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Oxidizer Surface Coating (U)

W.C. Simpson, C.J. Busso, S.J. Rehfeld

SHELL DEVELOPMENT COMPANY
A Division of Shell Oil Company
Emeryville, California

STATEMENT #2

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

Contract No. AF 04(611)-11644
Final Report
September 1966 - September 1967

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NOTICES

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OXIDIZER SURFACE COATING (U)

Sponsoring Agency: Air Force Propulsion Laboratory
Research and Technology Division
Edwards, California

Contract No. AF 04(611)-11644

FINAL REPORT

Period: September 1966-September 1967

Reported by: W. C. Simpson
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Date of Issue: January 1968

SHELL DEVELOPMENT COMPANY
A Division of Shell Oil
Emeryville, California

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FOREWORD

This report covers the work during the period September 1, 1966 through September 30, 1967 on Project Number 3148, element number 6.25.05.18.4 for the Air Force Rocket Propulsion Laboratory, Edwards, California under Contract AF 04(611)-11644 by Shell Development Company, Emeryville, California. Project Officer: Robert C. Corley, RCPS. Submitted October 1967.

This report contains classified information extracted from other classified documents.

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

W. H. EBELKE, Col., USAF
Chief Propellants Division

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ABSTRACT

(U)   This report describes the results of a project designed to study the influence of solid oxidizers on the curing of binders for solid propellants and to explore the possibilities of minimizing interaction of oxidizers and binder components by surface coating of the oxidizer or by introduction of chemical agents so that the binder systems might more nearly achieve their maximum physical properties. Kinetic studies showed that in binders involving epoxy resins and carboxyl groups in polybutadiene-acrylic acid-acrylonitrile terpolymers, the rate of the polymerization reaction is reduced and the epoxy groups are consumed faster than carboxyl groups in the presence of ammonium perchlorate (AP). The evaluation of over two hundred surface coatings adsorbed from solution on AP, deposited on a fluidized bed of the oxidizer or merely added to the propellant formulation is described. Coatings evaluated include polyethyleneimines, linear polyalkylenepolyamines, alkyl-amines, amides and polyamides, quaternary ammonium compounds, fatty acids and polymerized fatty acids, and a variety of polymers. Since consumption of epoxy groups in AP-epoxy resin mixtures was shown to be independent of amounts of AP present, it was concluded that this interaction is related to the solubility of AP in the binder system. Methods of chemically capturing AP or its ionization or decomposition products as they appear in solution were investigated. K, Rb and Cs salts which form perchlorates of very low solubility in organic system were effective in reducing the AP-epoxy interaction. A group of proprietary compounds including potassium salts of carboxylic, sulfonic and phosphonic acids decreased AP-epoxy interaction and reduced viscosity during propellant mixing by delaying the cure reaction. A most effective solution to the AP-epoxy interaction was to convert the polybutadiene-acrylic acid-acrylonitrile terpolymer to the K, Rb or Cs salts which resulted in reasonably rapid binder cures and much improved propellant physical properties.

(C)   A brief investigation of methods of reducing the interaction of hydroxylammonium perchlorate (HAP) with epoxy resins was made. Pretreatment of HAP with tolylene diisocyanate or use of a mixture of AP and HAP showed some promise.

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OXIDIZER SURFACE COATING (U)

SECTION I

OBJECTIVES OF THE PROJECT

(U)   It is recognized that the physical properties of solid propellant binders can be adversely influenced by interference of solid oxidizers such as ammonium perchlorate with the binder cure mechanism. In this project, our attention has been concentrated on binders consisting of epoxy resin-prepolymer combinations including epoxy-polybutadiene-acrylic acid-acrylonitrile systems and epoxy-carboxyl terminated polybutadiene. Ammonium perchlorate has been the oxidizer of primary interest, with some attention directed toward the more energetic hydroxyl ammonium perchlorate in the later stages of the project.

(U)   Our first objective was to attempt to define the nature of the oxidizer-binder intereference by examining the interaction of AP with various polyepoxides and by studying the influence of AP on the kinetics of the epoxy-carboxyl reaction as a function of AP concentration, temperature and catalyst type and concentration. These results provided the basis for test methods for examining candidate systems for rendering the oxidizer inert in binder components.

(U)   A second objective of the project was to evaluate the ability of a wide variety of surface coatings and treatments to minimize the interaction of oxidizer with binder components and reduce interference with cure mechanisms.

(U)   The third objective was to prepare fully formulated solid propellants with high loadings of solids and to evaluate the influence of a variety of oxidizer surface coatings and treatments on the curing and on the mechanical properties of the cured propellants.

(C)   The fourth objective was to explore the interference between hydroxylammonium perchlorate and binder systems and to evaluate some coatings and treatments as possible means of controlling their interaction.

SECTION II

SUMMARY OF RESULTS

(U)   Studies of mixtures of finely divided AP $(0.1 \ m^2/g)$ in various epoxy compounds agitated at 80°C over periods of several hundred hours showed that the disappearance of epoxy groups was greatest in aliphatic and in cyclo-aliphatic epoxides and least in aromatic epoxides. Among aromatic epoxides, the more pure the compound (as judged by approach to theoretical epoxy content and low hydroxyl content) the less epoxy content lost in contact with AP at 80°C. The loss of epoxy groups during these studies was shown to be independent of the amount of AP surface area presented to the resin, the

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decrease in epoxy content being the same whether 0.5%w or 80% AP was present in the mixture. These results suggest that the solubility of AP in the resin may play an important role in the epoxy-AP interaction.

Investigation of reaction kinetics in the model system EPON H-825-hexanoic acid-chromium octoate at 25, 60 and 80°C indicates that the reaction appears to be first order up to 80% completion and the reaction of epoxy and carboxyl groups is stoichiometric, i.e., 1/1. At 25°C the presence of AP does not influence the kinetics. At 60°C the presence of AP does not alter the stoichiometry of the reaction but the reaction is second order, the rate is decreased by AP and the response to catalyst addition is reduced. At 80°C the reaction is second order, the rate is reduced by AP and the stoichiometry is altered so that epoxide groups are consumed faster than carboxyl groups. The intereference of AP is greater when the hydrogenated analog of the diglycidyl ether of Bisphenol-A is used as the diepoxide. Similar studies ma_e with $KClO_4$ showed it to be completely inert in these systems with respect to both reaction rate and stoichiometry.

In order to determine whether a given surface treatment had produced a surface coating on AP and in order to obtain some information concerning wettability of the coating by binder components, a method for measuring contact angles on powders was developed and shown to give results in agreement with adhesion tension measurements and with measurements on large crystals. Of the coatings on AP examined from this point of view, a silane (Dri Film SC-77) and a group of proprietary phosphonic acid derivatives with long hydrocarbon chains were wet the least by epoxy resins.

Coatings were deposited on AP by adsorption of a variety of compounds from solution. Normal butyl alcohol was the most frequently used solvent because of the very low solubility of AP and reasonably high solubility of most coating compounds in this solvent. The evaluation of these coatings was made by mixing the coated AP (20%) with EPON H-825 (80%) in rotated vials at 80°C over periods of several hundred hours with periodic determinations of the epoxy content of the resin.

Polyethyleneimine coatings were studied extensively at levels of 0.25 to 8% basis AP and it was among the most effective coatings at the 1% level according to the above evaluation method. The effectiveness of these coatings appeared to be independent of molecular weight in the range 1,200 to 100,000 and ethoxylation of the polymer had no effect. Temperature of drying of the adsorbed coating of 60°C proved to be important since higher temperatures caused the formation of polyethyleneimine perchlorate with the liberation of ammonia which accelerated the reaction of the epoxy resin. Examination of the reaction kinetics in the model system EPON H-825-hexanoic acid-chromium octoate catalyst showed that the polyethyleneimine coating on AP increased the reaction rate but did not restore the epoxy/carboxyl stoichiometry to 1/1. Reaction of the polyethyleneimine coating on AP with polyallylglycidyl ether did not improve its protective quality further.

Linear polyalkylene polyamines adsorbed from solution on AP were evaluated and tetraethylenepentamine was found to be effective in reducing attack of AP on epoxy resins. The lower molecular weight polyalkylene polyamines accelerated the reaction. A diethylenetriamine-epoxy resin adduct was ineffective.

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Alkyl monoamines varying from methylamine to C_{22} amines were evaluated as coatings adsorbed on AP. Their effectiveness in reducing the attack of AP on epoxy resins was small and no influence of alkyl chain length was evident. Hexamethylenediamine was an ineffective coating but a polyoxy-propylenediamine (6 propylene oxide units) was almost as effective as the polyalkylene polyamines. Two cyclic diamines, metaphenylenediamine and menthanediamine were evaluated and the former was found to be a moderately effective coating while the latter was ineffective.

The amides, urea and formamide, were adsorbed on AP but these coatings did not reduce the attack of AP on epoxy resins. The polyamides of polymerized linoleic acid and diethylenetriamine (Versamid 125 and 140) were adsorbed from solution and both were found to be effective coatings, the higher molecular weight Versamid 125 being the most effective.

A series of quaternary ammonium compounds was adsorbed on AP with the hope of exchanging these cationic materials for the ammonium ion in the AP surface and producing an alkyl chain outer layer on the AP. Compounds varying from tetrapropylammonium halides through dioctadecyldimethylammonium halides were evaluated as coatings but these compounds were not found to provide any protection of the epoxy resin from attack by AP and in some cases the consumption of epoxy groups was accelerated by quaternary ammonium compound coatings.

Coatings of lauric acid, stearic acid and the trimer of linoleic acid were adsorbed on AP and evaluated. The order of increasing effectiveness of the coatings was stearic acid, lauric acid, trimer of linoleic acid with only the trimer of linoleic acid being sufficiently effective to be of interest.

Several polymer coatings on AP were deposited by adsorption and evaluated. Alkavinol (a proprietary copolymer of vinyl acetate and C_{12}-C_{18} alpha olefins hydrolyzed to the alcohol form) showed a small beneficial effect in reducing the attack of AP on epoxy resins. Polystyrene and polymethyl-methacrylate polymerized in the presence of AP in a nonaqueous system also showed a small beneficial effect as coatings. Nylon polymerized in the presence of AP accelerated the attack of AP on epoxy resins. Polyorthoxylene (about 8 monomer units) deposited from solution by evaporation was a moderately effective coating.

A proprietary potassium slat of a sulfated, ethoxylated long chain alcohol (NEODOL 25-3P) adsorbed from solution proved to be an ineffective coating for AP.

Several coatings were applied to AP by vaporizing the coating into a steam of nitrogen which was used to maintain a fluidized bed of the AP. Methylamine and diethylenetriamine coatings increased the rate of attack of AP on epoxy resins while ethyleneimine and a silane (Dri Film SC-77) produced a small decrease in rate of loss of epoxy groups.

Coatings of very fine particle silica powders (Cab-O-Sil and Aerosil) deposited on AP failed to moderate the rate of attack of AP on epoxy resins.

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A general conclusion which was reached as a result of study of over 90 coatings was tnat in order to be effective, a coating must be: 1) perfect and nonporous, i.e., no uncovered corners, edges or pinholes can be tolerated, 2) it must be insoluble in binder components at 80°C and 3) it must be tough enough to withstand the abrasive action of mixing in systems with very high solid contents.

In view of these stringent requirements which a coating must meet, we turned to another approach. Because of our finding that the consumption of epoxy groups in AP-epoxy mixtures at 80°C is essentially independent of the amount of AP present, we reasoned that this reaction is related to the solubility of the AP in the binder and we therefore began to investigate ways of chemically capturing AP or its decomposition products as they appear in solution. The perchlorates with lowest solubility in organic solvents are the K, Rb and Cs salts. Investigation of these three salts as coatings for AP showed them to be as effective as the most attractive coatings studied. It was also found that simple addition of K, Rb or Cs chlorides to an epoxy resin-AP mixture was effective as coating the AP with these perchlorates in a separate operation. Kinetic studies of the epoxy-carboxyl reaction in a model system containing AP showed that the presence of both KCl and RbCl resulted in an increase in the reaction rate but did not completely restore the stoichiometry to 1/1.

On the basis of these encouraging results we investigated a series of K salts whose anions might be expected to form insoluble ammonium compounds while the K serves to precipitate perchlorate ion as it comes into solution. The following salts were found to be effective in reducing the attack of AP on epoxy resins when added at a level of 1% basis AP: KBH_4, $KMnO_4$, $KCNO$, $K_4Fe(CN)_6$ and K_2PdCl_6 with last mentioned compound being the most effective. Ammonium compounds which might be expected to decompose at relatively low temperatures and thus reduce decomposition of AP by a mass action effect were also investigated. NH_4F was the most effective of this group but was not as effective as the best of the previously mentioned group of K compounds.

In view of the effectiveness of a variety of potassium compounds in reducing the reaction of AP with epoxy groups at 80°C, eighteen proprietary Shell compounds including potassium salts of carboxylic, sulfonic and phosphonic acids were evaluated from this point of view. Fifteen of the eighteen proved to be effective and seven of these were in the same class as the best polyethylene imine coatings and inorganic K salts as judged by the screening test involving prolonged mixing of AP and the additive with epoxy resin at 80°C.

Some of the early propellant mix work employing polybutadiene-acrylic acid-acrylonitrile terpolymer (PBAN-703)-EPON binder systems and potassium salts of organic acids as additives to reduce attack of AP on epoxy groups failed to cure. It was thought that this might be caused by the competition of the anion of the acid for the epoxy group. Since the anions of these K salts of organic acids were monofunctional they would tend to terminate polymerizing chains and prevent cure. We then reasoned that the anion of the K, Rb or Cs salt should be the anion which we want to react with the epoxy group in the resin. The K, Rb and Cs salts of the terpolymer PBAN were then made, the function of the cations being to capture any perchlorate

ions entering the binder. With these salts of PBAN the combination of relatively rapid binder cures and good binder physical properties were achieved in the presence of AP.

A ball penetration measurement was utilized to follow the state of cure of PBAN-EPON-AP systems to an advanced stage for beyond the point where samples could be dissolved for titrations. The presence of 20% or more AP in a mixtur 1 was shown to prevent cure of the PBAN-EPON system while under identical conditions with $KClO_4$ as the oxidizer the cure proceeds in a manner identical to the oxidizer-free system. Polyethyleneimine-coated AP with coating levels of 0.5, 1 and 2%w basis AP were evaluated in a PBAN-EPON binder and it was shown that the 2%w coating brought the curing rate reasonably close to that of the oxidizer-free system. Cure rate of the PBAN-EPON-AP system could be made to approach that of the neat binder when the AP was coated by dropping it through saturated aqueous solutions of KCl or RbCl which produced a layer of $KClO_4$ or $RhClO_4$ on the particle surface. The simple addition of KCl, RhCl or K oxalate to the binder-AP mixture was much less effective in preventing the interference of AP with binder cure than the above mentioned coating method as judged by the ball penetration assessment of state of cure. A carboxyl terminated polybutadiene (Thiokol HC-434)-EPON H-825-chromium octoate binder system was evaluated without any oxidizer, with 20% $KClO_4$ and with 20% AP present. The curing of these three systems at 80°C as followed by ball penetration showed that this binder system was insensitive to both $KClO_4$ and NH_4ClO_4.

Propell.. t formulations containing 14%w binder, 16%w aluminum powder and 70%w ammonium perchlorate were mixed, vacuum deaerated, molded and cured at 80°C on a rigid time schedule. Prior to the curing operation the viscosity of the mix was determined with the Brookfield Helipath at 80°C in order to evaluate the viscosity-reducing capability of a number of the additives in the propellant system. The viscosity of the PBAN-EPON H-825-Al-AP base system was 4×10^6 cps at 80°C. The mix viscosity was reduced to 1.6×10^6 cps by addition of 1% basis AP of VERSATIC® 911-P or the potassium salt of the monobutyl ester of eicosyl phosphonic acid or by conversion of 10% of the PBAN to the potassium salt. A reduction of viscosity to 1.7×10^6 cps was produced by addition of 1% basis AP of the potassium salt of Shell iso-C_{12} paraffin acid, or by coating the AP with 2% polyethyleneimine. A reduction of mix viscosity to 1.8×10^6 cps was observed when 10% of the PBAN was converted to the cesium salt. Viscosities in the range 2.4 to 2.8×10^6 cps were obtained when all of the PBAN was converted to K, Rb or Cs salts. The versatic, phosphonic and isoparaffinic acid salts and the polyethyleneimine probably work by retarding curing during mixing. The mechanics of viscosity reduction by K, Rb and Cs salts is not understood since these systems do not show any lack of cure. The potassium salt of a petroleum sulfonate and K_2PdCl_6 were also observed to materially reduce mix viscosity, probably by retarding the curing reactions.

The cured propellants were tensile tested at 25°C and 50% relative humidity at a strain rate of 2 inches per minute. The results on the PBAN-703, EPON H-825, Al, AP system with various treatments are summarized in the following table. Thus, several ways have been found to improve the physical properties of this propellant system considerably. The results should also be considered in comparison with those obtained when employing the

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completely inert but ballistically unattractive oxidizer $KClO_4$ in the same binder system which gave a tensile strength of 86 psi and 75% elongation at maximum stress.

Coating or Additive	Tensile Strength, psi	Elongation at Maximum Stress, %
None	11.2	60
PBAN converted to Rb salt	54	39
PBAN converted to K salt	43	35
10% PBAN converted to K salt	36	48
10% PBAN converted to Cs salt	29	57
PBAN converted to Cs salt	26	24
10% PBAN converted to Rb salt	19	54
1% KCl basis AP	18.5	50
1% $K_4Fe(CN)_6$ basis AP	18.3	60
1% polyethyleneimine on AP	12.9	26
2% polyethyleneimine on AP	9.8	42
1% NEODOL 25-P	2.8	35
1% SPAK-I C_{12}	(a)	(a)
1% VERSATIC 911-P	(a)	(a)
1% K petroleum sulfonate	(a)	(a)
1% K monobutyleicosyl phosphonate	(a)	(a)
1% K_2PdCl_6	(a)	(a)

a) Too soft to test.

(U) The binder system Thiokol HC-434 (carboxyl terminated polybutadiene)-EPON H-825 when used with 0.05% chromium octoate catalyst was found to be inert to both $KClO_4$ and NH_4ClO_4 and gave propellants with tensile strengths of 209 and 220 psi, respectively, with about 12% elongation at maximum stress.

(C) The possible application of some of the above findings to the oxidizer hydroxyl ammonium perchlorate (HAP) was explored. The interaction of HAP and EPON H-825 was too rapid to follow at 80°C but at 60° and 20° the rate of epoxy consumption was followed by titrations. Addition of 1% or 11% KCl basis HAP to the oxidizer-resin system accelerated the interaction at 60°C. Attempts to coat HAP with a layer of the monoepoxide phenylglycidyl ether were unsuccessful, no reaction being detected. Addition of 4% tolylene diisocyanate (TDI) to HAP failed to prevent its rapid reaction with epoxy groups in EPON H-825 at 80°C but addition of 43% TDI (0.33 moles TDI/mole HAP) produced a definite retarding effect on the reaction. A potassium petroleum sulfonate which was found to delay the cure in an AP-PBAN-EPON system failed to reduce the reactivity when added at a level of 2.5% basis HAP. It appears that the thermal decomposition of HAP to produce hydroxyl amine and perchloric acid at temperatures as low as 25°C makes its use in thermosetting resin systems (which can be cured by these decomposition products) an extremely difficult problem. In view of the rapid cure of the PBAN-EPON binder system in the presence of HAP and the slow cure in the presence of AP we explored the possibility of using a combination of AP and HAP as oxidizes. An exploratory experiment in which the AP/HAP ratio was 10/1 gave a promising result in the form of a more rapid cure than in the case where AP was the only oxidizer present.

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SECTION III

REACTIVITY OF UNTREATED AMMONIUM PERCHLORATE WITH EPOXY COMPOUNDS

Since some earlier Shell research demonstrated metal perchlorates to be effective EPON resin curing agents a series of small samples of EPON H-825 (ca 0.3 gram) over ca 0.24 gram AP in one milliliter open glass containers was statically aged in an 80°C (176°F) oven. Extent of reactivity was determined by removing samples at various intervals for epoxide analysis. The data showed a slow but definite loss of epoxide with time, about 20% loss at 150 hours, and the samples were sufficiently gelled after 240 hours to be insoluble in 9:1 chlorobenzene:acetic acid at room temperature.

