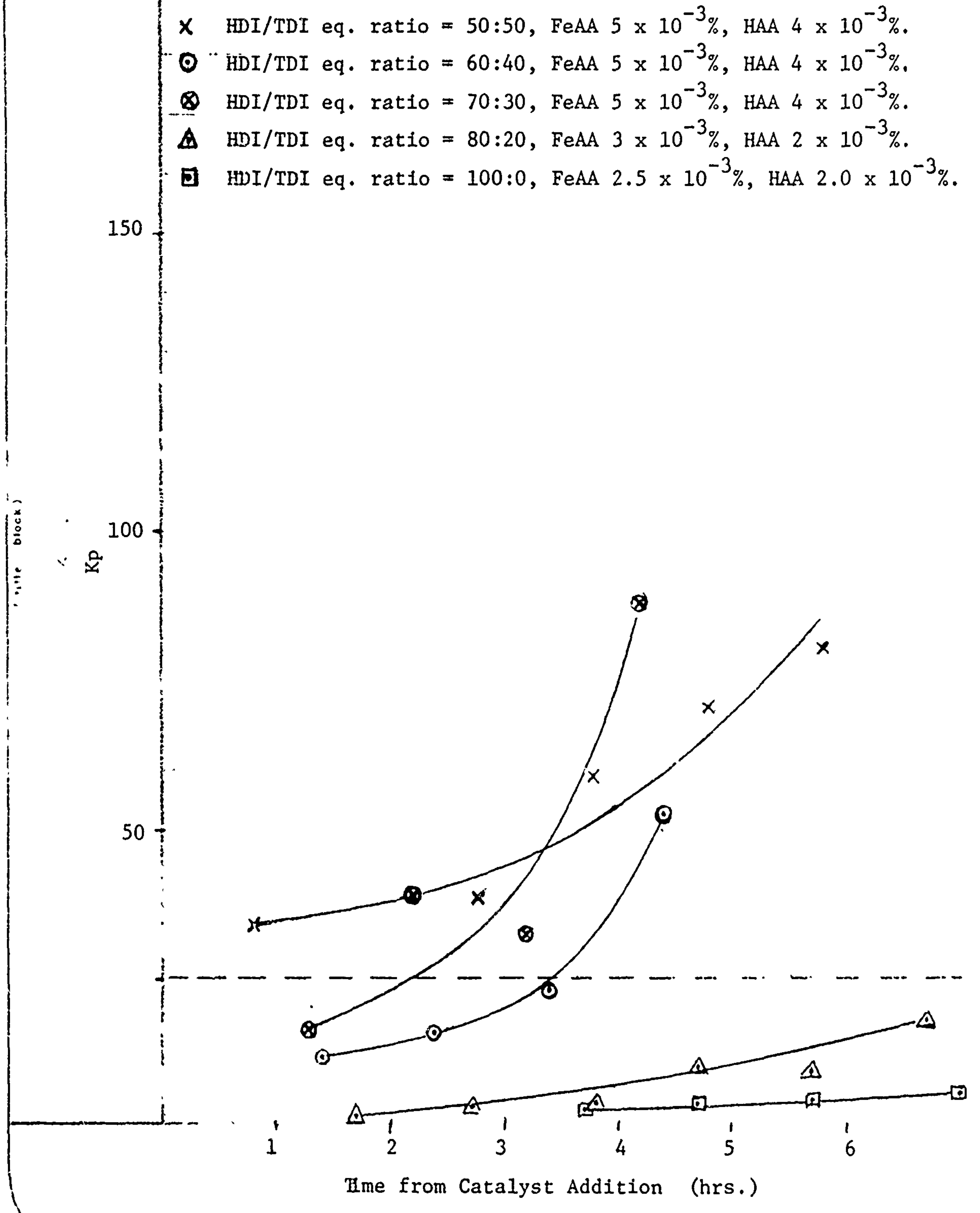


Figure 31b

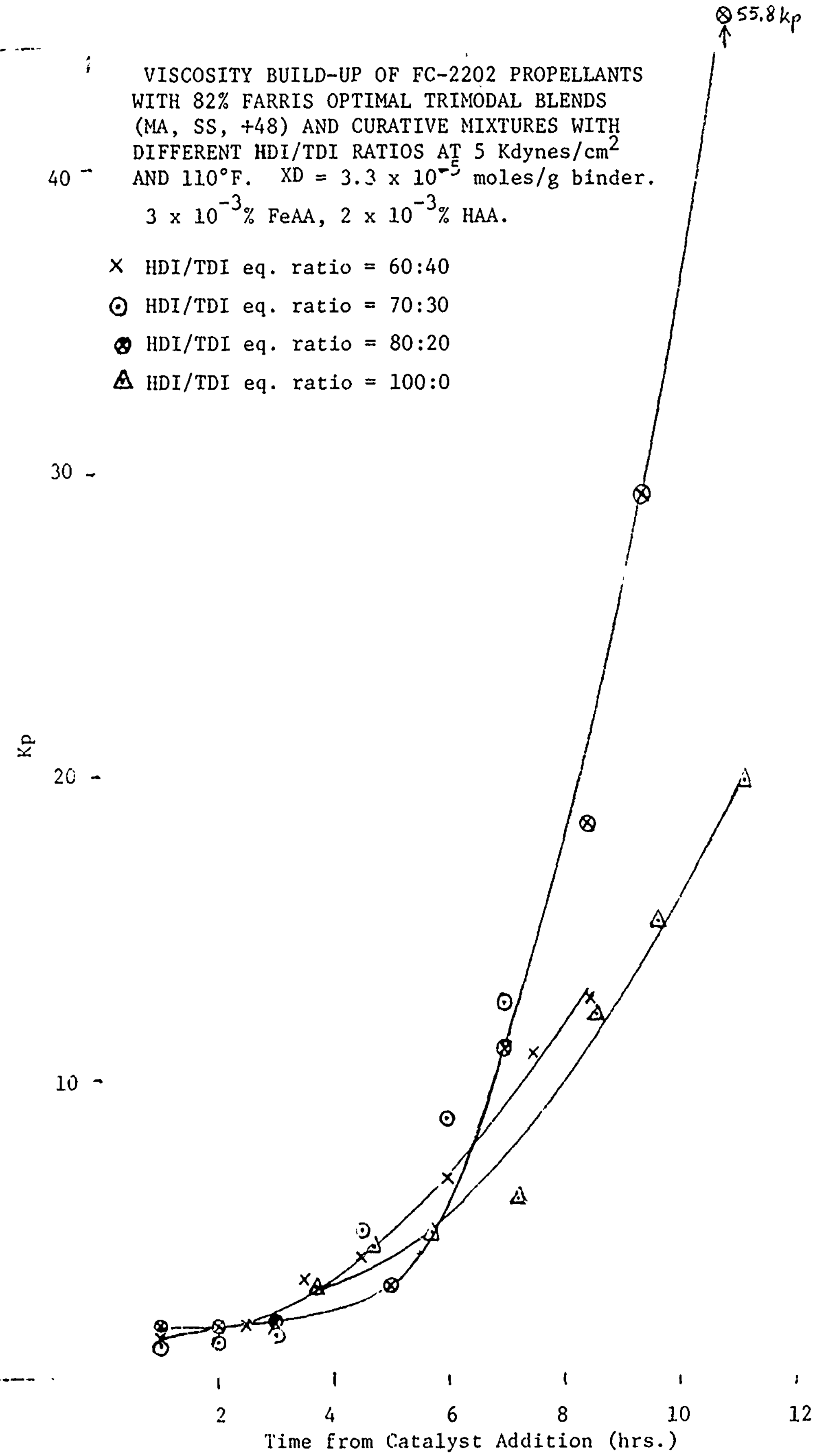

⊗ 55.8 kp
VISCOSITY BUILD-UP OF FC-2202 PROPELLANTS WITH 82% FARRIS OPTIMAL TRIMODAL BLENDS (MA, SS, +48) AND CURATIVE MIXTURES WITH DIFFERENT HDI/TDI RATIOS AT 5 Kdynes/cm^2 AND 110°F. XD = 3.3 x 10^{-5} moles/g binder. 3 x 10^{-3}% FeAA, 2 x 10^{-3}% HAA.
× HDI/TDI eq. ratio = 60:40
⊙ HDI/TDI eq. ratio = 70:30
⊗ HDI/TDI eq. ratio = 80:20
△ HDI/TDI eq. ratio = 100:0
Kp
40
30
20
10
2
4
6
8
10
12
Time from Catalyst Addition (hrs.)

Figure 32a

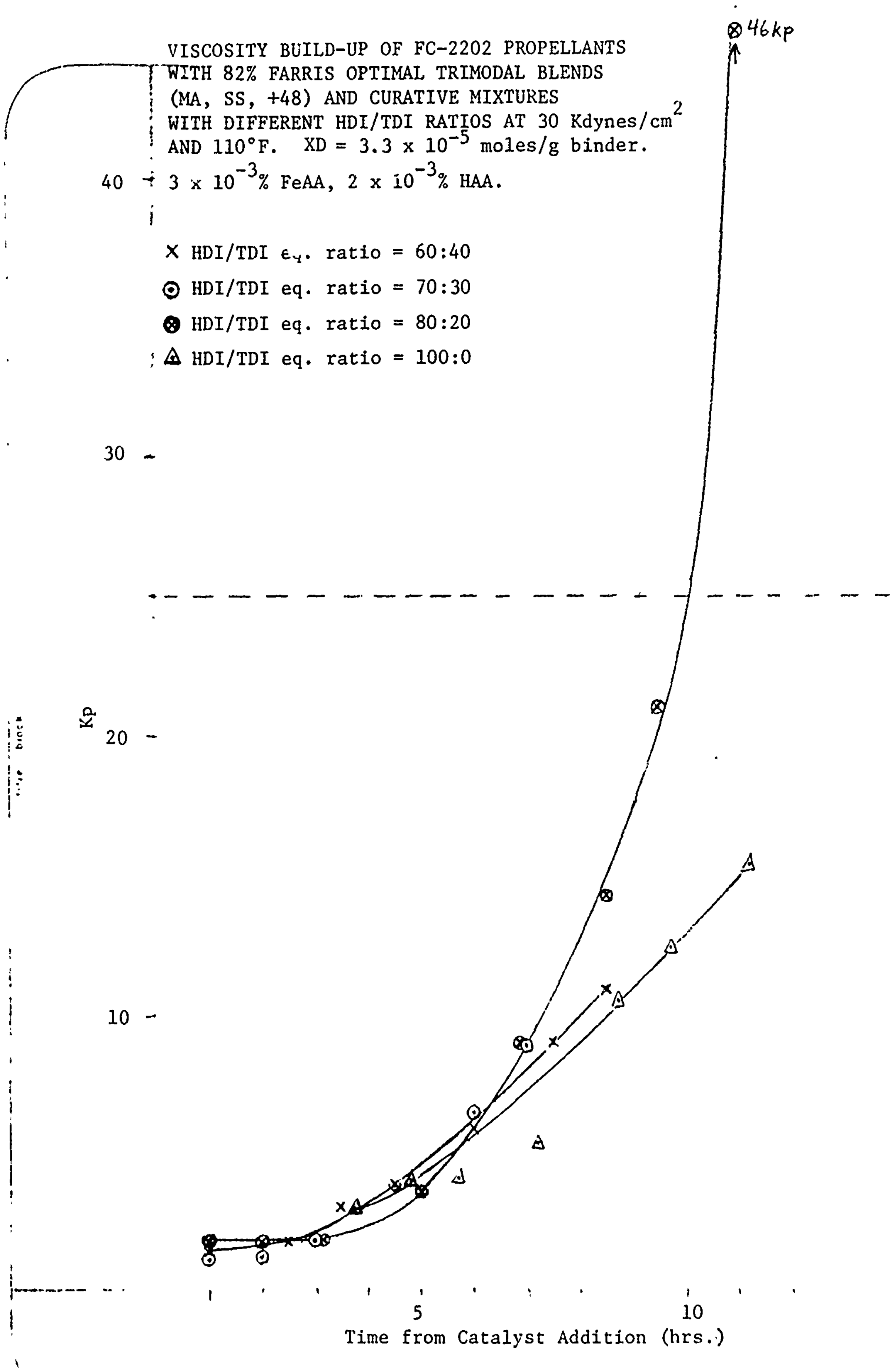

VISCOSITY BUILD-UP OF FC-2202 PROPELLANTS
WITH 82% FARRIS OPTIMAL TRIMODAL BLENDS
(MA, SS, +48) AND CURATIVE MIXTURES
WITH DIFFERENT HDI/TDI RATIOS AT 30 Kdynes/cm²
AND 110°F. XD = 3.3 x 10⁻⁵ moles/g binder.
3 x 10⁻³% FeAA, 2 x 10⁻³% HAA.
× HDI/TDI eq. ratio = 60:40
⊙ HDI/TDI eq. ratio = 70:30
⊗ HDI/TDI eq. ratio = 80:20
△ HDI/TDI eq. ratio = 100:0
⊗ 46kp
Kp
40
30
20
10
5
10
Time from Catalyst Addition (hrs.)