Further study of the AP/epoxy reactivity was conducted using an experimental set-up wherein the AP/epoxy samples were gently mixed. Reaction vessels were one-dram screw cap (Teflon liner) vials. Epoxy samples (usually about 0.3 g) plus the AP were weighed into the vials and then we added four 4 mm x 35 mm glass rods. The sealed vials were clipped normal to the face of a slowly rotating (~2 rpm) disc we constructed and installed in our Hotpak oven (see Figure 1 and 2). The tumbling action of the glass rods during rotation served to gently stir the samples. Epoxide values of aged samples were determined by immersing the vials (without caps) in 50 ml of 9:1 chloro-benzene:acetic acid solvent and stirring, with mild heating, until the contained sample was dissolved.

A. Epoxide Determination

Epoxide values in the presence of AP were determined by both visual and potentiometric procedures using either HBr or $HClO_4$ in acetic acid as titrants. Solvents used were toluene/acetic acid or chlorobenzene/acetic acid. AP concentrations up to 80%w of the sample do not interfere with the epoxide determination. The perchloric acid method has the advantage of a more stable titrant and somewhat sharper endpoints. Epoxy values reported here were determined by direct visual titrations using 0.1 N perchloric acid in glacial acetic acid, tetrabutylammonium iodide catalyst and crystal violet indicator. Sample solvent was 9/1 vol chlorobenzene/glacial acetic acid.

B. Reaction of Untreated AP With EPON H-825

Results from a series of EPON H-825 samples contacted with 5, 20 and 80%w untreated AP are plotted in Figure 3. These data indicate that about ten percent of the epoxide is consumed after 200 hours at 80°C and that rate and extent of reaction are not proportional to AP concentration.

To amplify our data on the untreated AP/EPON H-825 reaction rate at 80°C, we contacted the resin with low (5.0, 1.0 and 0.5%w) concentrations of AP at this temperature. Our data, see Table I and Figure 4 confirm that the reaction rate, at least down to 0.5%w AP, is independent of AP concentration. The relation between percent of the original epoxide consumed and time at 80°C for the AP/H-825 system is shown in Figure 5.
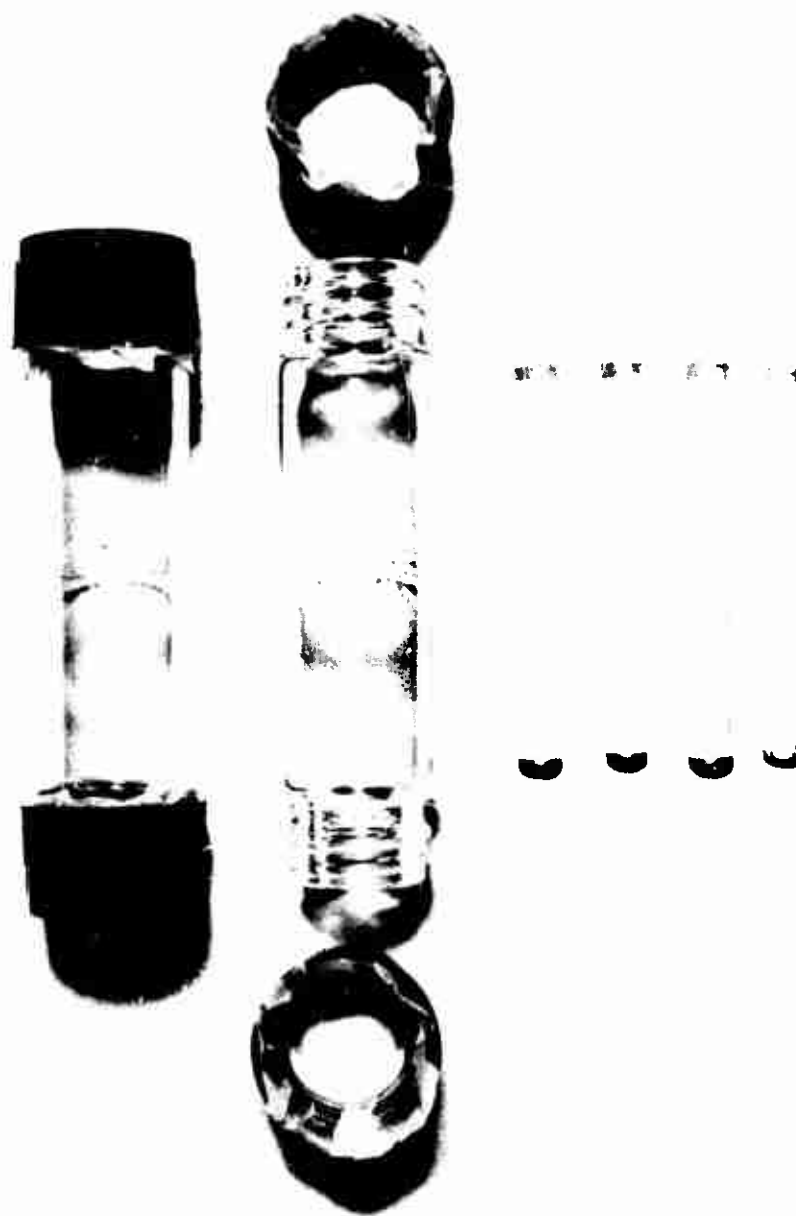
Figure 1. VIALS USED FOR AMMONIUM PERCHLORATE-EPOXY
REACTION RATE STUDIES

Figure 2. VIALS CONTAINING AP/EPOXIDE SAMPLES
POSITIONED ON ROTATING DISC IN
CONSTANT TEMPERATURE OVEN

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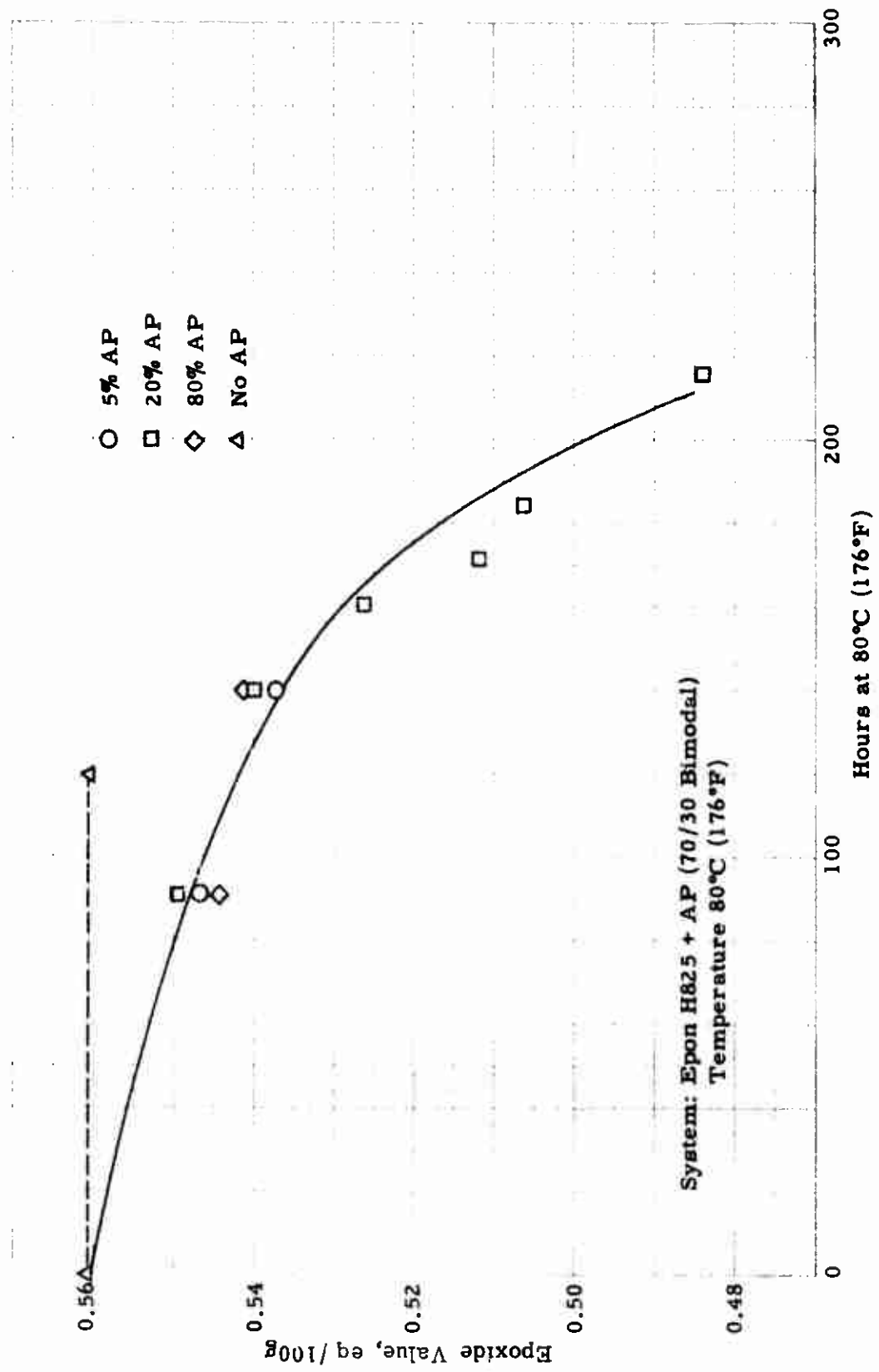
Figure 3. AMMONIUM PERCHLORATE – EPOXIDE REACTIVITY

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Table I. REACTIVITY OF "EPON" H-825 WITH LOW
CONCENTRATION OF AMMONIUM PERCHLORATE
AT 80°C

System: Continuous stirring
Initial Epoxy Value: 0.562 eq/100 g

System	Epoxy Value After Indicated Hours at 80°C		
	118 Hours	136 Hours	256 Hours
EPON H-825 + 5%w AP	0.529	-	0.482
EPON H-825 + 1.0%w AP	0.535	0.529	0.481
EPON H-825 + 0.5%w AP	-	0.529	0.483

C. Reaction of Untreated AP With Various Model Epoxy Compounds

In order to compare the influence of epoxide type on reactivity, phenylglycidyl ether and butylglycidyl ether were contacted for 119 hours at 80°C with 20%w AP. At the end of this time the phenylglycidyl ether had yellowed slightly but the epoxide value was essentially unchanged. The butyl-glycidyl ether was converted to a dark brown soft solid having <0.1 epoxy value. NMR spectra confirmed the absence of epoxide in the converted butyl-glycidyl ether sample and the lack of any significant change in the phenylglycidyl ether.

The greater reactivity of the aliphatic structure, due probably to greater AP solubility was also demonstrated using EPON 812. After 118 hours at 80°C in static contact with 20% its weight AP, EPON 812, the tris-glycidyl ether of glycerol, was converted to a hard, brittle solid.

The effect of resin purity and aromaticity on AP reactivity was determined by static contact of the following representative resins with AP at 80°C: EPON H-825 and DER 332 representing the purest commercially available Bisphenol-A type epoxies; EPON X-22, a pure crystalline diglycidyl ether of Bisphenol-A and a sample of the diglycidyl ether of hydrogenated Bisphenol-A. Our data, see Table II and Figure 6, indicate the highest purity bisphenol type resin to be least reactive and the cycloaliphatic resin to be very reactive. The reactivity of the cycloaliphatic is in line with our earlier findings with the aliphatic resins EPON 812 and butylglycidyl ether.
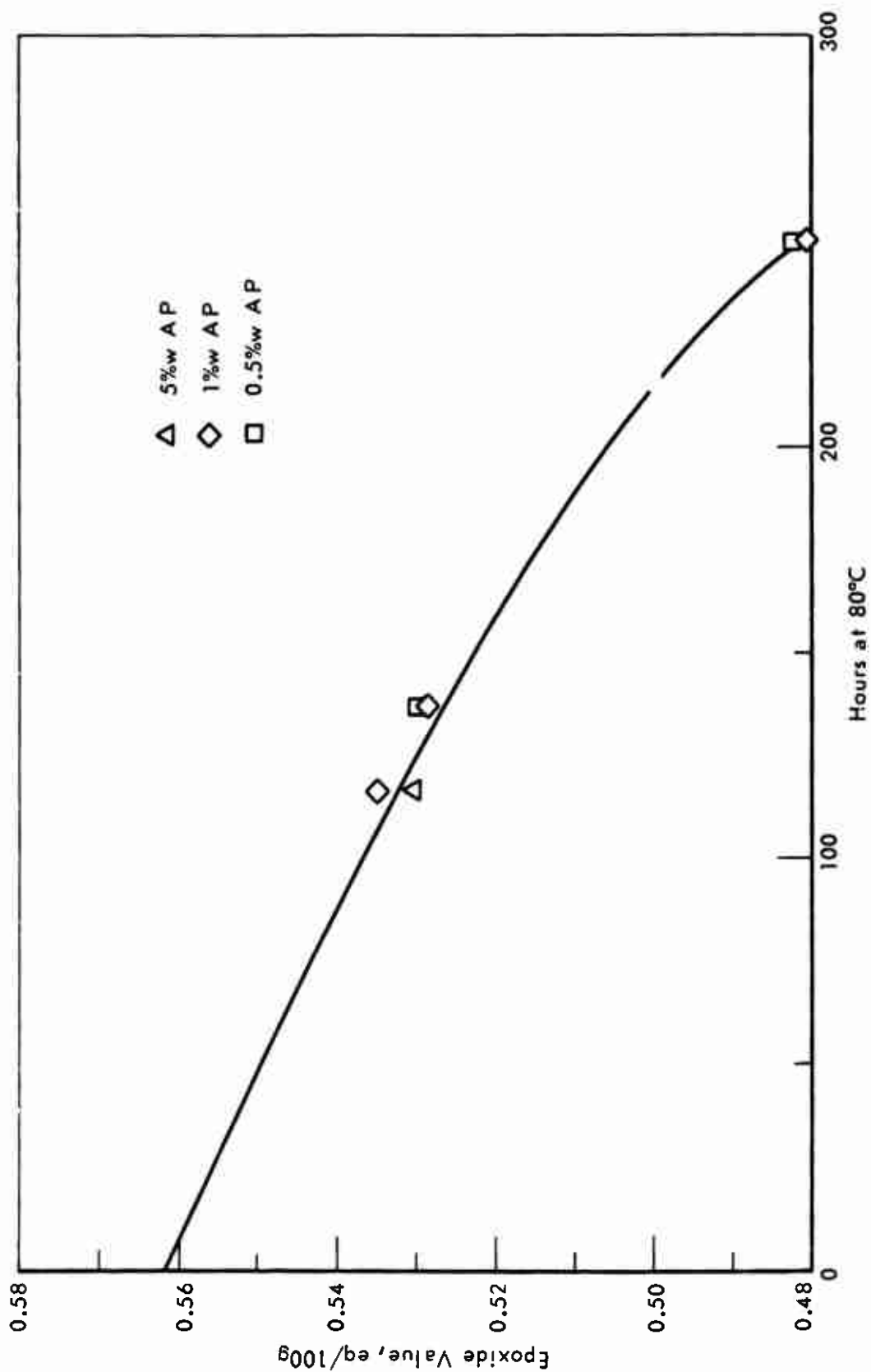
Figure 4. REACTIVITY OF EPON H-25 WITH LOW CONCENTRATIONS OF AMMONIUM PERCHLORATE AT 80°C

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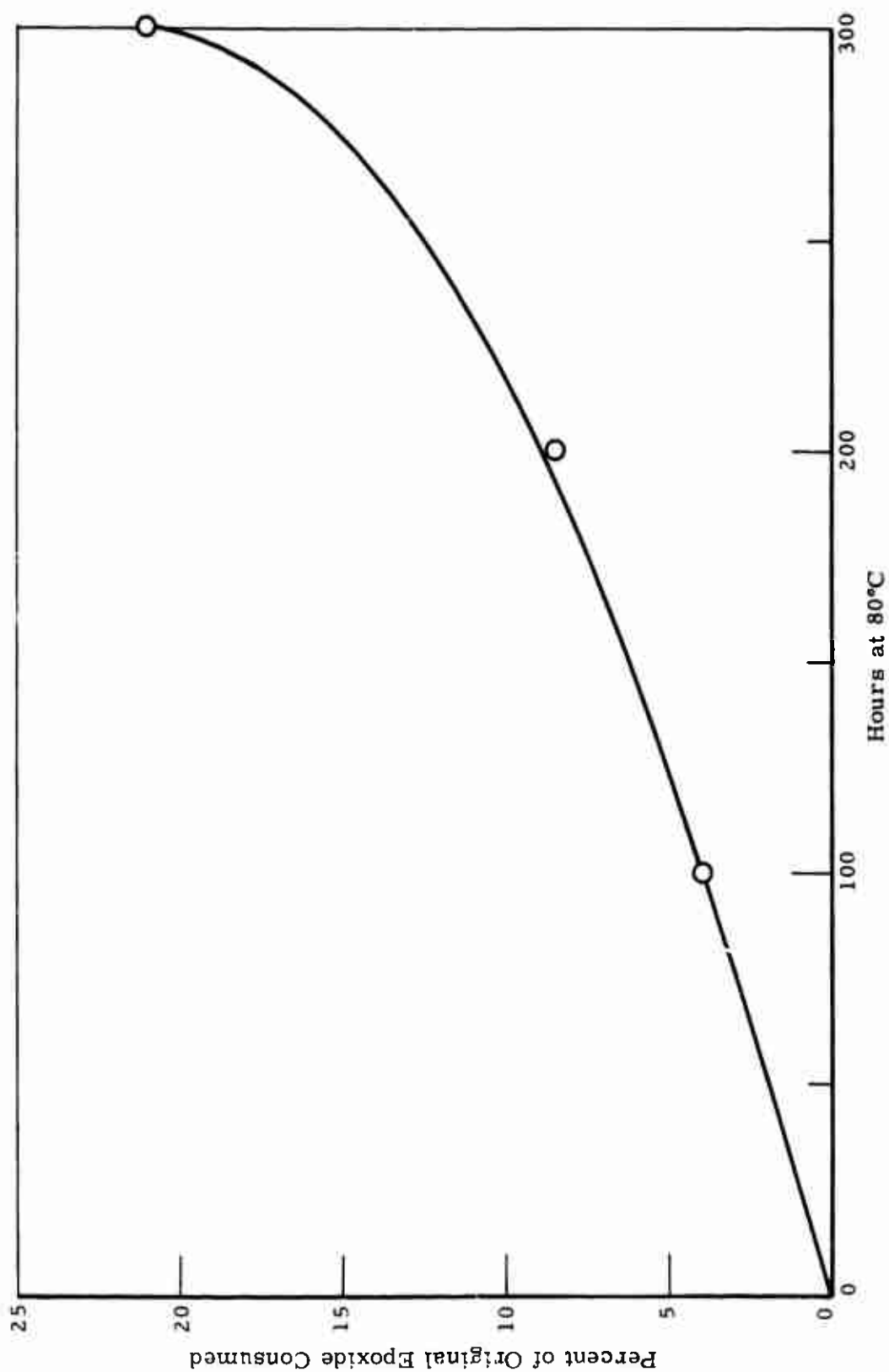
Figure 5. REACTION RATE OF 70/30 BIMODAL AMMONIUM PERCHLORATE WITH EPON H-825 AT 80°C

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Table II. REACTIVITY OF VARIOUS EPOXIES WITH AMMONIUM PERCHLORATE AT 80°C

System: Static contact. Five grams resin over one gram AP in 9 ml (20 mm x 30 mm) vial.

Epoxy Resin	Hydroxy, eq/100 g	H_2O Content, %$_w$	Epoxy Value, eq/100 g	"Purity" (% Theoretical epoxy Value)[a]	Epoxy Value After 288 Hours Contact With Ammonium Perchlorate at 80°C	Percent of Original Epoxide Consumed at End of 288 Hours at 80°C Over AP
EPON H-825 Lot 12GHJ831	0.02	0.18	0.565	96.2	0.522	7.6
DER 332	0.01	0.14	0.567	96.5	0.524	7.6
EPON X-22 Lot 1-62	0.01	0.36	0.579	98.6	0.545	5.9
Diglycidyl Ether of Hydrogenated Bisphenol-A	–	–	0.538	94.8	0.426	20.8

a) Theory for diglycidyl ether of Bisphenol-A = 0.5875 eq/100 g. Theory for diglycidyl ether of hydrogenated Bisphenol-A = 0.5673 eq/100.