Figure 32b

VISCOSITY BUILD-UP OF FC-2202 PROPELLANTS WITH 82% FARRIS OPTIMAL TRIMODAL BLEND (MA, SS, +48) AND A 60:40 EQ. RATIO OF HDI AND TDI WITH VARYING CATALYST CONCENTRATIONS AT 5 Kdynes/cm^2 AND 110°F

XD = 3.3 x 10^{-5} moles/g binder

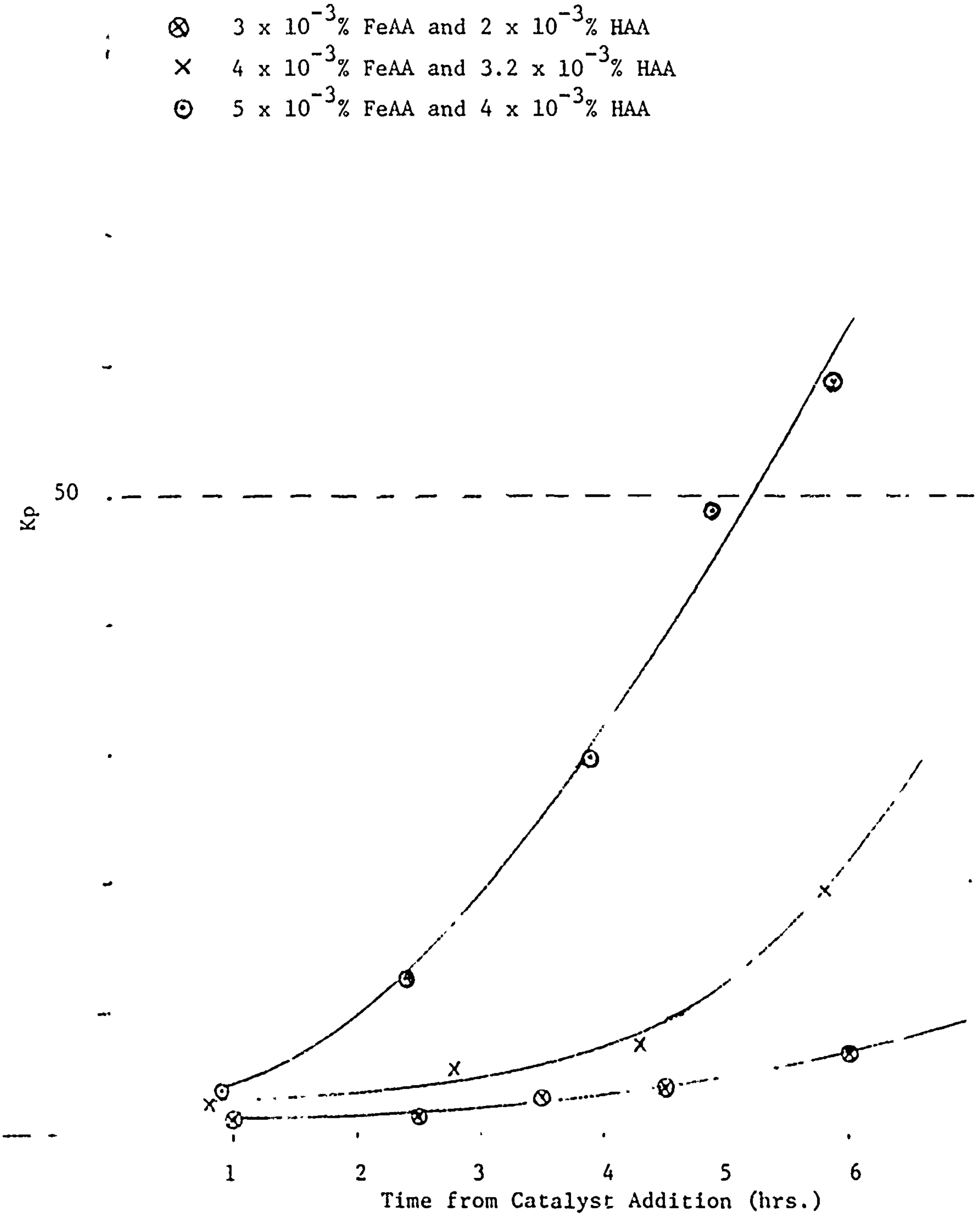


Figure 33a

VISCOSITY BUILD-UP OF FC-2202 PROPELLANTS WITH
82% FARRIS OPTIMAL TRIMODAL BLEND (MA, SS, +48) AND A 60:40
EQ. RATIO OF HDI AND TDI WITH VARYING CATALYST CONCENTRATIONS
AT 30 Kdynes/cm^2 AND 110°F

XD = 3.3×10^{-5} moles/g binder

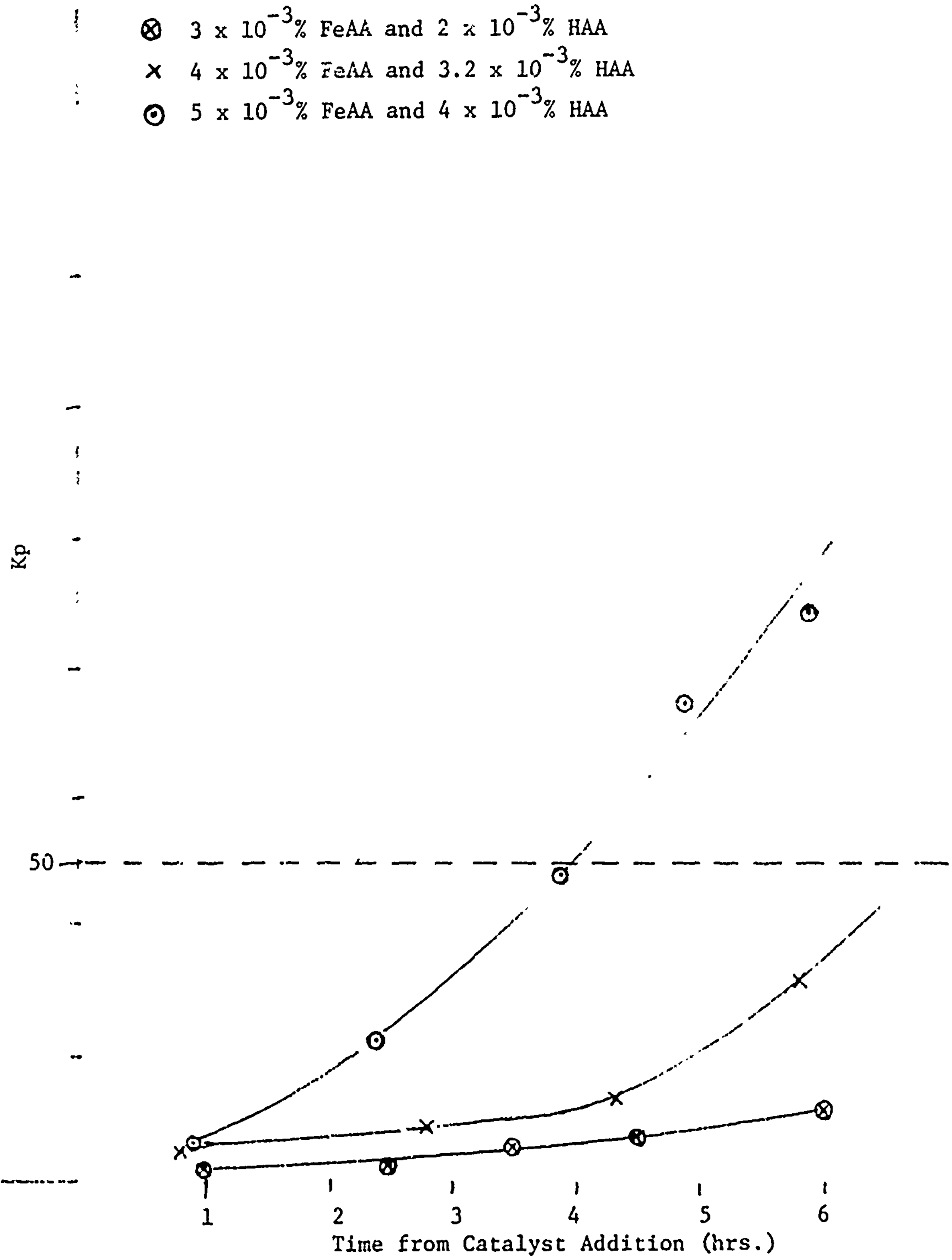


Figure 33b

VISCOSITY BUILD-UP OF FC-2202 PROPELLANTS WITH 82% FARRIS OPTIMAL TRIMODAL BLEND (MA, SS, +48), AND A 60:40 EQ. RATIO OF HDI AND TDI WITH VARYING CATALYST CONCENTRATIONS, AT 5 Kdynes/cm^2 AND 110°F

XD = 3.5×10^{-5} moles/g binder

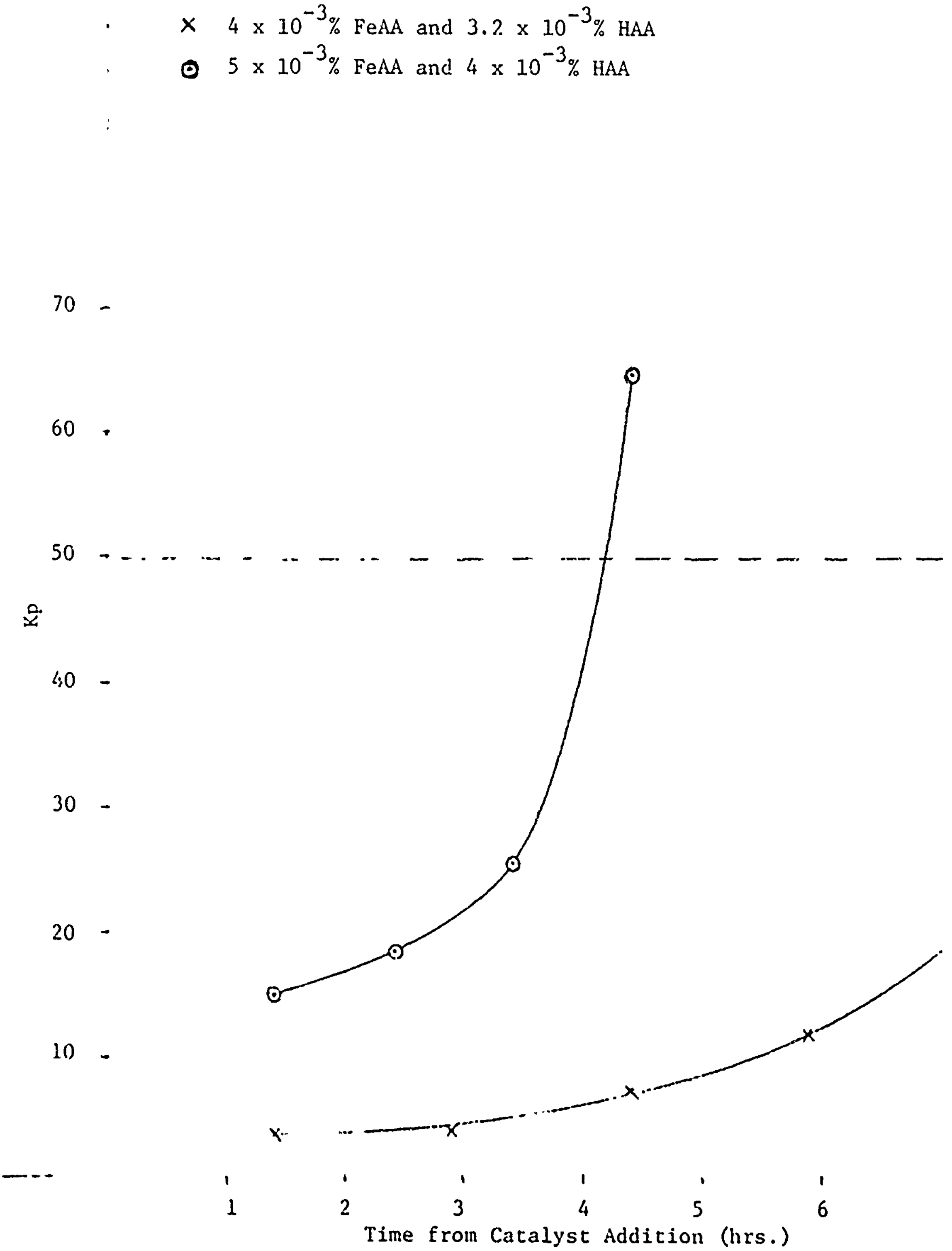


Figure 34a

VISCOSITY BUILD-UP OF FC-2202 PROPELLANTS WITH 82% FARRIS OPTIMAL TRIMODAL BLEND (MA, SS, +48), AND A 60:40 EQ. RATIO OF HDI AND TDI WITH VARYING CATALYST CONCENTRATIONS, AT 30 Kdynes/cm^2 AND 110°F