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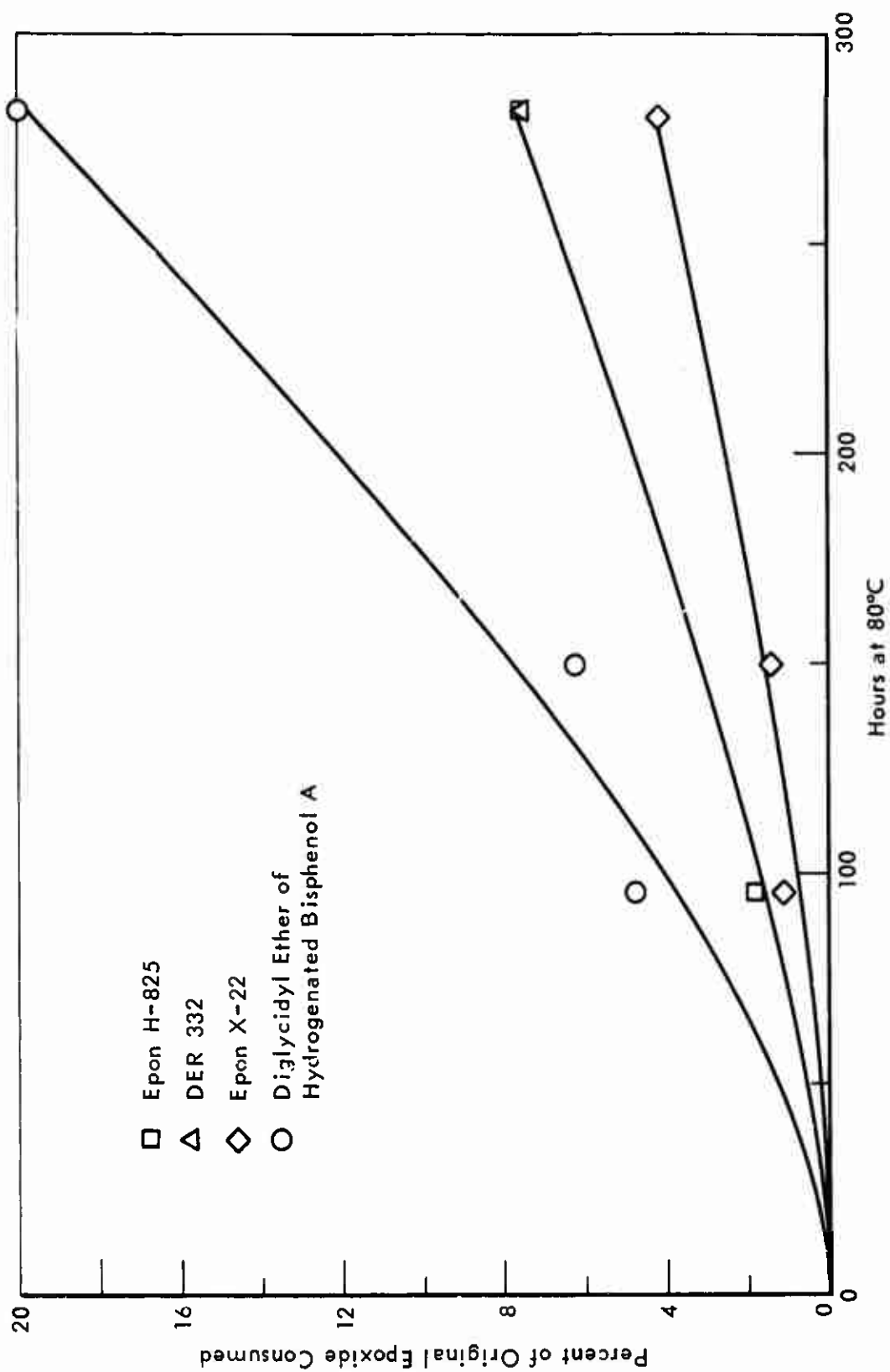
Figure 6. REACTIVITY OF VARIOUS EPOXIES WITH AMMONIUM PERCHLORATE AT 80°C
Static Contact

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SECTION IV

INFLUENCE OF AMMONIUM PERCHLORATE AND POTASSIUM PERCHLORATE
ON EPOXY-ACID REACTION KINETICS

In order to determine the effect of temperature on the magnitude of interference by ammonium perchlorate on epoxide-carboxyl reaction kinetics experiments using a model system, EPON H-825-hexanoic acid-chromium octoate, were conducted. Epoxy and acid consumption rates were determined at 25°C (77°F), 60°C (149°F) and 80°C (176°F) for samples containing varying catalyst concentrations both neat and in the presence of ammonium perchlorate.

Rate data for triphenylphosphine and benzyldimethylamine catalyzed systems at 80°C were also determined.

The base system used in our rate studies contained 1/1 epoxy to carboxyl equivalents, both epoxy and carboxyl initial concentrations were 0.344 eq/100 g. Weight percent concentrations were 60.34% EPON H-825 and 39.66% hexanoic acid (Aldrich Chemical Company, 99+%). Equivalent weights for EPON H-825 and hexanoic acid are 175 and 115, respectively.

One ounce glass containers containing the samples, ca 20 grams, plus a 1 x 4 cm glass rod (to improve mixing) were attached to a slowly revolving wheel in a constant temperature oven (see Figures 7 and 8). Aliquots were withdrawn at desired intervals for acid and epoxy analyses.

The 25°C (77°F) data for 0.1, 0.5 and 1.0% chromium octoate (on EPON H-825) and zero, 1% and 20%w ammonium perchlorate are plotted in Figures 9, 10 and 11.

Sixty degree data (140°F) for catalyst concentrations of zero, 0.1, 0.25 and 0.50% and ammonium perchlorate concentrations of zero to 50% are shown in Figures 12 through 16.

Rate data at 80°C (176°F) for: a) uncatalyzed, b) 1% triphenylphosphine catalyzed, c) 0.5% benzyldimethylamine catalyzed and d) 0.10% chromium octoate catalyzed systems, neat and in the presence of varying ammounts of ammonium perchlorate are plotted in Figures 17 through 21.

From the data obtained in this series of experiments the following conclusions may be drawn relative to the kinetics of this system and the influence of ammonium perchlorate (AP):

1) In the absence of AP, epoxide and acid consumption are stoichiometric and up to at least 80% completion the reaction follows the first-order rule, i.e., a plot of log C versus time is linear.

2) At 25°C (77°F) the presence of AP has no effect on the reaction kinetics.

3) At 60°C (140°F) the presence of AP does not alter the desired 1/1 epoxy/carboxyl reaction stoichiometry. However, AP does significantly reduce reaction rate relative to the neat system. Magnitude of rate reduction

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Figure 7. "PIGGYBACK" VESSELS USED FOR REACTION KINETICS STUDIES

Figure 8. "PIGGYBACK" VESSELS ATTACHED TO REVOLVING WHEEL
IN CONSTANT TEMPERATURE OVEN
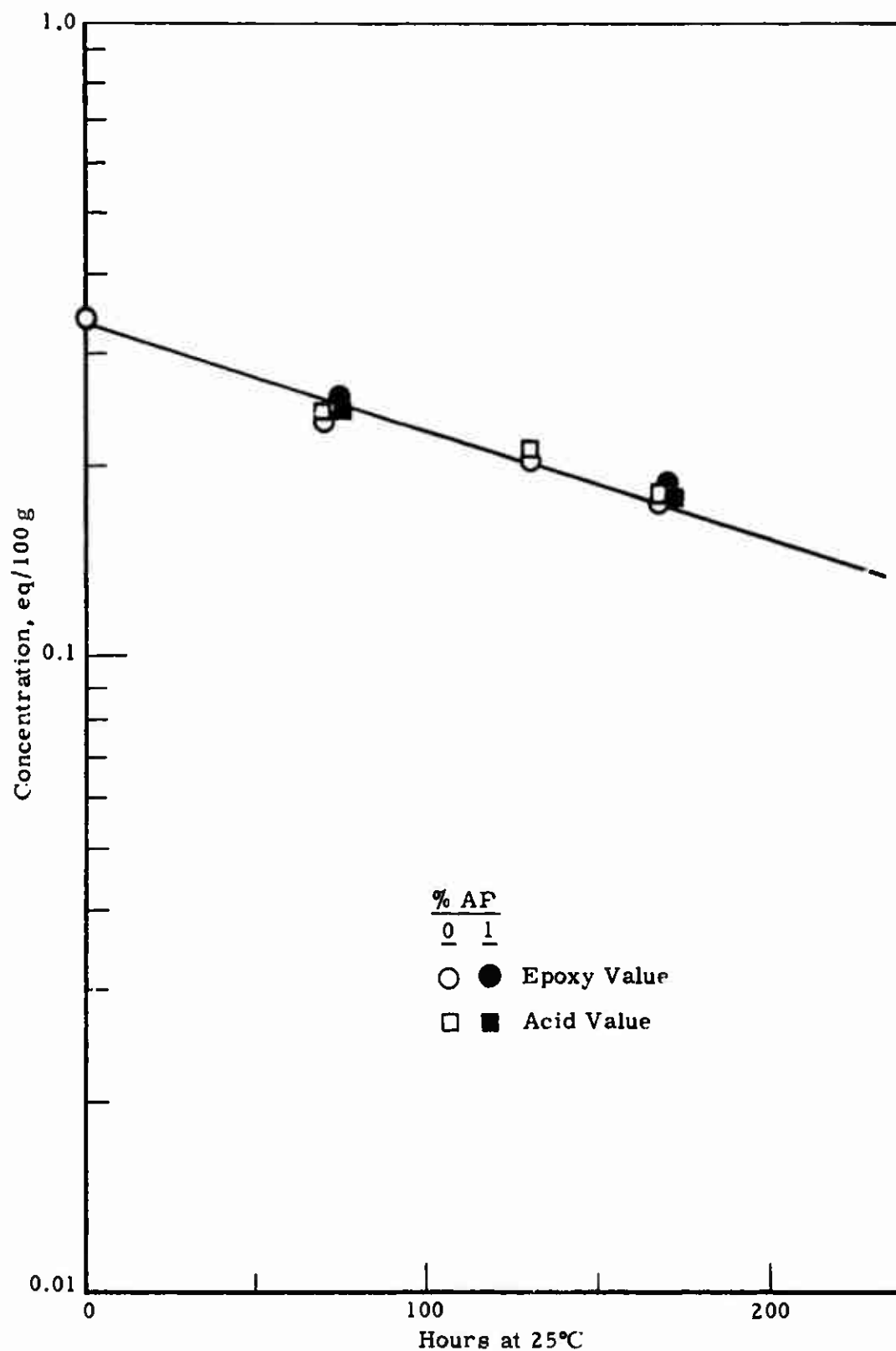
Figure 9. INFLUENCE OF AMMONIUM PERCHLORATE ON
REACTION KINETICS OF EPON H-825-HEXANOIC ACID-
0.1% Cr (OCT)₃ AT 25°C
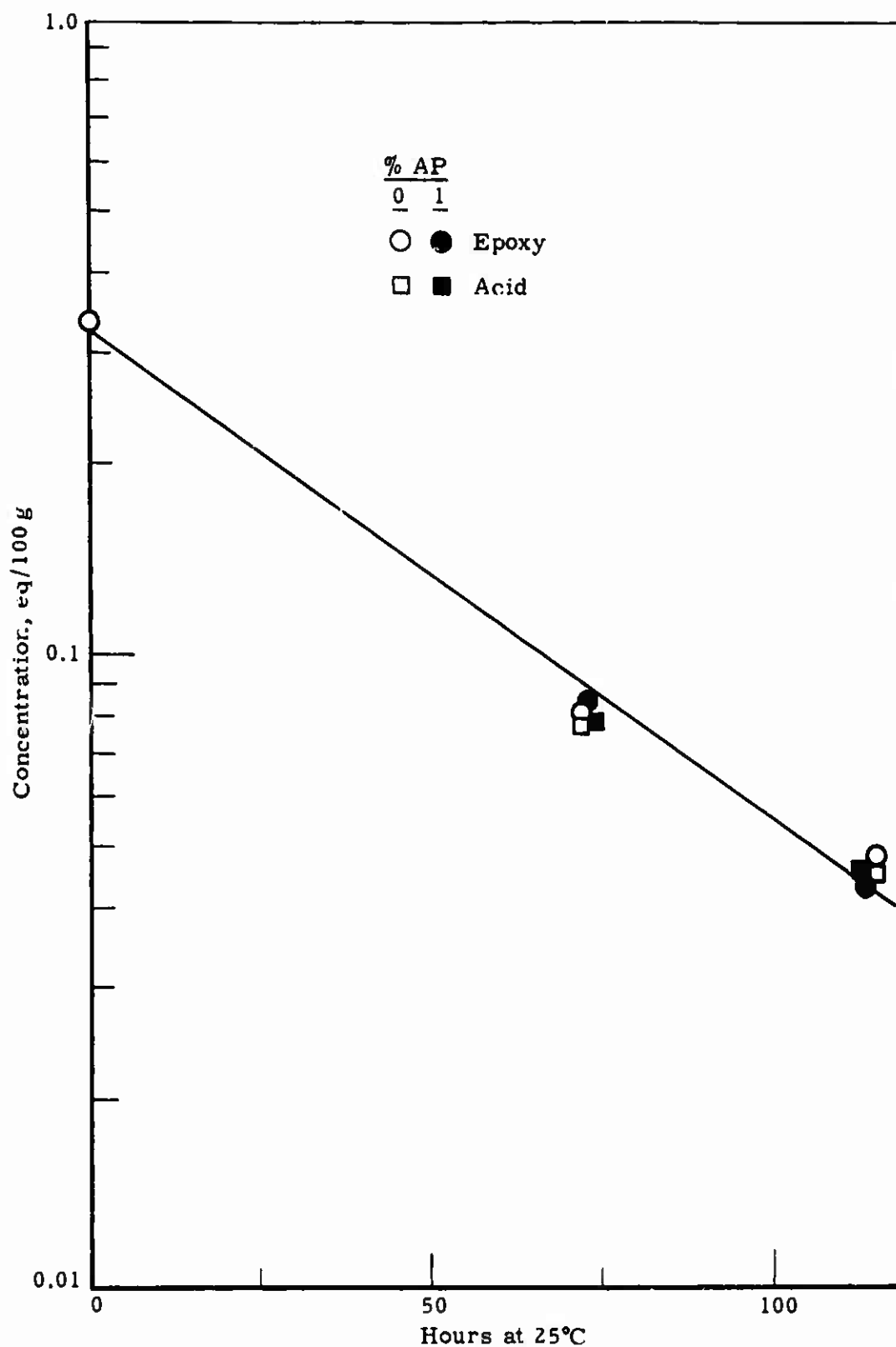
Figure 10. INFLUENCE OF AMMONIUM PERCHLORATE ON REACTION KINETICS OF EPON H-825-HEXANOIC ACID-0.5% Cr (OCT)₃ AT 25°C

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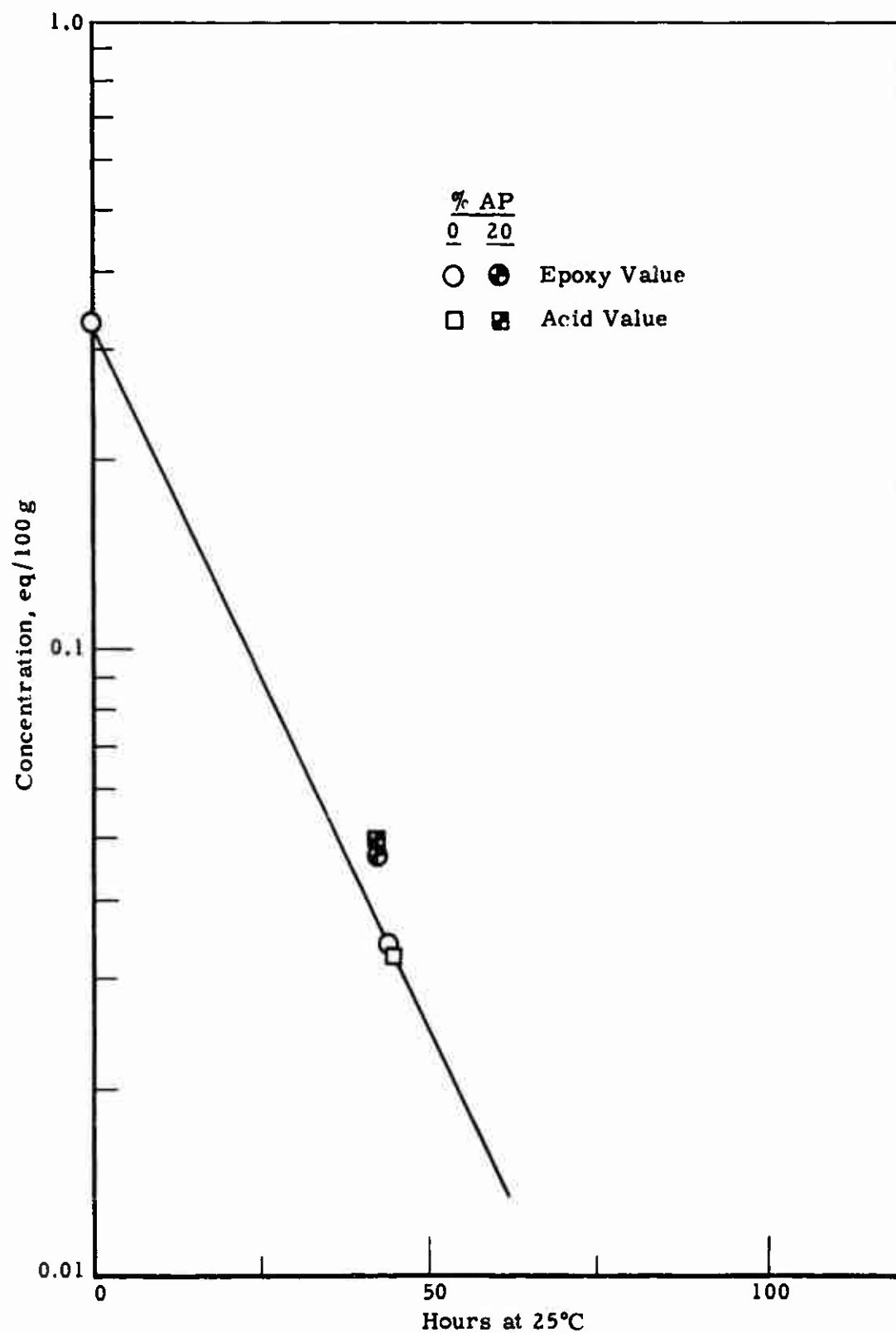
Figure 11. INFLUENCE OF AMMONIUM PERCHLORATE ON REACTION KiNETICS OF EPON H-825-HEXANOIC ACID- 1.0% Cr (OCT)₃ AT 25°C