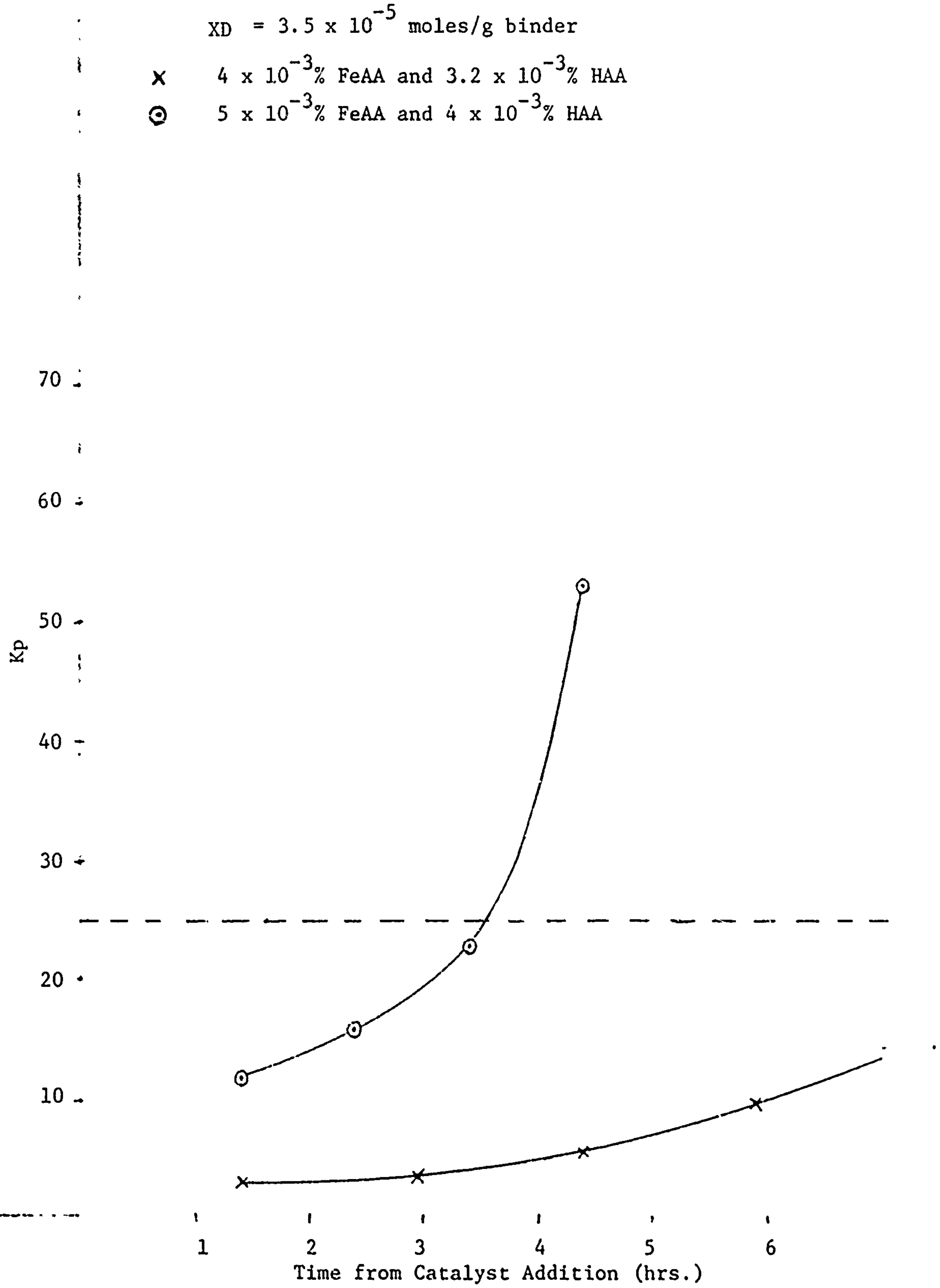


Figure 34b

VISCOSITY BUILD-UP OF FC-2202 PROPELLANTS WITH
84% FARRIS OPTIMAL TRIMODAL SOLIDS (MA,SS, +48) AT 30 Kdynes/cm^2
AND 110°F

XD = 3.3×10^{-5} moles/g binder

X Curative all HDI - 2.5×10^{-3}% FeAA, 2.0% HAA.

⊙ Curative HDI/TDI (60/40 eq. ratio) 4×10^{-3}% FeAA,
3.2×10^{-3}% HAA.

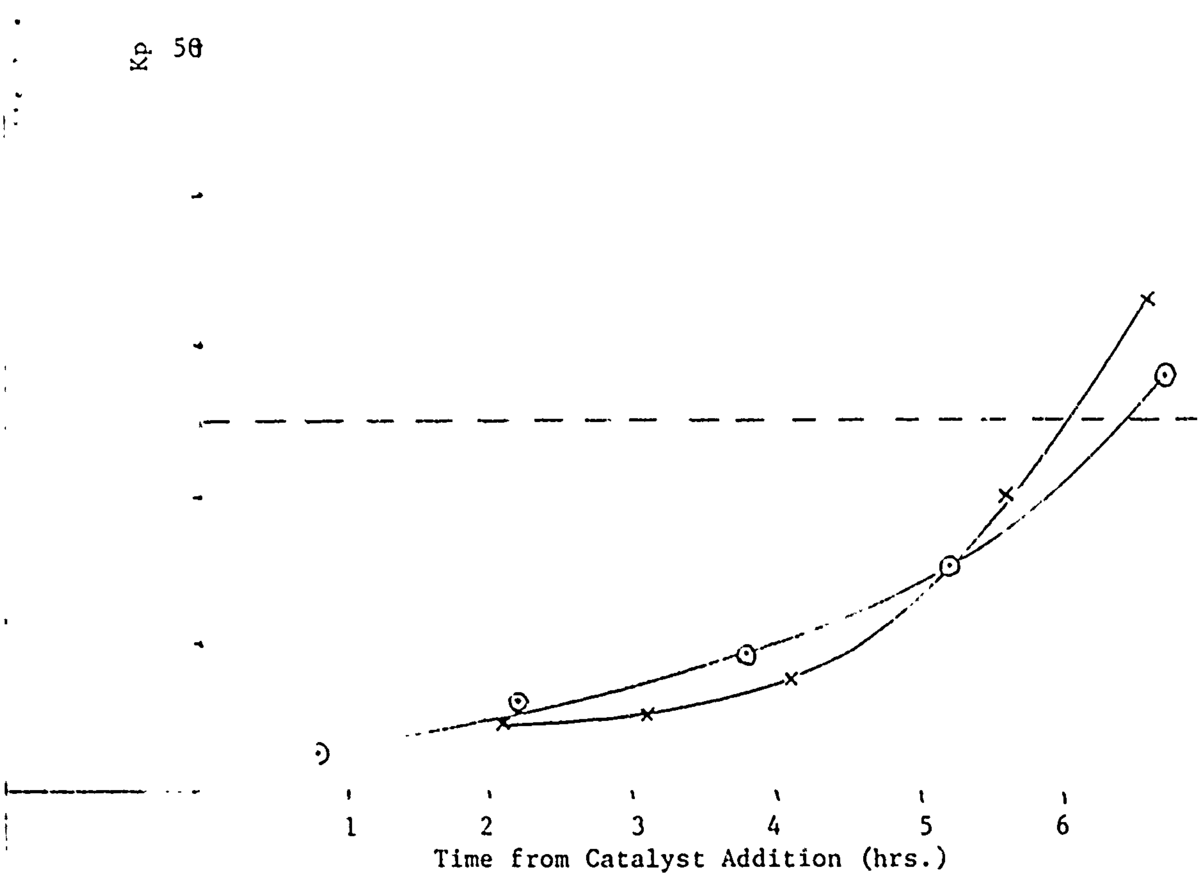
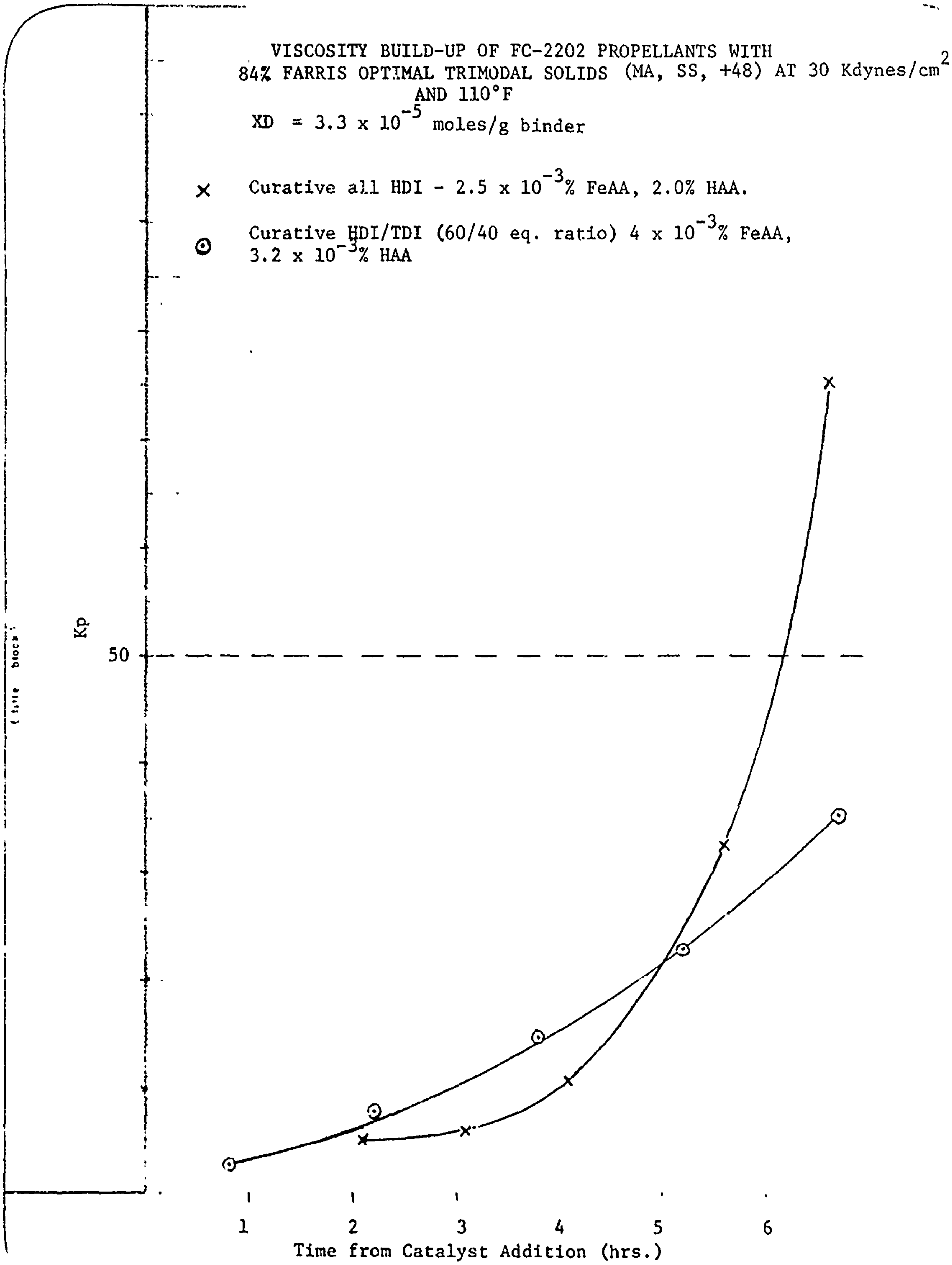


Figure 35a



VISCOSITY BUILD-UP OF FC-2202 PROPELLANTS WITH 84% FARRIS OPTIMAL TRIMODAL SOLIDS (MA, SS, +48) AT 30 Kdynes/cm^2 AND 110°F