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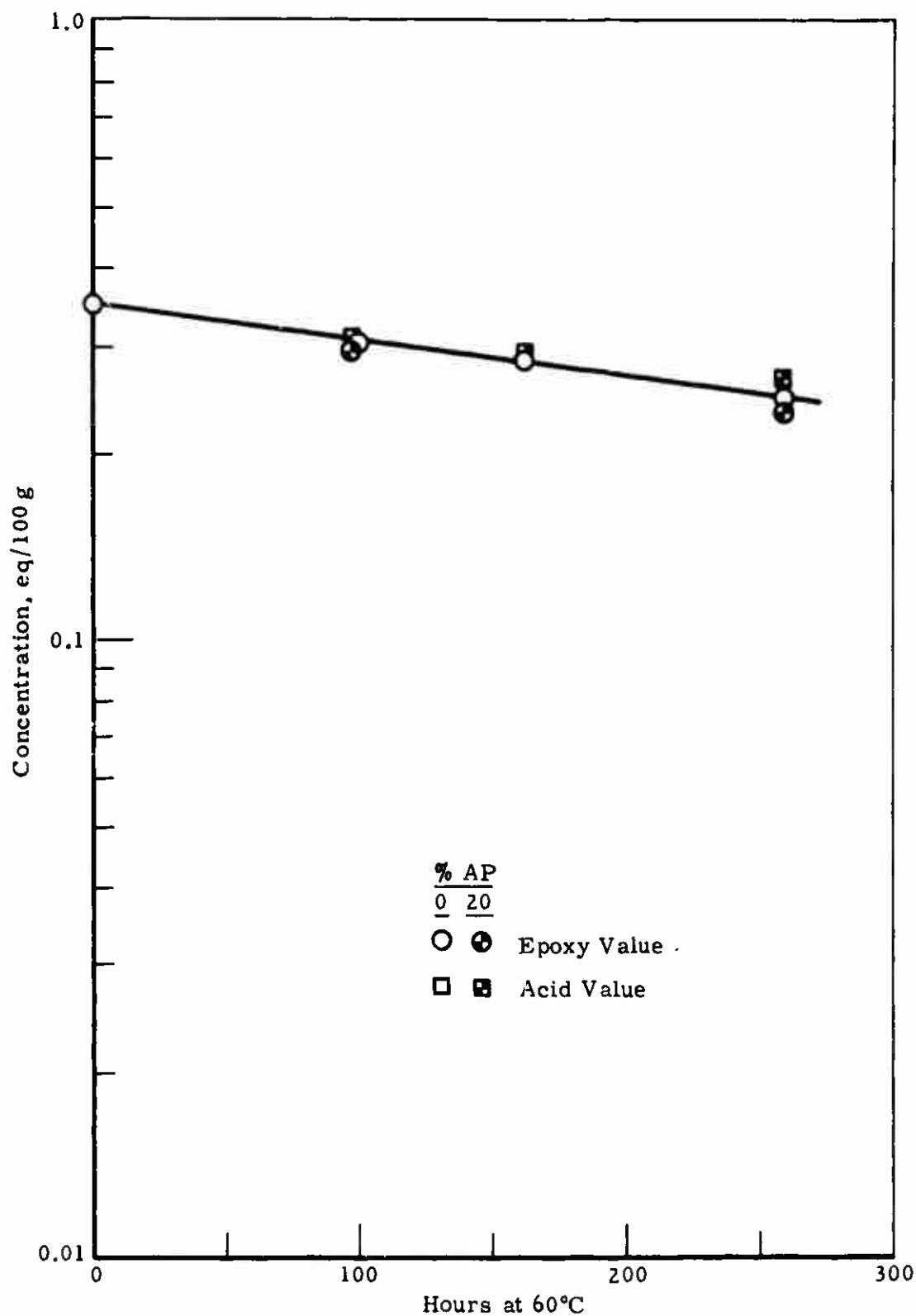
Figure 12. INFLUENCE OF AMMONIUM PERCHLORATE ON
KINETICS OF UNCATALYZED EPON H-825-HEXANOIC
ACID REACTION AT 60°C

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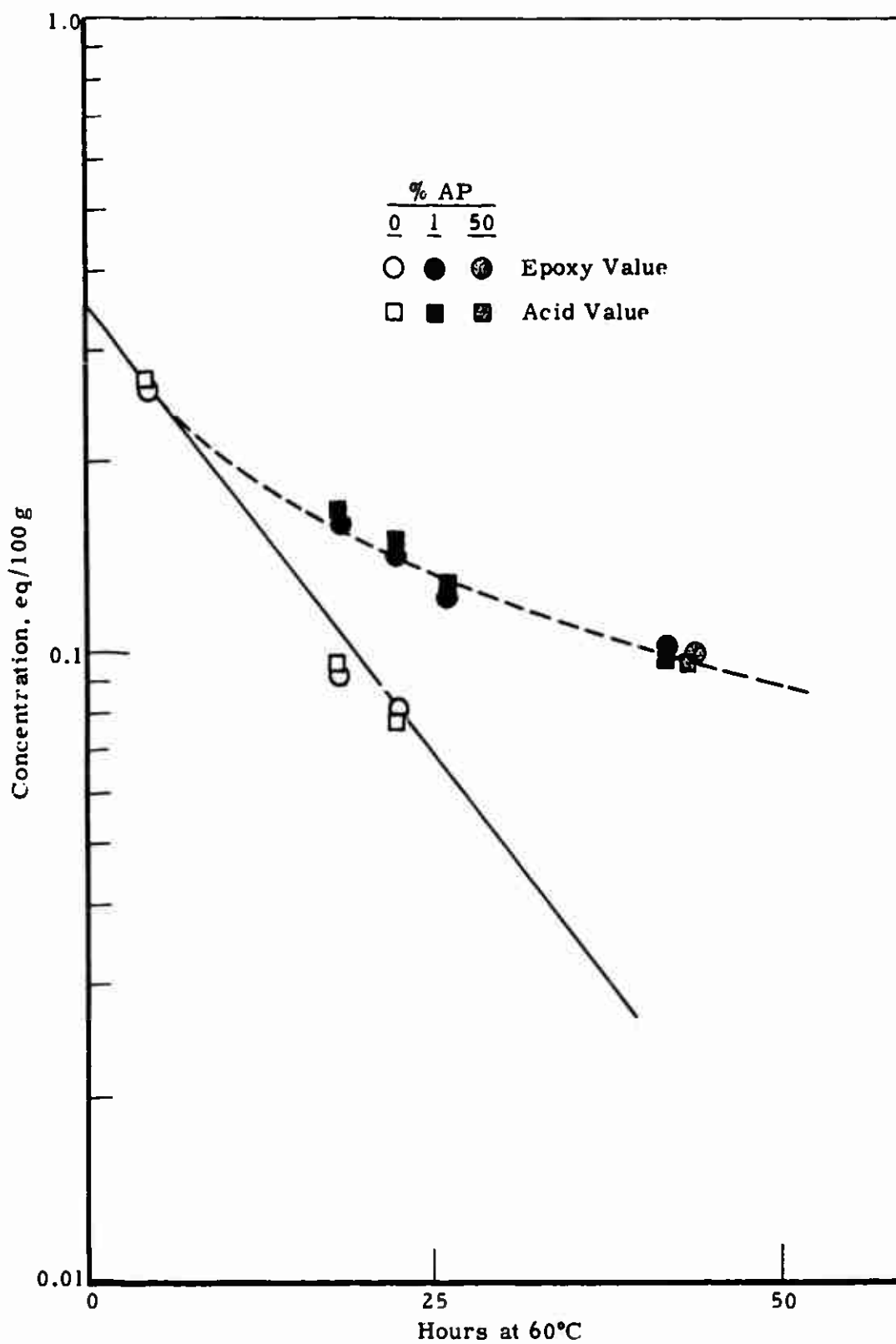
Figure 13. INFLUENCE OF AMMONIUM PERCHLORATE ON REACTION KINETICS OF EPON H-825-HEXANOIC ACID- 0.1% Cr (OCT)₃ AT 60°C

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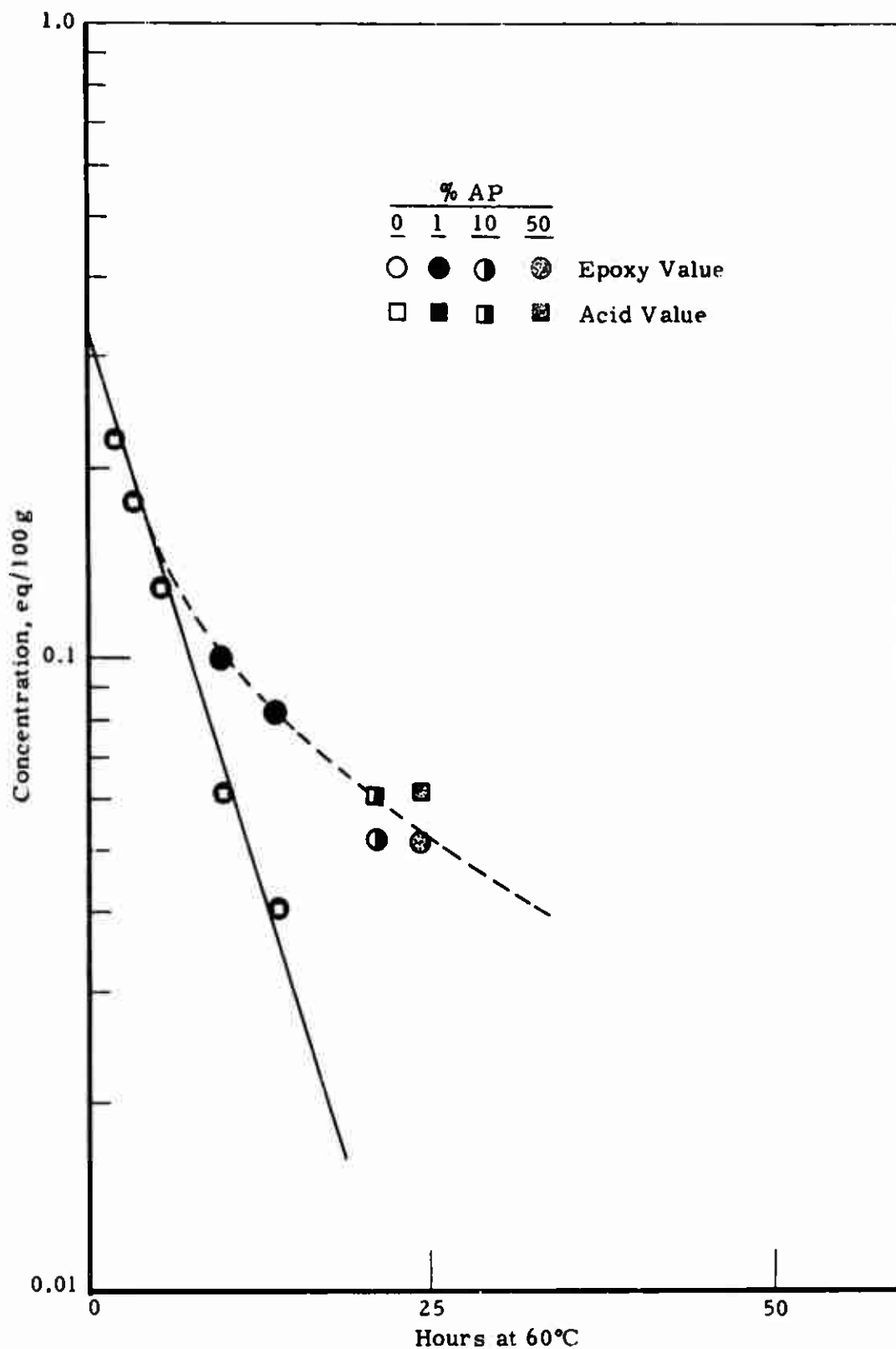
Figure 14. INFLUENCE OF AMMONIUM PERCHLORATE ON
REACTION KINETICS OF EPON H-825-HEXANOIC ACID-
0.25% Cr (OCT)₃ AT 60°C
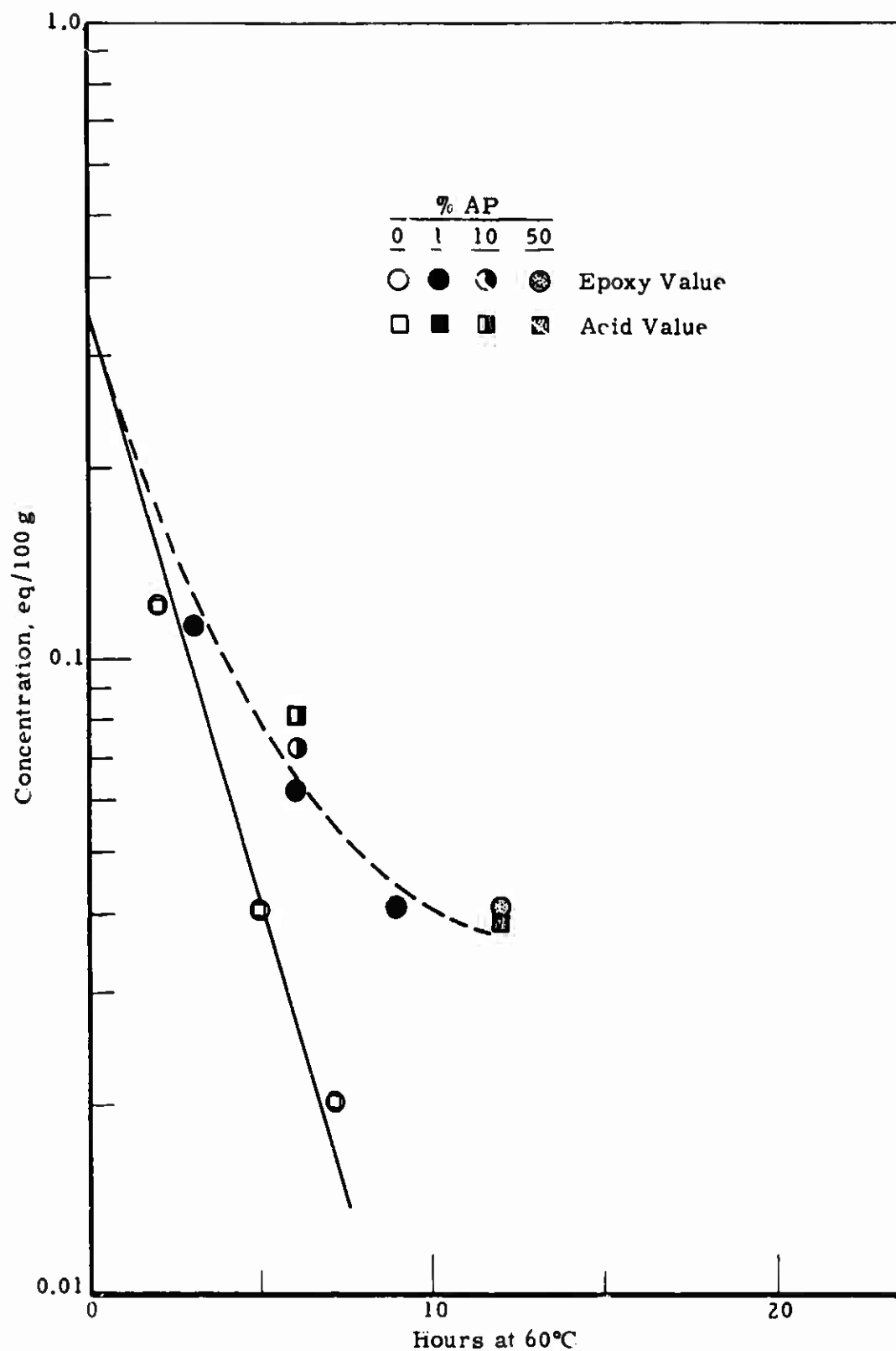
Figure 15. INFLUENCE OF AMMONIUM PERCHLORATE ON
REACTION KINETICS OF EPON H-825-HEXANOIC ACID-
0.50% Cr (OCT)₃ AT 60°C

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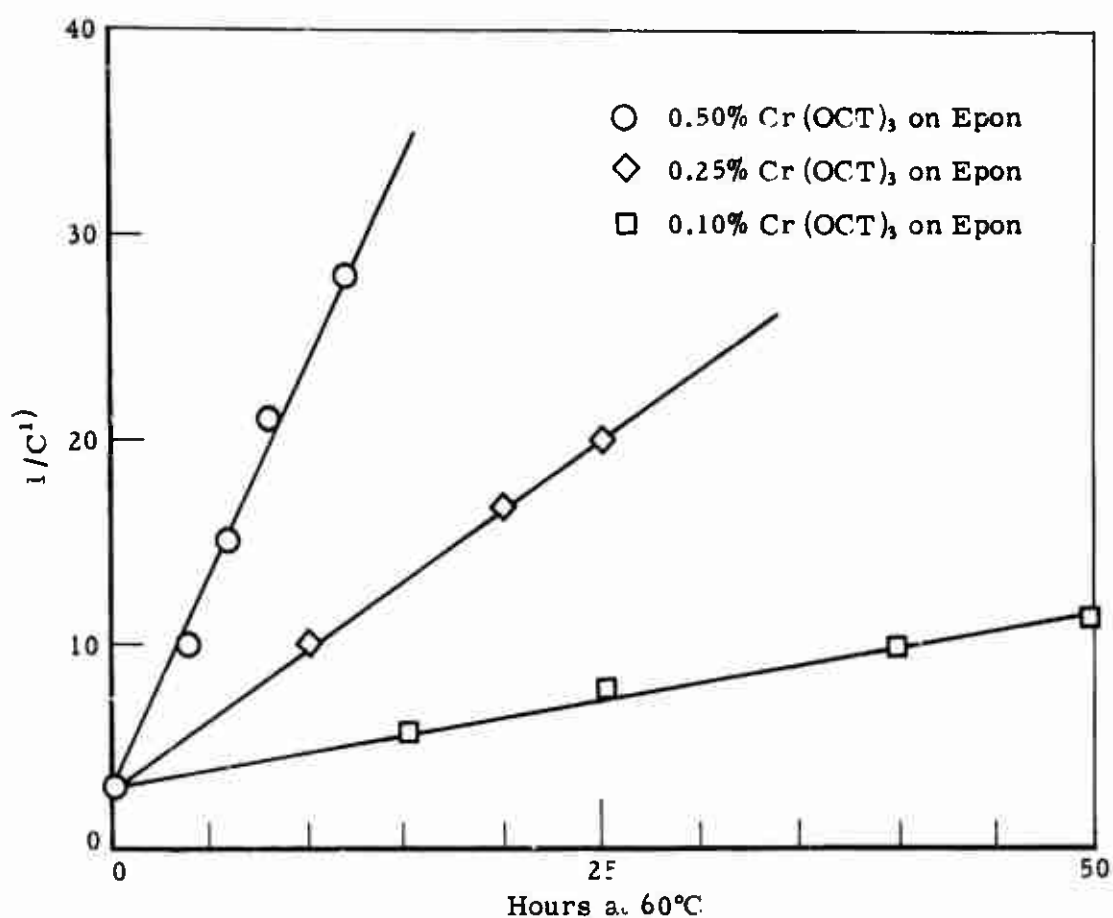
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Figure 16. REACTION RATE AT 60°C OF EPON H-825
HEXANOIC ACID-Cr (OCT)₃ IN PRESENCE OF
AMMONIUM PERCHLORATE

1) Epoxide or Acid Concentration, eq/100 g
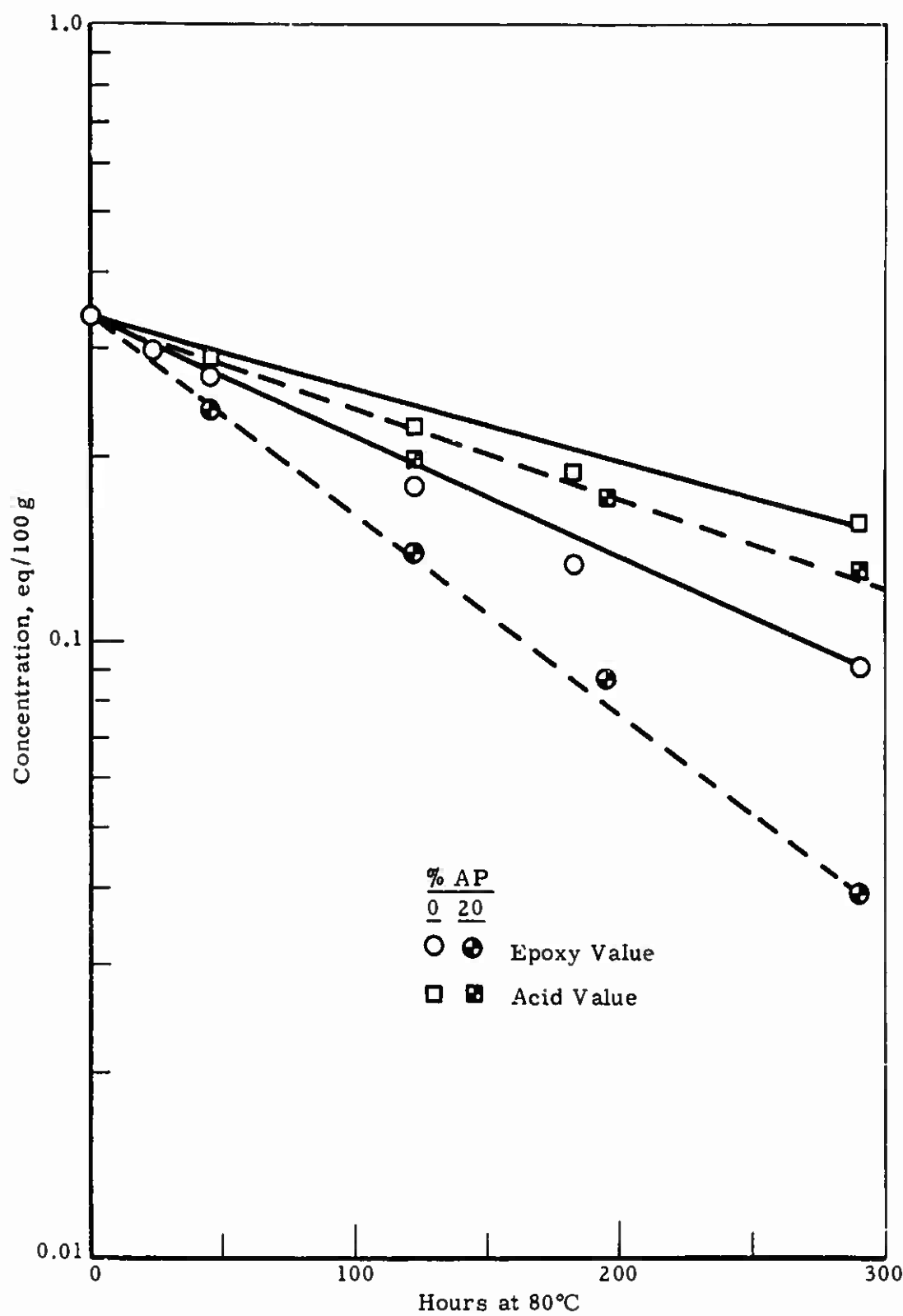
Figure 17. INFLUENCE OF AMMONIUM PERCHLORATE ON
KINETICS OF UNCATALYZED EPON H-85-HEXANOIC
ACID REACTION AT 80°C
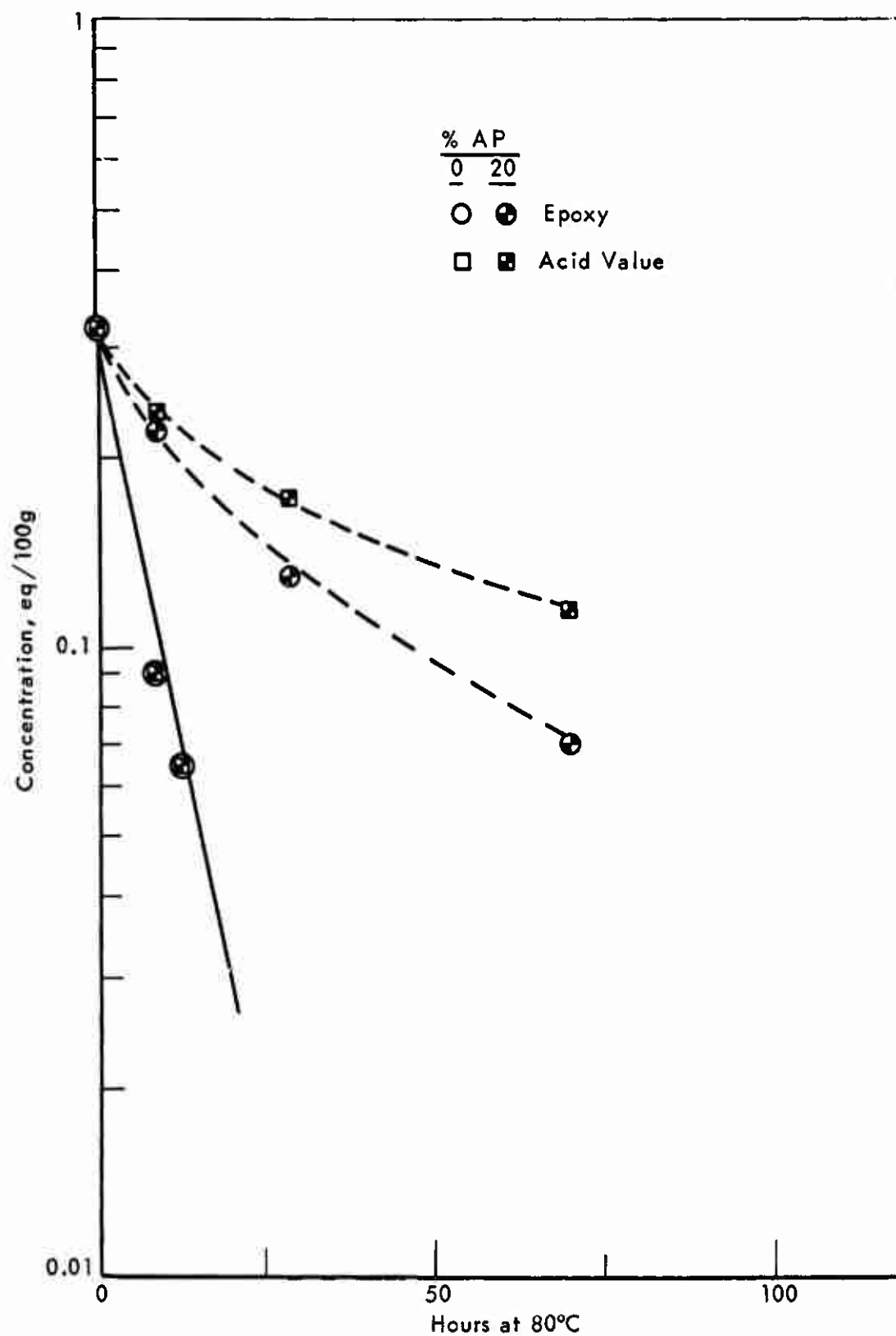
Figure 18. EPON H-825 – HEXANOIC ACID – 1% T PP
EFFECT OF AMMONIUM PERCHLORATE ON KINETICS

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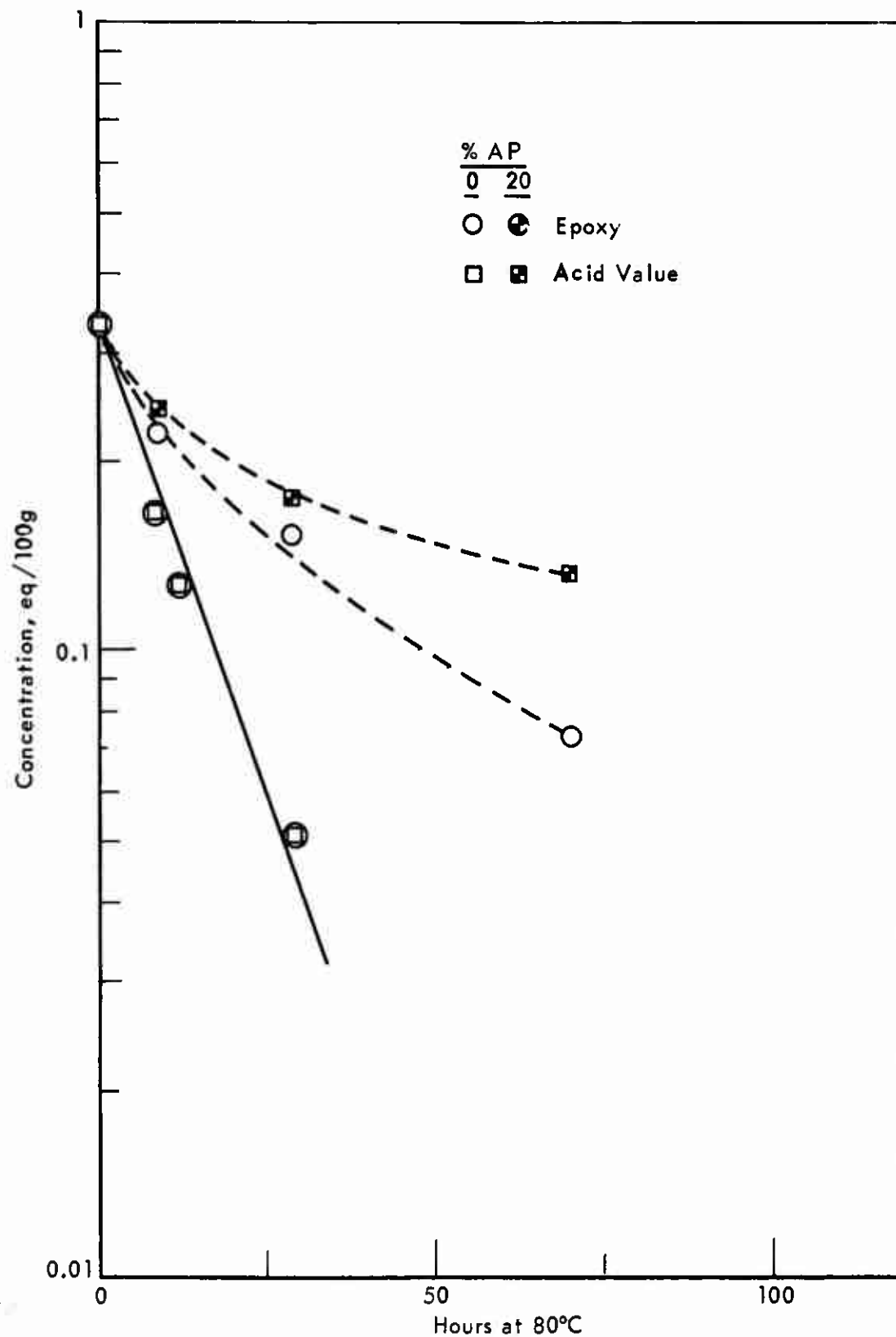
Figure 19. EPON H-825 - HEXANOIC ACID - 0.5% BDMA
EFFECT OF AMMONIUM PERCHLORATE ON KINETICS
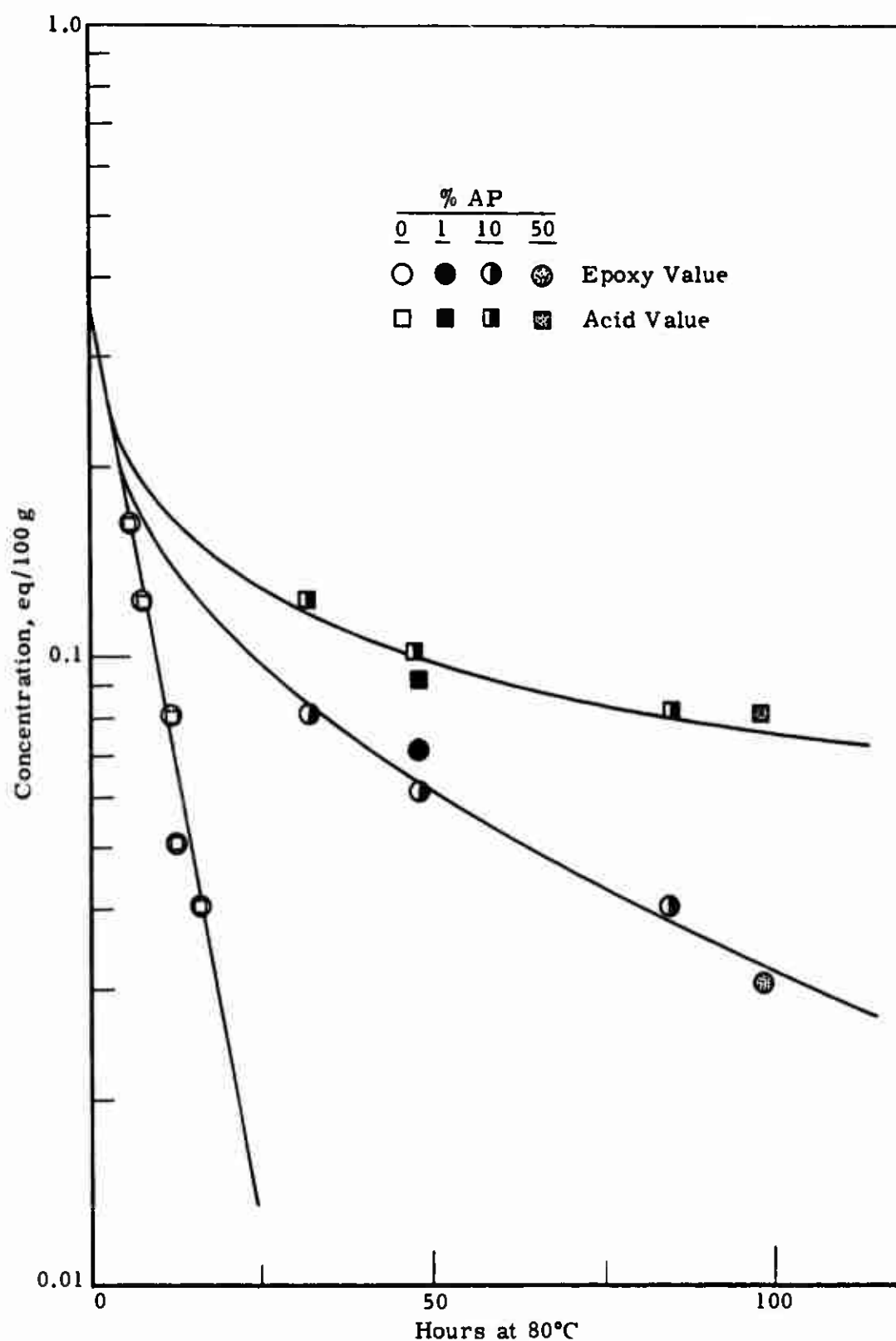
Figure 20. INFLUENCE OF AMMONIUM PERCHLORATE ON
REACTION KINETICS OF EPON H-825-HEXANOIC ACID-
0.10 Cr (OCT), AT 80°C
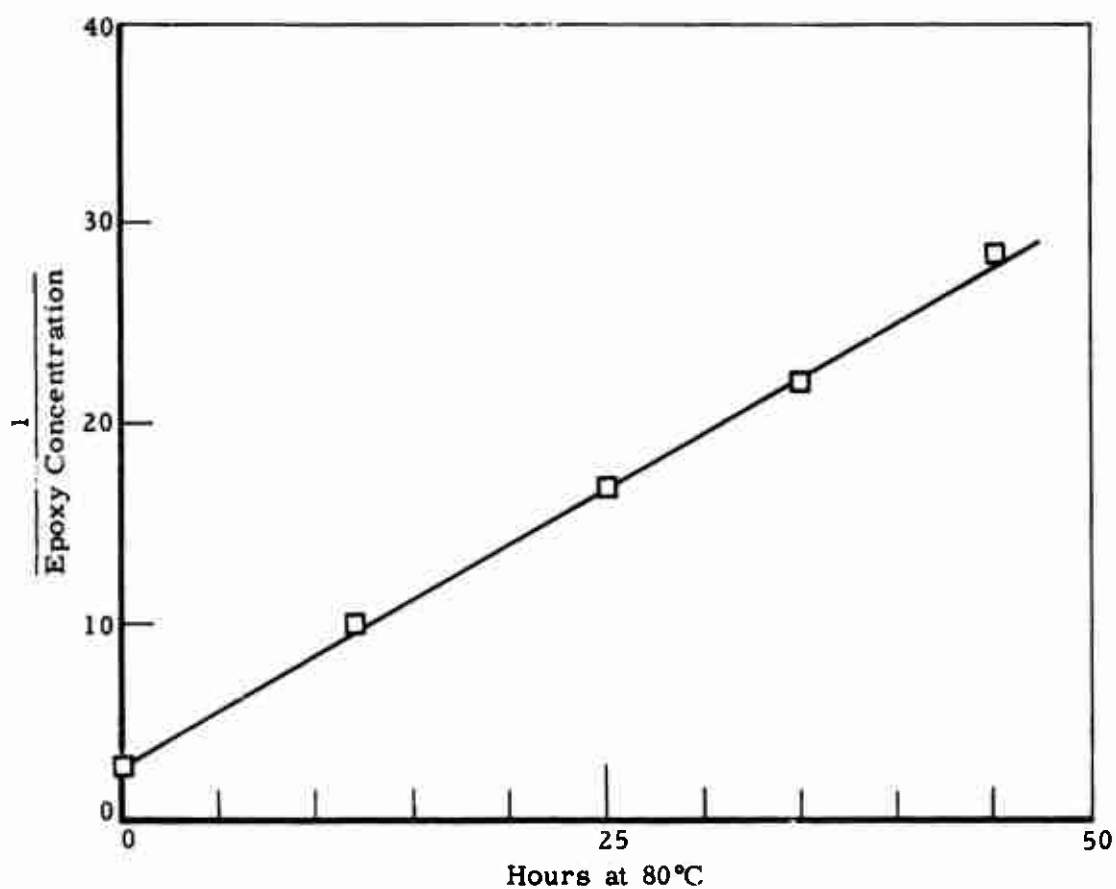
Figure 21. REACTION RATE AT 80°C OF EPON H-825-
HEXANOIC ACID-0.1% Cr (OCT)₃ IN PRESENCE OF
AMMONIUM PERCHLORATE

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based on time to 75% completion of reaction varies from 100% at 0.1% catalyst to 25% at 0.5% catalyst concentration. In addition, the reaction is second-order in the presence of AP (plot of $1/C$ versus time is linear).

4) At 80°C (176°F) AP not only reduces reaction rate, but significantly alters the epoxy-acid reaction stoichiometry so that epoxide is consumed at a greater rate than the acid. Epoxide consumption rate in the presence of AP follows the second-order rule.

Our results on this model system suggest that acid-epoxide binder systems containing an effective carboxyl-epoxide reaction catalyst and cured at 60°C or below will cure more slowly in the presence of AP but should develop ultimate mechanical properties equivalent to similar systems containing inert filler.

To supplement our finding that the saturated system is more reactive with AP than the conventional aromatic BPA derived resin (see Figure 6), we determined the reaction rate of the saturated resin with hexanoic acid, neat and over 20%w AP. Our data, see Figure 22, show the reaction rate of the saturated resin in the neat system to be faster than EPON H-825. However, the influence of AP in the reducing reaction rate and interfering with epoxy-carboxyl stoichiometry is relatively greater with the saturated resin.

Since $KClO_4$ was found to be inert toward EPON H-825 in our screening test at 80°C, see No. 77 in Table XVII it was of interest to confirm the inactivity of this salt in our epoxy-acid system. Kinetic data on the model system, neat and in the presence of 20%w $KClO_4$ (see Figure 23) confirms that potassium perchlorate is inert in this system at 80°C with respect to both rate and stoichiometry.