XD = 3.3×10^{-5} moles/g binder

Figure 35b

VISCOSITY BUILDUP OF IDENTICAL 1800g BATCHES OF FC-2202 PROPELLANT AT 5 Kdynes/cm^2 AND 110°F

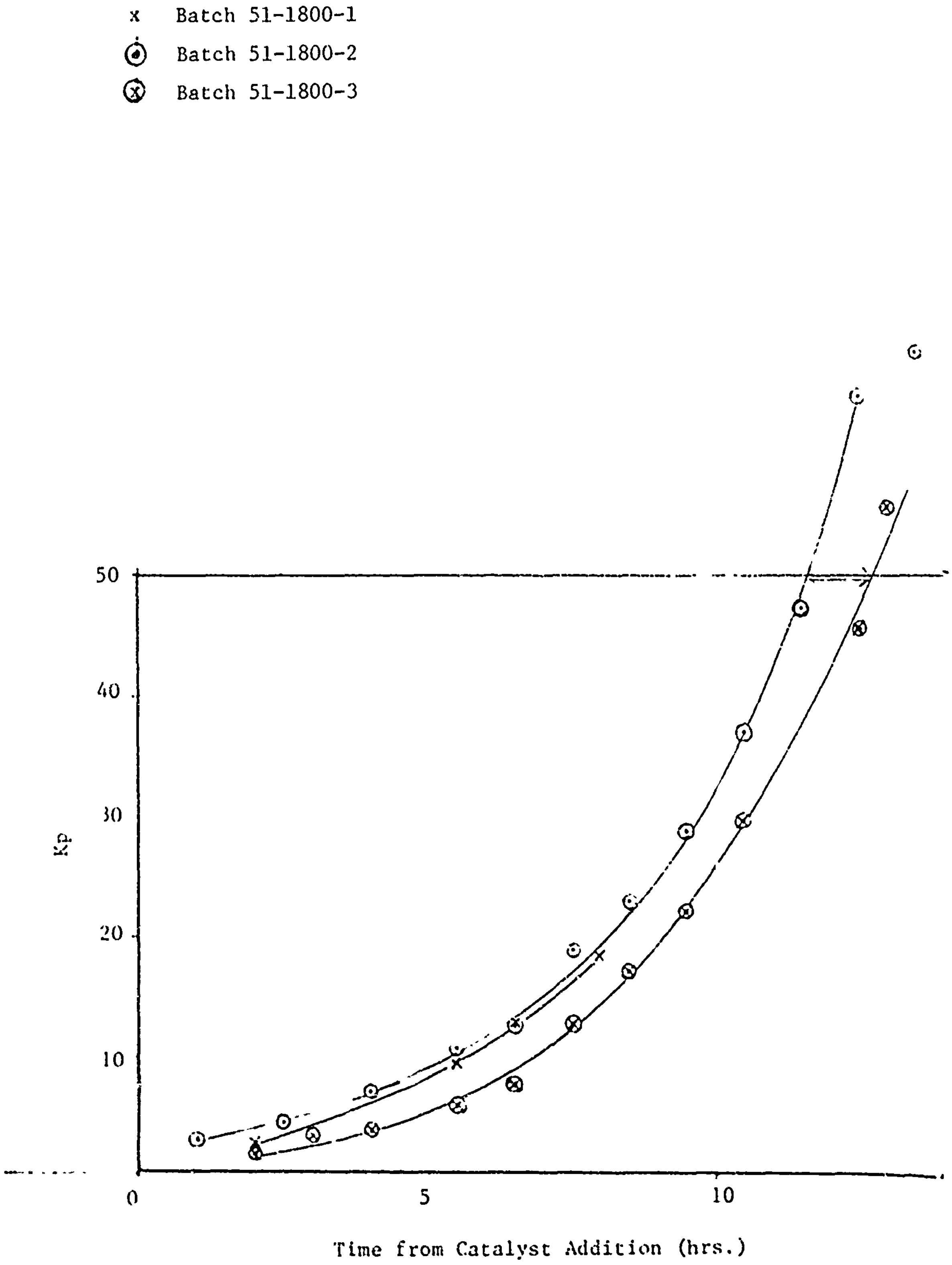


Figure 36a

VISCOSITY BUILDUP OF IDENTICAL 1800g BATCHES OF FC-2202 PROPELLANT AT 30 Kdynes/cm^2 AND 110°F

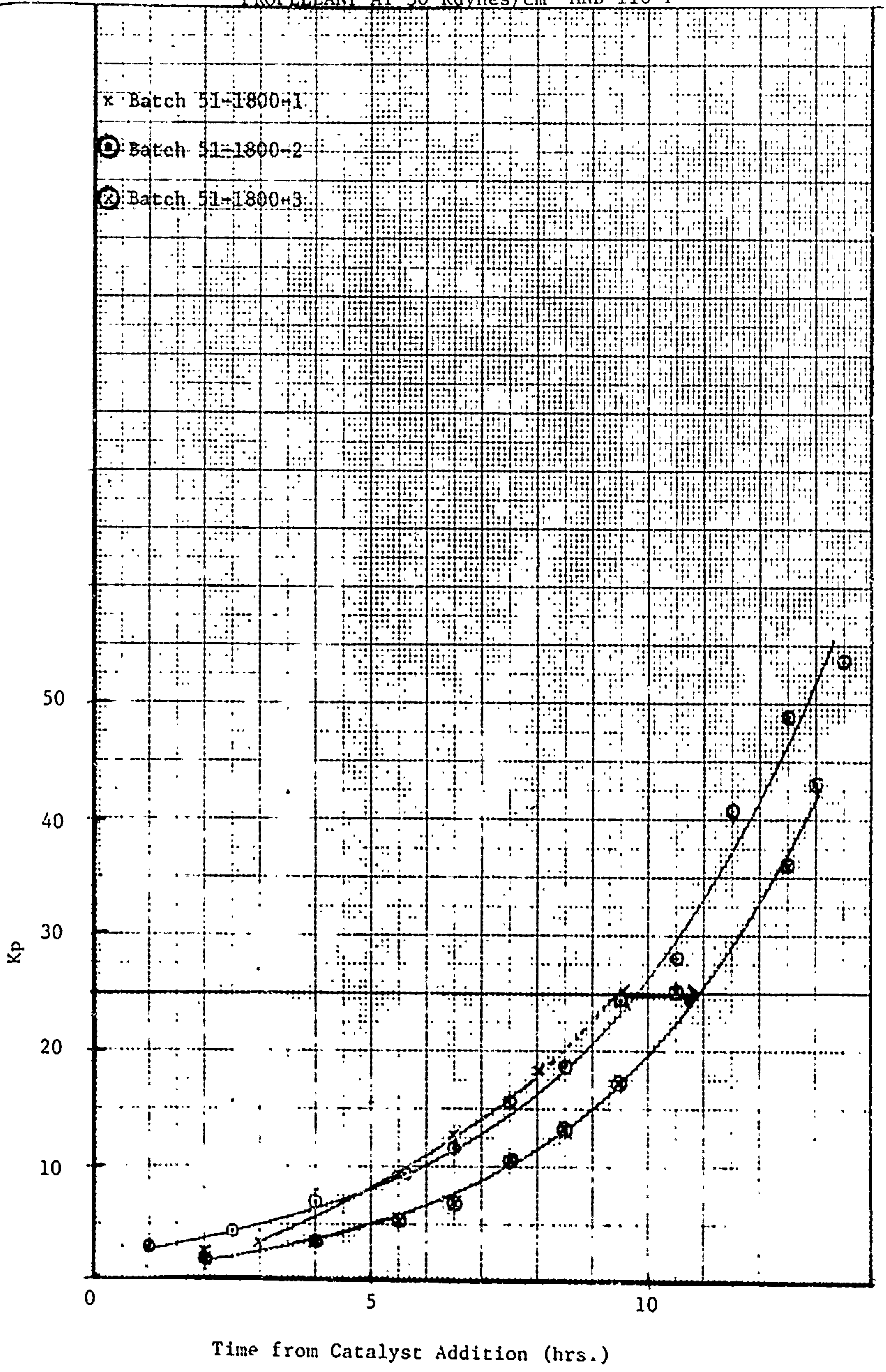