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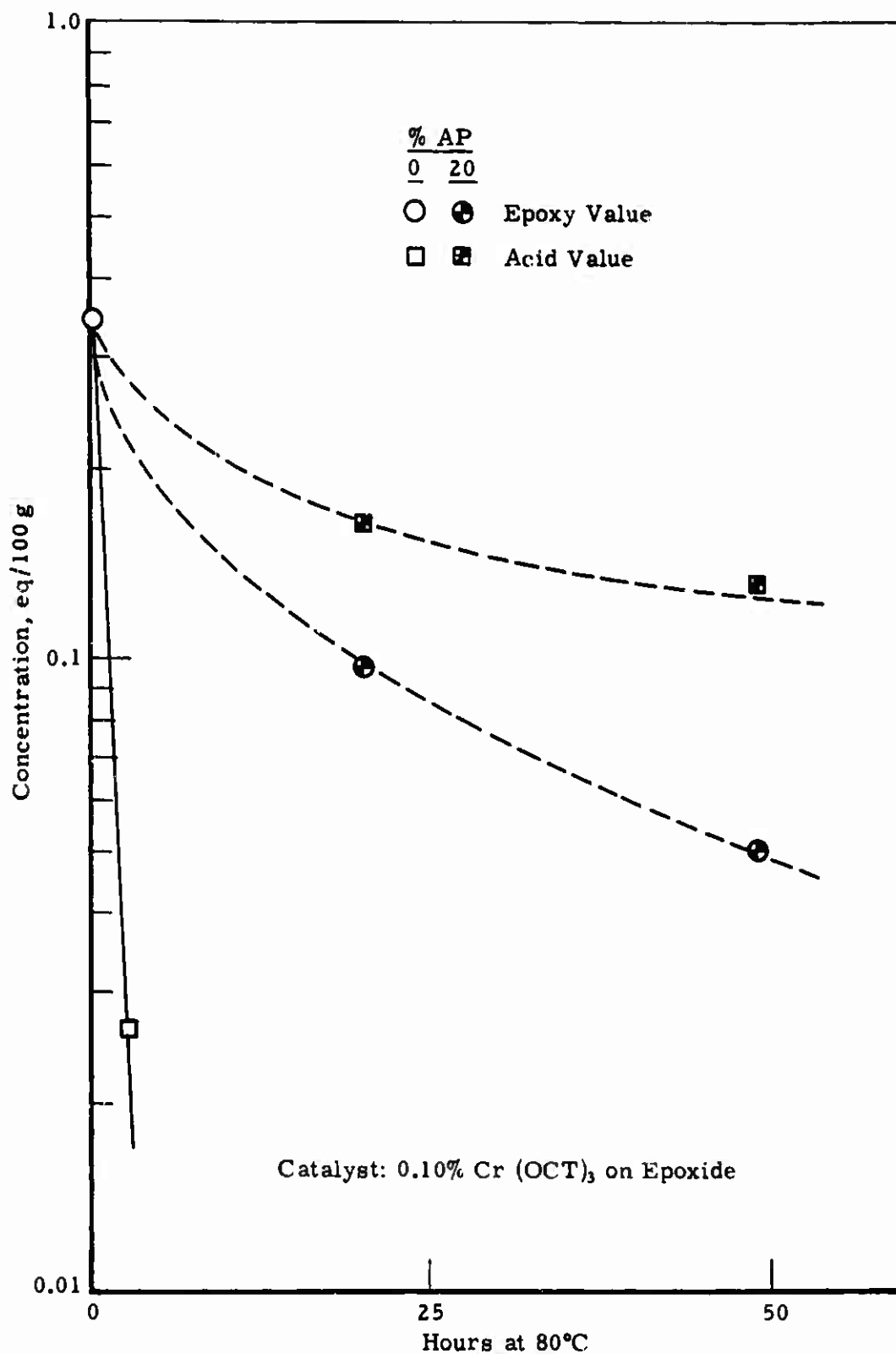
Figure 22. INFLUENCE OF AP ON KINETICS OF GLYCIDYL ETHER
OF HYDROGENATED BISPHENOL A-HEXANOIC ACID REACTION
AT 80°C

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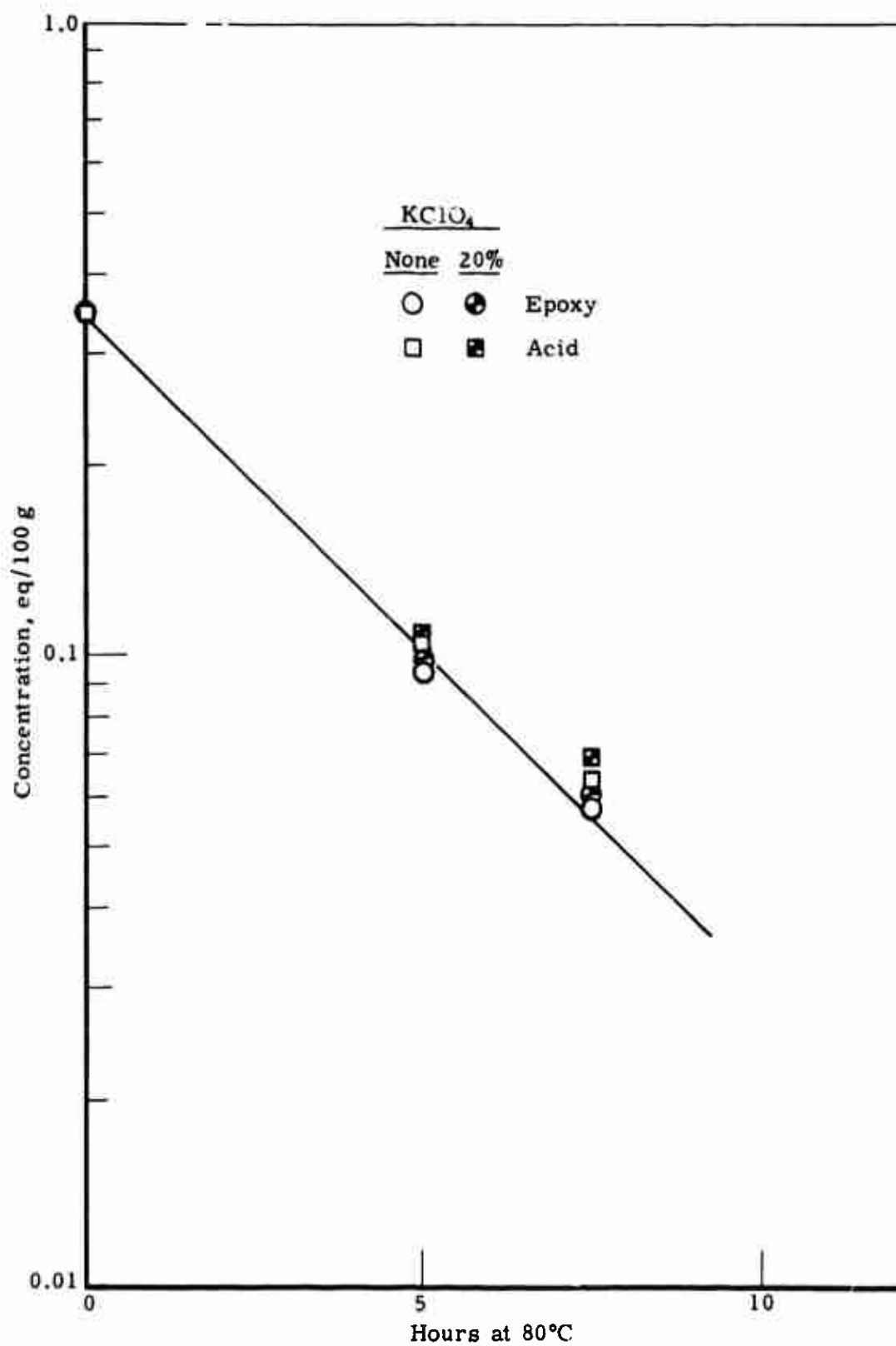
Figure 23. INFLUENCE OF KCLO$_4$ ON KINETICS
OF EPON H-825-HEXANOIC ACID-Cr (OCT)$_3$
SYSTEM AT 80°C

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SECTION V

PARTICLE SIZE DISTRIBUTION OF AMMONIUM PERCHLORATE
AND POTASSIUM PERCHLORATE USED

A. Ammonium Perchlorate

In selecting ammonium perchlorate for the work reported here, prime
consideration was given to the fact that powders produced by conventional
crushing and grinding operations have void contents in the 35-40%v range
which lead to a binder requirement in a propellant considerably exceeding the
stoichiometric amount which can be oxidized by the ammonium perchlorate. It
is therefore, desirable to reduce e void content of the powdered solid in
order to bring binder requirements closer to a stoichiometric relationship
with the oxidizer. This problem of reducing the void content of particulate
matter is an old one encountered in a number of fields. For example: the
particle size distribution which will allow the largest amount of coal to be
stored in a given volume has been explored; the mineral aggregate size
distribution requiring the least asphalt in mixes for bituminous pavements
has been the subject of much study, and the dependence of permeability of oil
sands on particle size distribution has also been studied.

Two general solutions to this type of problem have been developed:
the use of smooth maximum density particle size distributions such as that
proposed by Nijboer[1] and others and the use of bimodal mixtures as described
by Furnas[2] and others. The use of the smooth maximum-density gradings
require extensive sieving and recombination of fractions while the bimodal
distribution approach requires only the blending of the proper amounts of two
appropriately chosen size fractions.

The bimodal mixture approach was chosen in our work on reaction
kinetics and on screening of coatings and additives. The two size ranges
comprising the mixture were: 1) Trona ammonium perchlorate having a size
range of 50 to 300 microns and 2) a powder produced from this material by
Mikropulverization at 9650 rpm through a 0.013-in. herringbone screen and
having a size range from about 6 to 300 microns. From measured apparent dry
densities of mixtures of the two components, the void content of the mixtures
was calculated. These calculations indicated a minimum void content of 27%v
with 72%w of the Trona ammonium perchlorate and 28%w of the Mikronized
material.

The particle size distributions of these materials including that
of the bimodal mixture are summarized in Table III. The data for the bimodal
mixture are plotted in the form of a bar graph in Figure 24 and the midpoints
of the size ranges are employed in plotting the same data in Figure 25. The
surface area of the bimodal mixture was found to be $0.095m^2/g$ by krypton
adsorption.

In our propellant studies, e so called trimodal ammonium perchlorate
mix obtained from Thiokol was used. We also produced such a mixture from our

1) See References.

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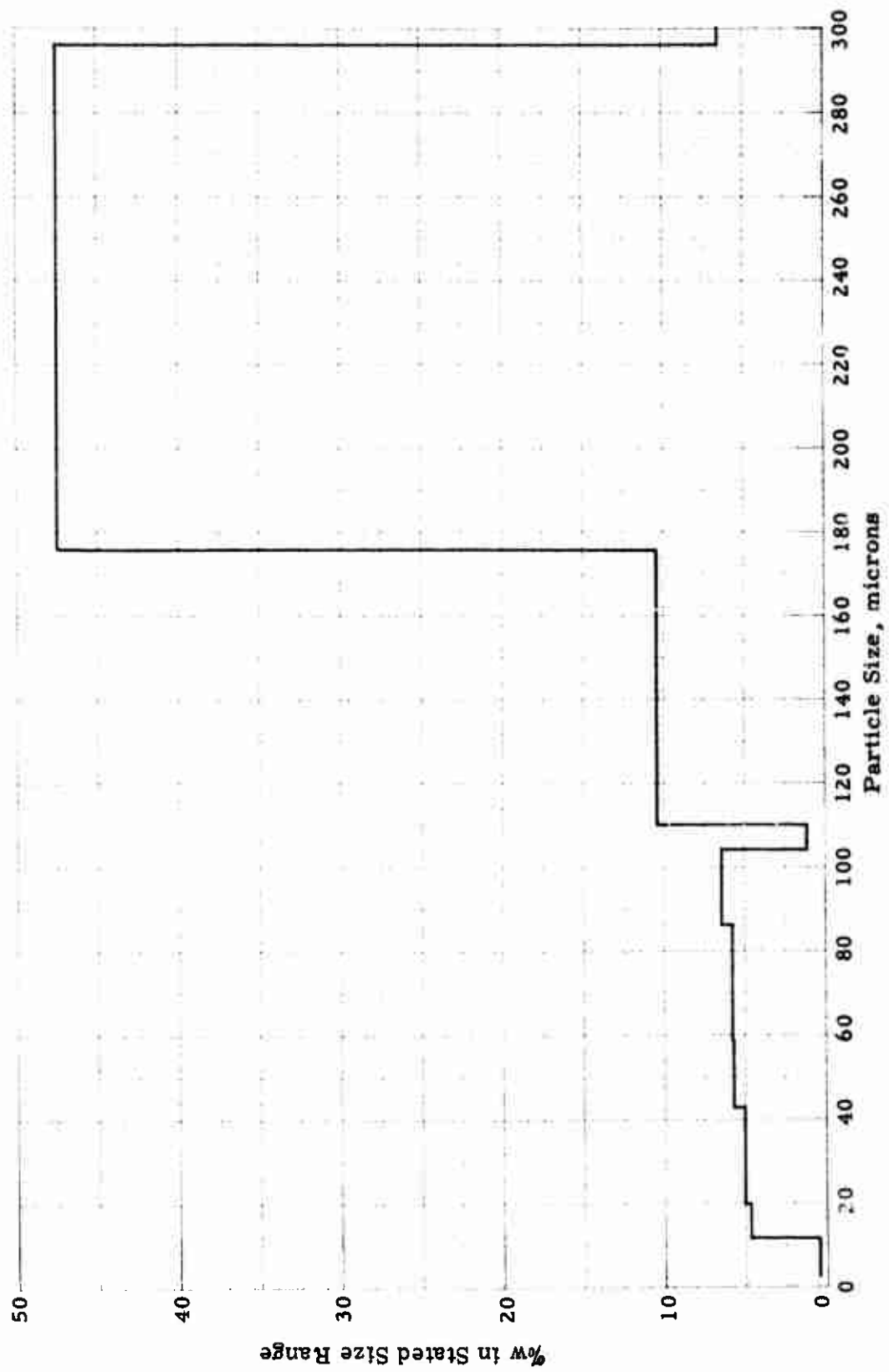
Figure 24. PARTICLE SIZE DISTRIBUTION OF AMMONIUM PERCHLORATE USED
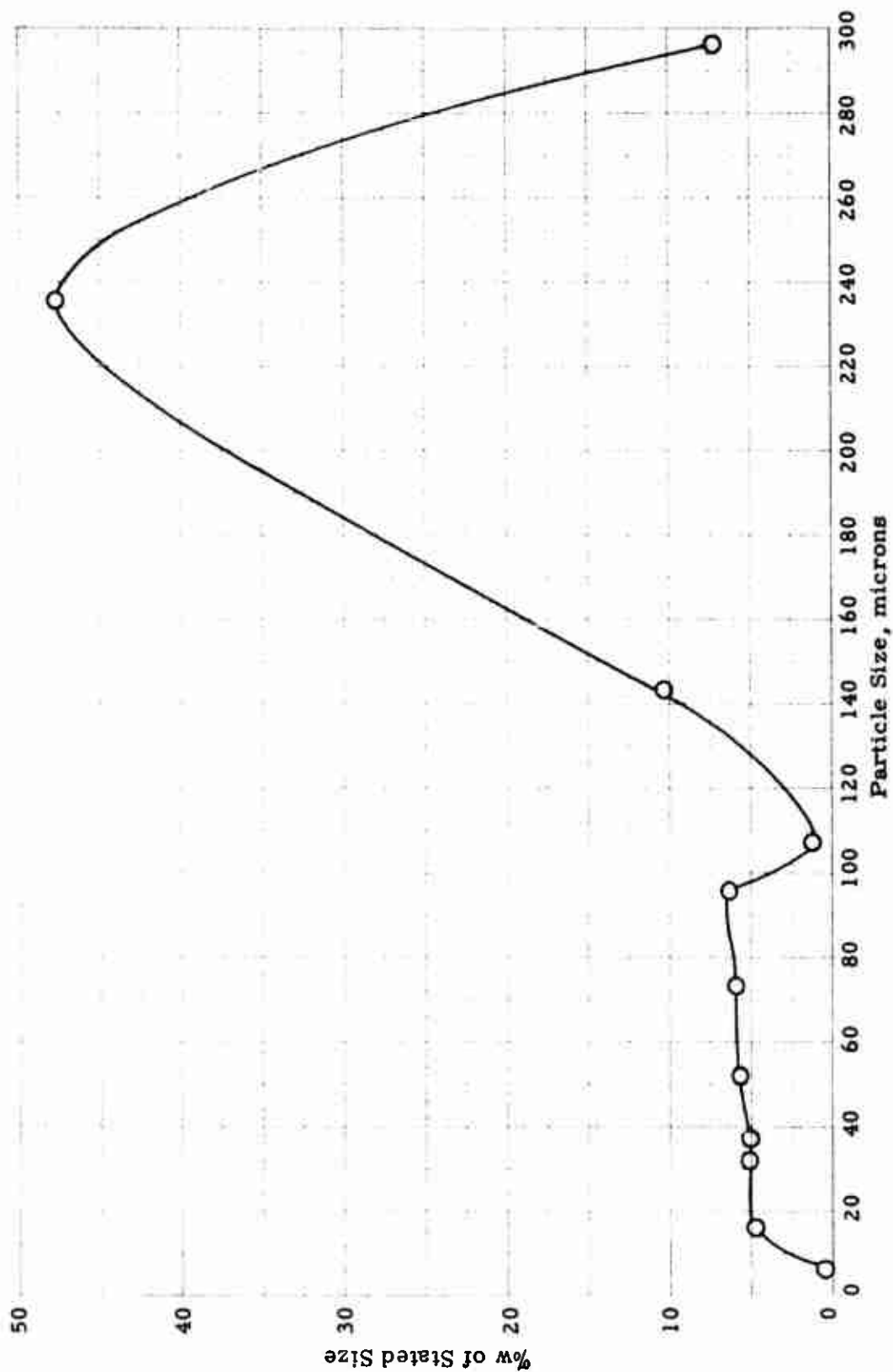
Figure 25. PARTICLE SIZE DISTRIBUTION OF AMMONIUM PERCHLORATE USED

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own supplies of micropulverized, unground and recrystallized ammonium perchlorate. This mixture had the following size distribution:

Size Range, microns	% weight
589 - 500	3.0
500 - 354	22.0
354 . 149	22.5
149 - 53	22.5
53 - 10	30.0
	100.0

Table III. PARTICLE SIZE DISTRIBUTION OF AMMONIUM PERCHLORATE
FRACTIONS AND OF THE BIMODAL MIXTURE USED IN THIS PROJECT

Surface Area of Bimodal Mixture by Krypton Adsorption:
0.095 square meters per gram.

Mesh Size, Microns	%w Passing Stated Sieve Size			%w in Stated Size Range
	Trona AP as Received[a]	Mikropulverized at 9650 rpm[b]	72%w Trona + 28%w Mikro-pulverized at 9650 rpm	72%w Trona + 28%w Mikro-pulverized at 9650 rpm
295	90	(99.3)[c]	92.7	7.2
175	25	(97.0)	45.2	47.6
110	12.5	92.1	34.8	10.4
104	11	(91.8)	33.6	6.4
86.2	4	(86.3)	27.2	5.9
58.5	1	73.6	21.3	5.8
43.1		55.6	15.6	5.0
31.6		37.7	10.6	5.2
19.4		19.1	5.4	4.9
10.31		1.8	0.5	

a) Sieved dry through standard sieves.
b) Wet sieved with n-heptane using electroformed micromesh sieves.
c) Figures in parentheses read from log probability plot of the data.

B. KClO$_4$ for Use in Propellant Studies

Some of our studies of the attack of perchlorates on epoxy groups in EPON H-825 showed that KClO$_4$ has no influence on tne epoxy content of this resin at 80°C even after several hundred hours of contact. For this reason, KClO$_4$ was of interest as a reference material in some of our propellant formulation studies. Since KClO$_4$ would not interfere with the epoxy-acid reaction, it might be expected that a propellant containing KClO$_4$ would attain mechanical properties which reflect the binder properties attainable when t ` highly filled system is cured without interference with the chemistry of the curing system.

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In order to explore this possibility, $KClO_4$ was prepared with a particle size distribution patterned after that of the AP mixture used in our propellant formulation work. The $KClO_4$ was obtained by first sieving the analytical grade salt to obtain the desired small size fractions. Some of the material was then dissolved in hot water and recrystallized slowly to produce the larger size fractions. The composition of the blend and the particle size ranges of the fractions are summarized below. This blend had a coarse appearance because of the high maximum size used.

%w	Sieves	Size Range, Microns
25	20-35	833-500
22.5	45-100	354-149
22.5	100-270	149-53
30	270	<53

The use of this material in propellant formulation studies is reported in Section XX.

SECTION VI

WETTABILITY OF AMMONIUM PERCHLORATE AND OF SURFACE COATINGS BY EPOXY RESINS

A. Direct Measurement of Contact Angles on Powders

In order to determine whether a given treatment had produced a surface coating on the AP and in order to obtain some idea about the nature of the coating, a screening test was needed which could be used to survey the effectiveness of a number of treatments fairly rapidly before proceeding to more time-consuming studies of binder reaction kinetics in the presence of the surface-treated oxidizer. Measurement of the contact angle of liquids of interest on the coating provided a basis for such a screening test. Our previous experience with characterization of surfaces and with determining molecular orientation in surface layers by contact angle measurements proved to be useful in this approach.

The structure of ammonium perchlorate is analogous to that of $BaSO_4$, $KMnO_4$ and $KClO_4$[3] and is dominated by oxygen atoms in tetrahedral arrangements around the chlorine atoms. The cations are a relatively conspicuous feature of the crystal model. The surface energy of such a highly oxygenated substance should be of the same order of magnitude as inorganic oxides, i.e., several hundred ergs/cm^2. Organic liquids whose surface tensions are in the range 10 to 60 ergs/cm^2 would thus be expected to wet ammonium perchlorate well with a zero contact angle. Adsorption of organic liquids by the ammonium perchlorate in such a way as to produce an autophobic situation in which the liquid does note completely wet its own adsorbed oriented monolayer can lead to measurable contact angles of organic liquids on ammonium perchlorate in spite of its high surface energy. When a low energy surface coating is deposited on the ammonium perchlorate, the ability of organic

liquids in general to wet the surface will be reduced and higher contact angles will be observed. Specifically, if the critical surface tension for wetting of the surface coating (γ_c) is less than the surface tension (γ_L) of the liquid of interest, the contact angle will not be zero and the larger the value of $\gamma_L - \gamma_c$ the higher the contact angle of the liquid will be.[4]

Several ways of making contact angle measurements on coated AP were considered. The most obvious approach is to grow AP crystals of sufficient size to accommodate a liquid drop with a diameter of at least one to two millimeters. Such crystals could then be coated and the contact angle of binder components could then be studied. It was learned that attempts to grow AP crystals large enough for this type of measurement have already been made successfully by others, but no information on the experimental techniques used were found in the literature. Other approaches were then considered.

The contact angle, θ, of a liquid of known surface tension, γ_L, on a finely powdered solid can be determined by measuring the adhesion tension of the solid-liquid system ($\gamma_L \cos \theta$) and dividing the adhesion tension by γ_L. Any method of measuring surface tension of liquids becomes a method of measuring adhesion tension when the contact angle of the liquid on the solid surface is not 0° (where $\cos \theta = 1.0$). Two experimental methods for measuring adhesion tension on solids were considered: 1) the displacement pressure method of Bartell et al[5] and 2) the wetting balance method of Gustalla.[6]

In Bartell's pressure of displacement method, a disc of known dimensions is formed by packing the powdered solid in a reproducible manner in a cell. The liquid of interest is allowed to contact one face of the disc and air pressure is applied to the other side. The pressure required to prevent the liquid from wetting the disc further (advancing angle) or to cause it to just begin to recede (receding angle) gives $\gamma_L \cos \theta$, the adhesion tension. The surface tension of the liquid is determined by another method such as the drop volume, pendant drop or du Nouy ring method and $\cos \theta$ is calculated. The results are rather sensitive to the reproducibility of packing of the powder but it appears to be of sufficient interest for this work that construction of the device has been undertaken.

In Gustalla's wetting balance method, a piece of the solid of known perimeter is gradually withdrawn from the liquid in which it has been immersed. The force required to withdraw the solid a known amount is measured with a balance and a buoyancy correction is made. The force per unit of perimeter is $\gamma_L \cos \theta$, the adhesion tension. The value of γ_L is determined independently and $\cos \theta$ is obtained. We have the necessary equipment for this method in the form of a Wilhelmy balance and a du Nouy tensiometer. The major problem is to obtain a piece of the solid of sufficient size or to devise a way to produce a polycrystalline surface of the material of known perimeter.

In thinking of methods of producing a polycrystalline surface of AP for use in Gustalla's wetting balance method, we realized that if the surface were sufficiently flat we might be able to measure contact angles directly. Two methods of producing polycrystalline surfaces of AP were tried. The first consisted of slowly withdrawing a clean microscope slide from a saturated solution of AP in methanol. When this operation was repeated several times the slide appeared to be covered with a layer of AP crystals. Microscopic

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inspection of the slide indicated that the glass surface was not completely covered with AP and contact angles of liquids were not stable with time because of partial wetting of both AP and glass.

A second method of producing a polycrystalline AP surface consists of coating a glass microscope slide with a thin layer of an adhesive and dusting the surface with fine AP powder. The method which worked best consisted of depositing a 2-micron layer of rubber on a clean microscope slide by dipping the slide into latex and drying at room temperature, followed by sieving AP through an electrically grounded 325-mesh screen (44 microns) onto the slide. More screened AP powder is placed on the slide and a smooth AP surface is produced by rolling and skidding a smooth cylindrical object such aa a glass rod along. Microscopic examination shows the AP layer to be about 60 microns thick. The AP surface is relatively smooth when compared to the dimensions of liquid drops (1 to 2 mm) placed on them for contact angle determination.

Contact angles were measured with a Bauach and Lomb microscope and Gaertner goniometer eyepiece of the type shown in Figure 26 with a total magnification of about 20X. The microscope slides on which the AP powder or other substrate was deposited were mounted on a movable stage on an Ealing triangular aluminum optical bench. Contact angles can be determined to the nearest 0.1 degree, but the reproducibility between liquid drops is of the order of 1 to 2 degrees. Table IV shows the average values (four or more drops) of contact angles of EPON 826, a diglycidyl ether of bisphenol-A, on various types of surfaces including some exploratory coatings deposited on AP powder.

Table IV. AVERAGE CONTACT ANGLES OF "EPON" 826 ON
SEVERAL TYPES OF SURFACES

Backing + Surface	Contact Angle of EPON 826, Degrees
Clean glass + commercial paraffin	71
Clean glass, dried at room temperature, 50% relative humidity	16
Clean glass + 2 μ rubber film	76
Clean glass + rubber film + AP powder	24
Clean glass + rubber film + AP powder + Dri Film 88 ex solution	73
Clean glass + rubber film + AP powder + Dri Film SC-77 ex gas phase	73
Clean glass + rubber film + AP powder + "MB2TDDP" ex benzene solution	25
Clean glass + rubber film + AP powder + "OCTAB" ex aqueous solution	46

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Figure 26. CONTACT ANGLE MEASURING MICROSCOPE

From these measurements it can be seen that EPON 826 wets AP rather well, giving a low contact angle. Hydrocarbon surfaces such as paraffin and rubber (styrene-butadiene) are poorly wet by the epoxy resin. When AP is treated with Dri Film 88 (a silane varnish manufactured by General Electric for coating electrical equipment) by depositing it from mineral spirits solution, a hydrocarbon surface coating results as indicated by the high contact angle. Similarly, when AP is treated with Dri Film SC-77 in the vapor phase (a mixture of monomethyl trichlorosilane and dimethyl dichlorosilane) a hydrocarbon coating results, again as indicated by the high contact angle.

A preliminary attempt to coat AP with a quaternary ammonium compound "OCTAB" (octadecyl dimethyl benzyl ammonium chloride) from a 0.4% aqueous solution was only partially successful, raising the contact angle to only 46°. This treatment was studied in more detail using a variety of quaternary ammonium compounds.

The technique of producing a polycrystalline AP surface appeared to offer a fairly rapid method for screening surface treatments and it seemed worthwhile to check the values of contact angles on AP by an independent method before proceeding further.

B. Contact Angles on Powdered Ammonium Perchlorate by Adhesion Tension Measurement

A device was constructed for measuring the adhesion tension $(\gamma \cos \theta)$ of a liquid for a powdered solid following the basic ideas of Bechhold[7] for measuring pore diameters in solids and of Bartell and Jennings for use on powders. The purpose of this work was to obtain an independent means of determing contact angles of liquids on powdered solids for comparison with values measured by the microscopic technique on polycrystalline powder surfaces.

Consider a liquid with surface tension, γ, advancing by capillary forces along a capillary or pore of radius, r, in a solid or between particles of a solid on which the contact angle of the liquid is, θ. The force pulling the liquid into the capillary is then the product of the perimeter of the capillary, $2\pi r$, and the component of surface tension along the axis of the capillary, $\gamma \cos \theta$. If the movement of the liquid into the capillary is opposed by applying air pressure to the other end, the force applied is the product of the cross-section area of the capillary, πr^2, and the applied force per unit area, P. Then when the opposing forces are just balanced we have:

$$\pi r^2 P = 2\pi r \gamma \cos \theta \tag{1}$$

or

$$rP = 2\gamma \cos \theta \tag{2}$$

or

$$P = 2\gamma \cos \theta / r. \tag{3}$$

Thus, if we know the contact angle of a liquid on a solid and the surface tension of the liquid we can determine the radius of pores within a porous solid or the effective radius of interstices between particles of a nonporous

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powder. This is the basis of the pore size distribution determination by the mercury porosimeter[8-11] where the pressure required to just cause mercury to enter the pores is measured.

We can also see from expression (3) that the cosine of the contact angle of a liquid on a solid powder can be determined if we know the effective radius of the interstices between the particles, the surface tension of the liquid and the pressure required to counter balance the capillary movement of the liquid in the interstices between the particles. Our approach was:

1) to devise a cell to hold finely powdered AP to which air pressure can be applied to counter balance capillary pressures,

2) to measure r, the effective radius of interstices between AP particles with mercury and

3) to determine cos θ for EPON 826 on untreated AP powder for comparison with values from microscopic measurements on polycrystalline powder surfaces.

Our mercury porosimeter, manufactured by the American Instrument Co., was investigated for possible use in making the desired measurement. It proved to be incapable of handling nonporous solid powders because no means of confining the powder sample is provided. Building of a cell similar to that described by Bartell and Jennings[5] was considered but the time required for the machine work appeared to be excessive. Finally, it was decided that the function of holding a bed of finely packed solid powder could be performed adequately by an in-line millipore filter holder of the type used on hypodermic syringes and identified as "Swinney Hypodermic Adapters" (Millipore Filter Corporation). Instead of placing a 1/2-inch diameter millipore filter in the holder, a piece of rubber tubing 1/2-inch OD and about 3/16-inch long was packed with AP powder and, with a 200-mesh stainless screen on each end to confine the powder, was placed in the filter holder. In order to prevent AP powder from escaping from this chamber a fraction of a bimodal mixture in the 100-200 mesh range (147 to 74 microns) was used for the experiments. A sketch of the apparatus is shown in Figure 27.

In order to determine the average effective radius of the interstices, r, between the AP particles with mercury we need a value for the surface tension of mercury and a value for the contact angle of mercury on AP. A large number of determinations of the surface tension of mercury have been reported, among the most reliable of which is the value used by Fowkes;[12] 484 dynes/cm at 20°C. The contact angle of mercury on various solids has also been much discussed in the literature in connection with the mercury porosimeter. Most of the values reported are in the range 130 to 140° for materials such as charcoal, alumina, cracking catalysts, petroliferous strata, porous iron, leather and coal. We measured the contact angle of mercury on AP powder by the microscopic method and found an average value of 133° in reasonable agreement with the value usually used in mercury porosimeter work.

A packed bed of 100-200 mesh AP powder weighing 0.458 g was placed in the Millipore filter holder and a small pool of mercury was placed on the bed. Air pressure was slowly applied to the system and when the pressure was

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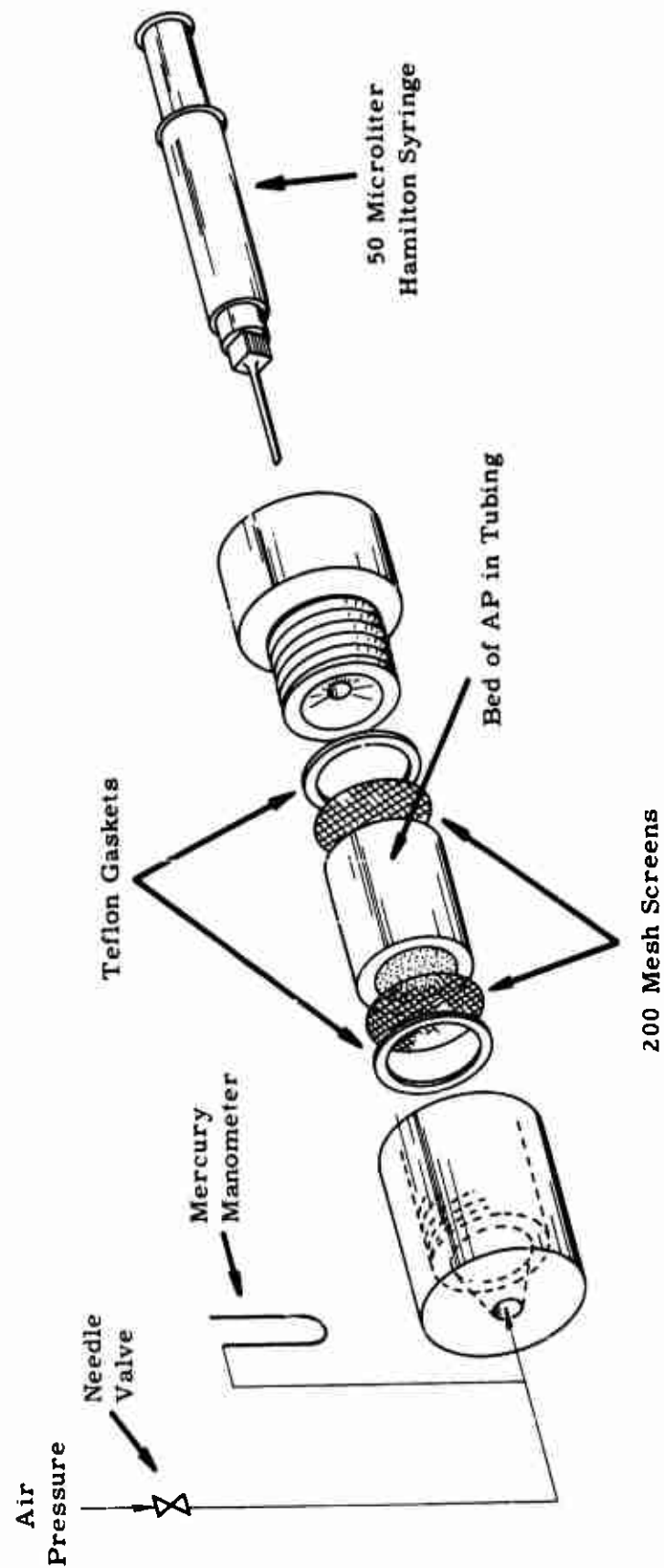
Figure 27. DEVICE FOR PORE SIZE AND ADHESION TENSION MEASUREMENTS
Swinney Hypodermic Adapter - Expanded View

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just sufficient to force mercury into the interstices between the AP particles, the pressure dropped. The average of six determinations gave a pressure of 283 mm Hg. When this value was used in expression (3) along with the surface tension and contact angle of mercury, a value of the effective pore radius, r, of 17.5 microns was obtained.

A new bed of AP powder prepared in the same manner was placed in the holder and EPON 826 was placed on the atmospheric pressure side of the bed. The EPON 826 tends to enter the bed by capillarity and the air pressure on the opposite side of the bed required to just reverse the EPON 826 flow was measured. Reversal of flow was observed in the 50 microliter syringe. The average of four determinations was 36.9 mm Hg pressure. The surface tension of EPON 826 as determined by the du Nouy tensiometer using a technique for viscous liquids developed earlier was 47 dynes/cm.

Using a value of r of 17.5 microns, a value of γ of 47 dyens/cm, a value of P of 36.9 mm Hg and the appropriate constants to give consistent units, we obtained from expression (3) a value of cos θ of 0.9159 for EPON 826 an AP. This corresponds to 23.7°. This is in excellent agreement with our microscopic measurements on AP powder which gave an average value of 24° as reported in Table V. We consider this good agreement to indicate that the more rapid and convenient microscopic contact angles on polycrystalline powders can be used with confidence rather than the more complicated pressure of displacement method.

C. Wetting of Ammonium Perchlorate Crystals by Epoxy Resin

Several crystals of ammonium perchlorate were grown by slow evaporation of aqueous solutions at room temperature over a period of about ten days. The largest of these had a flat face about one centimeter on a side. These are not large single crystals but are well-organized mosaics of small single crystals producing at least one face flat enough for contact angle measurements. The contact angle of EPON H-825 measured on this crystal was 24°, in agreement with our results from measurements on powders previously reported.

A verbal communication from Dr. Lionel Dickinson of Stanford Research Institute indicated that they have a crystallization process for ammonium perchlorate and might be able to supply crystals. We also received a communication from Dr. Arnold Adicoff of the U.S. Naval Ordinance Test Station (NOTS) at China Lake describing some of their work in 1964 and 1965 relating to adhesion of propellant binder systems to ammonium perchlorate crystals. Dr. William McBride of the Naval Ordinance Test Station, China Lake, California has developed a technique for growing single crystals an inch or more on a side.

D. Wettability of Ammonium Perchlorate Coated With Proprietary Phosphonic Acid Derivatives

A group of surface active compounds which has been under proprietary development by Shell research laboratories for a variety of applications is based on phosphonic acid. The general formula of phsophonic acid is $RP(O)(OH)_2$. They may be considered as derivatives of phosphoric acid in which one of the hydroxyls is replaced by an organic radical directly bonded

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to phosphorus. The compounds which have been included in this study to date include phosphonic acids in which the alkyl group has been varied, phosphonic acid mono and diesters, aluminum salts of the acids and their monoesters and a group of ethoxylated acids and their mono and diesters.

The material in the bimodal ammonium perchlorate passing 325 mesh (44 microns) was screened out and a polycrystalline layer anchored to 2 micron rubber films on clean microscope slides. The phosphonic acid derivatives were deposited on these ammonium perchlorate layers by applying solutions of the compounds dropwise and allowing the solvent to evaporate. The ethoxylated derivatives were applied as 1% isopropyl alcohol solutions and all the remaining compounds were applied as 1% benzene solutions. In order to be sure that the solvents (particularly benzene) used in application of the phosphonic acid derivatives had not dissolved rubber from the substrate and redeposited it on the surface of the powder we also coated clean, bare microscope slides with the phosphonates and contact angle measurements were made on these specimens as well as on the coated ammonium perchlorate specimens. The liquid used in these contact angle measurements was EPON H-825, a slightly more pure diglycidyl ether of Bisphenol-A than the 826 product used earlier.

The results of these measurements are summarized together with the structures of the coating compounds in Table V. The contact angle of the epoxy resin on uncoated ammonium perchlorate was 22 degrees. All of the phosphonic acids, esters and salts which have not been ethoxylated produce surface coatings which are not wet as well by the epoxy resin as the uncoated ammonium perchlorate. The aluminum salt of the monobutyl ester of 2-thia-dodecyl-phosphonic acid, eicosyl phosphonic acid, and its monobutyl ester, all produce surface coatings which are hydrocarbon-like in their wetting charac-teristics. The aluminum salt of the monobutyl ester of eicosyl phosphonic acid is slightly less effective as a coating and the monobutyl ester of 2-thiadodecyl-phosphonic acid is much less effective.

A series of ethoxylated (5, 10 and 20 ethylene oxide groups) acids, mono and dimethyl esters of phosphonic acid derivatives was also studied. These materials would be expected to produce high enrgy surface coatings which would be wet very well by the EPON-H-826. This proved to be the case, the coatings being wet better by the epoxy resin than is the uncoated ammonium perchlorate. The ethoxylated products are not recommended for this application but they should be screened at a later date as viscosity-control and surface bonding additives.

A general conclusion which can be drawn from a comparison of the contact angle data on coated ammonium perchlorate and on coated glass is that the coating compounds must orient very similarly on the two substrates in view of the good agreement of the contact angles in Table V.