Figure 36b

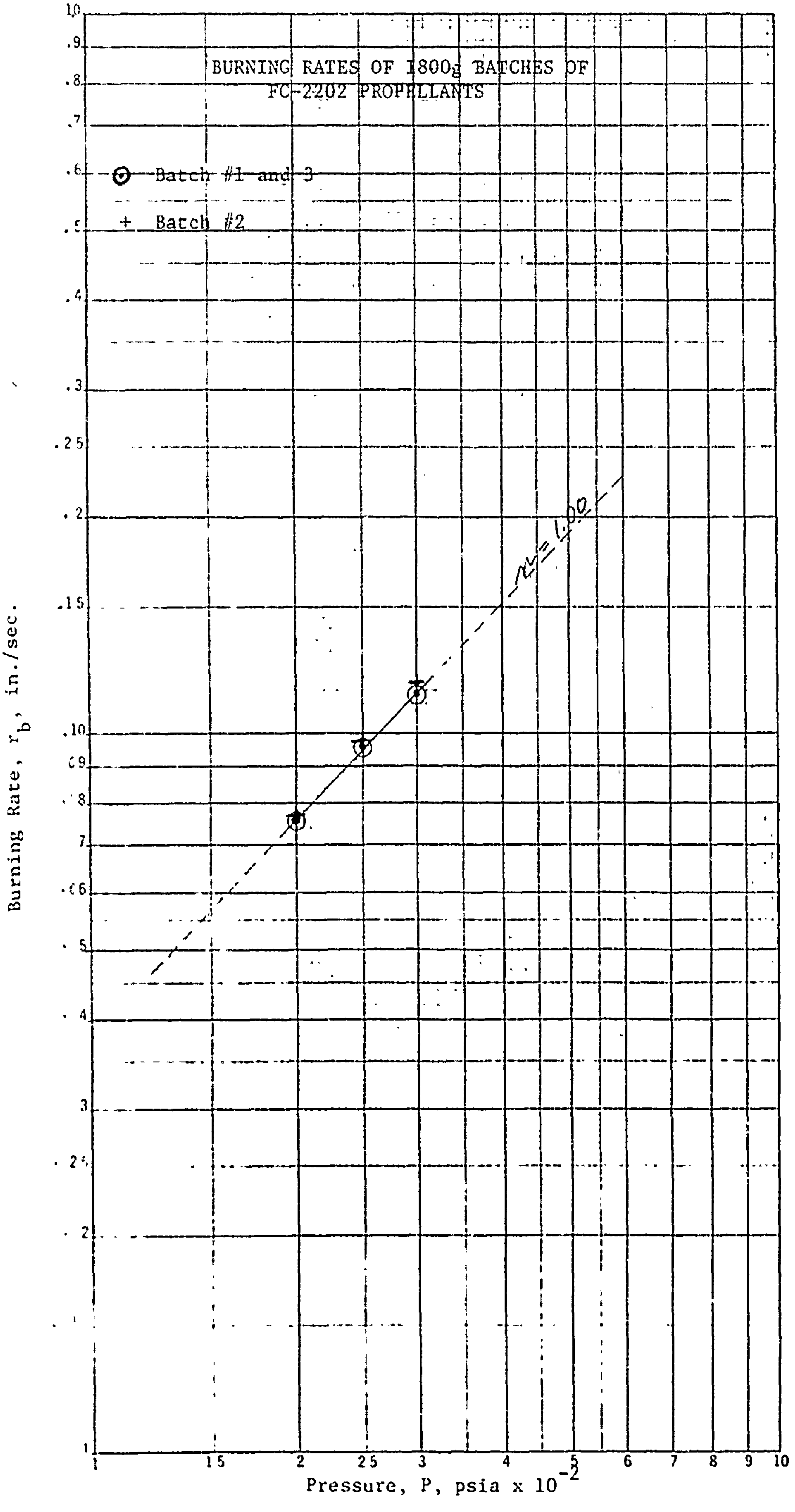

BURNING RATES OF 1800g BATCHES OF FC-2202 PROPELLANTS
⊙ Batch #1 and 3
+ Batch #2
n = 1.00
Burning Rate, r_b, in./sec.
1.0
.9
.8
.7
.6
.5
.4
.3
.25
.2
.15
.10
.09
.08
.07
.06
.05
.04
.03
.025
.02
.01
1
1.5
2
2.5
3
4
5
6
7
8
9
10
Pressure, P, psia x 10^{-2}

Figure 37