E. Wettability of Miscellaneous Compounds as Ammonium Perchlorate Coatings

Another group of specimens representing a variety of compounds has been screened. These compounds were deposited on the bimodal mixture of ammonium perchlorate from hydrocarbon solution as described in a later section. The coatings amounted to 0.5%w. The coated material was screened to remove the particles smaller than 44 microns and this powder was anchored to microscope slides by a 2 micron rubber film on the slide. The contact angle

Table V. COATING AMMONIUM PERCHLORATE WITH PROPRIETARY PHOSPHONIC ACIDS, ESTERS AND SALTS - INFLUENCE OF THE COATING ON THE CONTACT ANGLE OF EPON® H-825 ON THE SOLID (Coating Applied to AP Powder Smaller Than 44 Microns Anchored to a Microscope Slide With 2 Micron Rubber Film)

Coating Material	Structure	See Evaluation Number	Contact Angle of EPON H-825, Degrees	
			Coating On AP	Coating On Glass
None (Uncoated AP)	-	-	22	-
Aluminum Salt of Monobutyl Ester of 2-Thiadodecyl Phosphonic Acid (AlMB2)	$Al(O\text{-}P\text{-}CH_2\text{-}S\text{-}C_{10}H_{21})_3$, $\uparrow O$, $O\text{-}C_4H_9$	12,19	75	74
Eicosyl Phosphonic Acid (EPA)	$HO\text{-}P\text{-}C_{20}H_{41}$, $\uparrow O$, HO	13	70	72
Monobutyl Ester of Eicosyl Phosphonic Acid (MBE)	$HO\text{-}P\text{-}C_{20}H_{41}$, $\uparrow O$, $O\text{-}C_4H_9$	14	71	71
Aluminum Salt of Monobutyl Ester of Eicosyl Phosphonic Acid (AlMBE)	$Al(O\text{-}P\text{-}C_{20}H_{41})_3$, $\uparrow O$, $O\text{-}C_4H_9$	11,20	63	63
Monobutyl Ester of 2-Thiadodecyl Phosphonic Acid (MB2)	$HO\text{-}P\text{-}CH_2\text{-}S\text{-}C_{10}H_{21}$, $\uparrow O$, $O\text{-}C_4H_9$	7	36	31

Table V (Contd). COATING AMMONIUM PERCHLORATE WITH PROPRIETARY PHOSPHONIC ACIDS, ESTERS AND SALTS - INFLUENCE OF THE COATING ON THE CONTACT ANGLE OF EPON® H-825 ON THE SOLID (Coating Applied to AP Powder Smaller Than 44 Microns Anchored to a Microscope Slide With 2 Micron Rubber Film)

Coating Material	Structure	Contact Angle of EPON H-825, Degrees	
		Coating Coating On AP	On Glass
4,7,10,13,16-Pentaoxa-18-hydroxyoctadecyl-phosphonic acid (5O18-OL18)	$HO-\overset{\overset{O}{\shortparallel}}{\underset{HO}{P}}-CH_2-CH_2-CH_2-O-(CH_2-CH_2-O)_5H$	10	12
Monomethyl ester of above compound (M5O18-OL18)	—	9	12
Dimethyl ester of above compound (DM5O18-OL18)	—	9	9
4,7,10,13,16,19,22,25,28,31-Decaoxa-33-hydroxytritriacontylphosphonic acid (10O33-OL33)	$HO-\overset{\overset{O}{\shortparallel}}{\underset{HO}{P}}-CH_2-CH_2-CH_2-O-(CH_2-CH_2-O)_{10}H$	14	13
Monomethyl ester of above compound (M10O33-OL33)	—	10	12
Dimethyl ester of above compound (DM10O33-OL33)	—	10	12
Dimethyl Ester of 4,7,10,13,16,19,22,25,28,31,34,37,40,43,46,49,52,55,58,61-Ficosaoxa-63-hydroxytrihexacontylphosphonic acid (DM20O63-OL63)	$CH_3-O-\overset{\overset{O}{\shortparallel}}{\underset{CH_3O}{P}}-CH_2-CH_2-CH_2-O-(CH_2-CH_2-O)_{20}H$	7	11

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of EPON H-825 was measured on these coated specimens. The results are given in Table VI in order of decreasing contact angle. On the basis of these contact angle data only the Dri Film Coating appears particularly promising.

Table VI. MISCELLANEOUS COMPOUNDS AS AMMONIUM PERCHLORATE COATINGS, 0.5%w

Coating Compound	Contact Angle of EPON H-825, Degrees
Dri Film SC-77	74
Glycidyl ether of C_{11} fluoroalcohol	38
Glycidyl ether of C_3 fluoroalcohol	35
OCTAB	26
Butyl glycidyl ether	23
Z-6040	23
A-186	19
Phenyl glycidyl ether	17
Y-4351	
None	22

SECTION VII

SURFACE COATING OF AMMONIUM PERCHLORATE BY ADSORPTION FROM SOLUTION

A. Polyethyleneimine

Ethylene imine is converted into a cationic species by reaction with an acid or with an alkyl halide as follows:
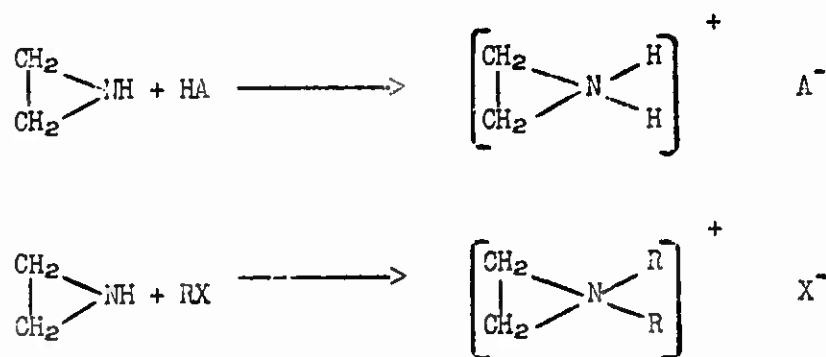
The cationic species reacts with additional ethylene imine to initiate polymerization. The polymers produced are known to be branched and contain primary, secondary and tertiary amine groups. They may be represented by the general structure:

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$$NH_2 - (CH_2-CH_2-N)_x - (CH_2-CH_2-NH)_y -$$
$$\begin{array}{c} | \\ CH_2 \\ | \\ CH_2 \\ | \\ NH_2 \end{array}$$
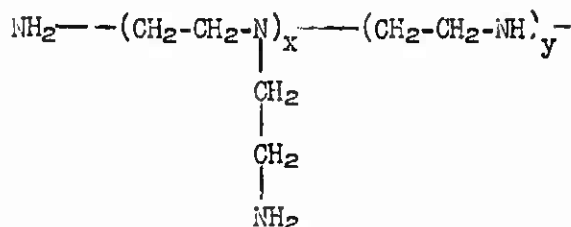
The commercial products of this type made by Dow Chemical Company are reported to contain primary, secondary and tertiary amine groups in the approximate ratio 1:2:1.

Ammonium perchlorate powder anchored on a microscope slide was treated with n-butanol solutions of a series of five polyethyleneimines and the solvent removed by drying at $130°C$. The contact angles of EPON H-825, a diglycidyl ether of bisphenol A were measured with the following results:

Coating on AP	Contact Angle of EPON H-825
Montrek 12	14°
Montrek 18	15°
Montrek 600	34°
Montrek 600E	38°
Montrek 1000	38°

The polyethyleneimine coatings appear to present relatively polar surfaces to the EPON H-825 in view of the rather low contact angles observed. The five polymers in this series are believed to differ primarily in molecular weight. On the basis of viscosity, the molecular weight increases with increasing code number. Montrek 600, 600 E and 1000 contain some water.

Montrek 18 and Montrek 1000 were used to coat ammonium perchlorate for subsequent chemical reactivity tests. The Montrek 18 was applied as follows: One gram of Montrek 18 was added to 100 ml of n-butanol which had been saturated with ammonium perchlorate at room temperature. Ten grams of bimodal AP was added with stirring and within a few seconds the AP particles began to agglomerate into larger lumps and their surface gradually took on a yellow color. The odor of ammonia was detected but no visible bubbling at the particle surface was observed. The mixture was agitated for an hour with a magnetic stirrer at room temperature, filtered and vacuum dried at $60°C$. A portion of this light yellow solid, LR 9950-39, was used in chemical reactivity tests described later as number 22 in Section XVIII.

A portion of the AP treated with Montrek 18 was exposed to formaldehyde vapor at $60°C$ for one hour with the objective of reacting surface NH or NH_2 groups. The following reaction of polyethyleneimine with aldehydes and ketones is well known.

$$R_1 - NH + \overset{R_2}{\underset{H}{\overset{|}{C}}} - \overset{O}{\overset{||}{C}} - R_3 \longrightarrow R_1 - \overset{R_2}{\underset{H}{\overset{|}{N}}} - \overset{OH}{\overset{|}{C}} - R_3$$
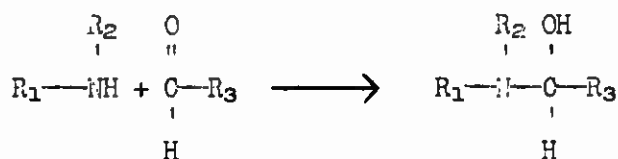
The color of the coated AP changed to orange during the formaldehyde treatment. The contact angle of EPON H-825 was raised from 15° to a value of 25° by the formaldehyde treatment. This product, LR 99950-39F, was used in chemical reactivity tests described later as number 21 in Section XVIII.

Ammonium perchlorate was coated with Montrek 1000 by adsorption of the polymer from a 1% solution in n-butanol at room temperature using the same procedure described for Montrek 18. The results of chemical reactivity tests described later as number 23 indicated this coating (LR-9950-41) to be a promising candidate for further study. A second preparation (LR 9950-43) was made using n-butanol containing 0.6% water as the solvent for the Montrek 1000. Analysis of the filtrate following the treatment of AP indicated that the solid oxidizer had adsorbed or reacted with 86.1% of the Montrek 1000 added. This represents a coating comprising 8.6%w of the AP which is considerably above the level of 1% set as a goal of this project. The promising results at this level led us to begin a series of surface treatments with smaller amounts of the polyethyleneimine Montrek 1000.

Three 100 ml solutions containing 1%, 0.5% and 0.1% respectively of Montrek 1000 in n-butanol (no water added) were used to treat 10 g batches of AP. The mixtures were mechanically stirred for 5 minutes at room temperature and filtered. The treated AP was vacuum dried at 60°C and the filtrates were evaporated to dryness to determine the amounts of Montrek 1000 taken up by the AP. The results were:

LR 9950-46 Sample	A	B	C
Concentration of Montrek 1000 Solution	1.0	0.5	0.1
% of Montrek 1000 taken up by AP	91.8	88.3	77.2
Coating, %w basis AP	9.2	4.4	0.77

These results indicate a definite interaction between the AP and the polyethyleneimine. Chemical reactivity tests on specimen 46 A continued to be encouraging as shown in run Number 26 in Section

The five polyethyleneimine products of the Montrek series manufactured by Dow Chemical Company were examined for water content in order to determine the exact polymer content. In addition, the approximate molecular weights of the polymers were obtained from Dow. The results are shown in Table VII. Two of the samples are essentially anhydrous while the remainder are approximately 40% solutions in water. The Montrek 600 E is the ethyoxylated derivative of Montrek 600 with approximately equal molar quantities of ethylene imine and ethylene oxide. With the information in Table VII and the solubility data for AP in H_2O and in n-butanol, it is possible to calculate the amount of polyethyleneimine adsorbed on AP from n-butanol after evaporation of the filtrate. The residue from the filtrate should contain the AP dissolved in the n-butanol, the AP dissolved in the water in the Montrek and the unadsorbed polyethyleneimine. Using this approach, the amounts of polyethyleneimine adsorbed in all previous preparations was recalculated. The calculated amount of coating on AP was somewhat reduced in the cases of Montrek 1000, 600 and 600 E, while the Montrek 12 and 18 calculations were unaffected.

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Table VII. COMPOSITION OF POLYETHYLENEIMINE SAMPLES

	%w Water (Karl Fischer)	Nominal Molecular Weight
Montrek 12	0.64	1,200
Montrek 18	0.15	1,800
Montrek 600	65.8	60,000
Montrek 600 E	58.1	120,000[a]
Montrek 1000	57.8	100,000

a) This includes ethylene oxide reacted with the poly-
    ethyleneimine. Analysis shows approximately one
    ethylene oxide group so that the molecular wt is
    approximately doubled by ethoxylation. Elemental
    analysis indicates the following average composition:

$$\left[H_{1.51} \; (N-CH_2-CH_2)_{1.16} \right] \left[(O-CH_2-CH_2)_{1.02} \cdot OH_{0.206} \right]$$

$$\qquad\qquad\qquad\quad 1194 \qquad\qquad\qquad\qquad\qquad 1052$$
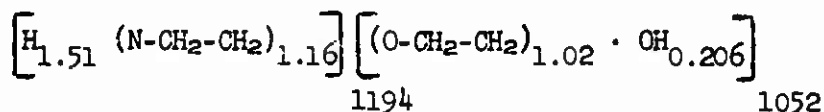
Two new series of AP treatments with polyethyleneimines were made by
adsorption from solutions in n-butanol at levels designed to produce coatings
of about 4% and 2% polyethyleneimine basis AP. All five of the available
Montrek products were used at each of these levels to produce two series of
products LR 9950-82 A-E and LR 9950-85 A-E. One change in coating procedure
which was made in the case of these two series was that the temperature of
drying was raised to 100°C and was prolonged to about 72 hours which resulted
in considerable yellowing of the specimens because of reaction between the
coating and AP. The amounts of polyethyleneimine adsorbed on the AP and the
available data on evaluation of chemical activity of the specimens in epoxy
resin at 80°C are summarized in Table VIII. Most of the early preparations
showed less attack of the coated AP on EPON H-825. The only known difference
between these preparations was the tempeature and duration of drying of the
coated AP.

As a result of these experiments, we concluded that the polyethyl-
eneimine coatings probably reduce the interference of AP with binder reactions
by reacting with AP or its decomposition products as they dissolve in the
binder. A reaction between AP and polyethyleneimine can be made to take place
during the drying operation after adsorption from solution. This is evident
by yellowing of the coated AP and by evolution of NH_3. It is believed that
this reaction during drying is undesirable because the capacity of polyethyl-
eneimine to react with dissolving AP in the binder is exhausted by the
pre-reaction during drying. In order to test this idea, a 21 g batch of AP
was coated with polyethyleneimine (Montrek 12) by adsorption from n-butanol
solution to give a coating of 0.84% basis AP. The coated AP was divided into
three batches and dried 24 hours at 25°C, 60°C and 100°C, respectively. The
100°C drying produced a noticeable yellowing of the specimen. These materials
were tested for reactivity with EPON H-825 at 80°C with the results shown in
Table IX. These results confirm in a systematic way that the pre-reaction of
polyethyleneimine with AP during drying reduces its effectiveness as a coating
for AP.

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Table VIII. SUMMARY OF POLYETHYLENEIMINE TREATMENTS OF AMMONIUM
PERCHLORATE AND EVALUATION OF CHEMICAL ACTIVITY IN
EPOXY RESIN AT 80°C

(See Section XVIII for complete evaluation data.)

20%w coated AP in EPON H-825 with continuous mixing

LR 9950-	Activity Evaluation No.	Montrek No.	Coating on AP, %w	Hours at 80°C	% of Initial Epoxy Content Retained
46-A	26	1000	6.1	288	90.7
46-B	36	1000	2.9	263	74.2
46-C	35	1000	0.9	263	80.4
56-A	44	1000	0.3	233	79.0
61-A	46	12	7.7	283	92.7
61-B	45	18	4.2	283	90.4
61-C	41	600	3.4	282	93.9
61-D	43	600 E	4.2	282	91.5
61-E	42	1000	5.8	282	93.0
82-A	83	12	4.5	235	77.3
82-B	84	18	4.1	237	78.5
82-C	85	600	5.0	237	82.4
82-D	86	600 E	4.7	237	90.7
82-E	87	1000	5.0	237	88.0
85-A	94	12	2.4	138	Gelled (<70)
85-B	91	18	2.4	138	Gelled (<70)
85-C	90	600	2.4	186	Gelled (<70)
85-D	89	600 E	1.8	186	Gelled (<70)
85-E	93	1000	2.3	186	Gelled (<70)

Table IX. INFLUENCE OF DRYING TEMPERATURE OF AP COATED WITH
MONTREK 12 ON REACTIVITY IN "EPON" H-825 AT 80°C

(See Section XVIII for complete evaluation data.)

0.84% Coating basis AP, 20% coated AP in EPON H-825

LR 9950-	Evaluation No.	Drying Temp, °C, 24 hr	% of Initial Epoxy Content Retained		
			77 Hr	168 Hr	239 Hr
93-A	130	25	94.2	84.1	Gelled
B	131	60	90.2	84.6	66.3
C	132	100	75.9	Gelled (<70)	-
No coating	-	-	97.4	91.7	83.6

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A puzzling fact, which remains unexplained, is that specimens of AP coated with low levels of polyethyleneimine (in <u>Table VIII</u> see samples 85A-E with 1.8 to 2.4% coating) the epoxy-coated AP system gelled at relatively short times, indicating that the reaction with epoxy groups is more rapid than in the case of uncoated AP in epoxy resin. Similarly, in the case of the specimens with a 0.84% coating (95-A, B, C in <u>Table IX</u>), the epoxy value has been reduced to a lower value in all three cases than in the case of the uncoated AP-epoxy resin system.

The possibility that polyethyleneimine is reacting with AP was further investigated by mixing 5 g of Montrek-600 with 0.5 g of AP at room temperature. The AP reacted with the polyethyleneimine and ammonia began to be evolved promptly and continued for several hours. On standing overnight, the viscous Montrek-600 became a taffy-like mass. It is possible that the tertiary amine groups in polyethyleneimine are reacting with ammonium perchlorate as follows:

$$NH_2\text{-}CH_2\text{-}CH_2\text{-}N\text{-}CH_2\text{-}NH_2 + NH_4ClO_4 \longrightarrow NH_3 \uparrow + NH_2\text{-}CH_2\text{-}CH_2\text{-}\overset{\displaystyle \overset{NH_2}{\underset{}{|}} \overset{CH_2}{\underset{}{|}} \overset{CH_2}{\underset{}{|}}}{N}\text{-}H \; {}^+ \; ClO_4^-$$
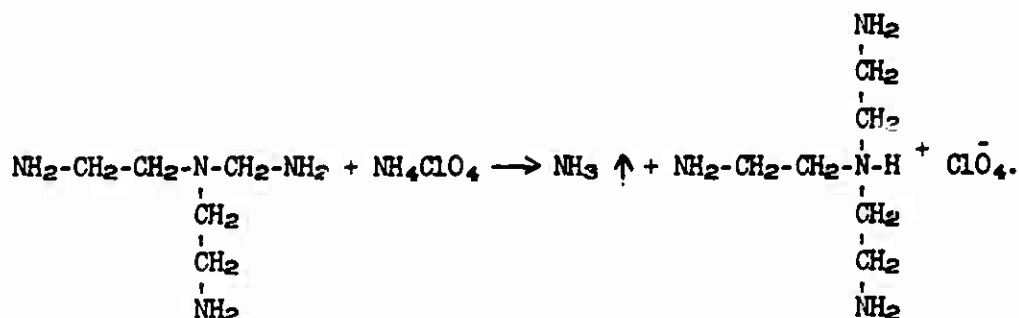
It should be possible to check this by measurement of the NH_3 evolved and by a separate determination of tertiary nitrogen content by p-toluenesulfonic acid titration. The reaction was carried to the point where the ammonium perchlorate consumption reached 0.3 moles of NH_4ClO_4 per mole of imine and the product became higher melting and rubbery. Attempts to dissolve this orange-colored product in alcohols were unsuccessful, but it is readily soluble in water.

Another series of coatings was produced by adsorption of polyethyleneimines from n-butanol on to AP at relatively low coating levels of 2% and less basis AP. Low, intermediate, and high molecular weight Montrek products were used and an ethoxylated intermediate molecular weight product as well. These products were dried in a uniform manner consisting of a 30-minute period at 60°C in a vacuum oven followed by 16 hours at 60°C at atmospheric pressure. This sequence was chosen in order to minimize the chemical reaction between polyethyleneimine and AP which has been studied earlier. The results of the adsorption experiments are summarized in <u>Table X</u>. These coated AP specimens were evaluated for chemical reactivity in EPON H-825 at 80°C as described in a later section as evaluations 142 through 153. With the exception of samples 97 A and 97 C, all reduced the consumption of epoxy groups by AP at 80°C.

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Table X. COATING OF AP WITH
POLYETHYLENEIMINE BY
ADSORPTION FROM N-
BUTANOL SOLUTION

%w Coating Basis AP

LR 9950 No.	Montrek No.			
	12	600	600E	1000
96 A-D	0.36	0.38	0	0.19
97 A-D	0.56	0.63	0.50	0.95
98 A-D	1.71	2.0	2.0	2.0

All the polyethyleneimine coatings produced on ammonium perchlorate by adsorption from solution in n-butanol followed by filtration and drying have been reviewed and their chemical reactivity toward epoxy groups in EPON H-825 has been summarized in **Figure 28**. All samples known to have been overheated have been deleted from this plot in view of the formation of polyethyleneimine perchlorates demonstrated earlier. The results of the remaining chemical reactivity tests at 80°C over a period of 280-290 hours are shown in the figure. From these results, we conclude that there is no clear cut influence on chemical reactivity of molecular weight of the polymer in the range 1,200 to 100,000 and no indication that ethoxylation of a 60,000 molecular weight polymer to form a 120,000 molecular weight product influences the chemical reactivity. These results support the earlier conclusion that a 2%w coating on AP may be required to produce the level of protection of epoxy resin from attack by ammonium perchlorate obtainable with this material.

Two small-scale preparations with 0.5% and 2.0%w coatings of the polyethyleneimine Montek 1000 were made (LR 9950-107 A and B) in order to follow by means of ball penetrometer measurements the curing in a practical binder system with a trimodal mixture of AP obtained from Thiokol. The results of these tests, discussed in a later section, generally support the conclusion regarding the superiority of a 2%w coating of the Montek polymer overtthe 0.5% coating from the point of view of reducing interference of ammonium perchlorate with the epoxy-carboxyl reaction in a binder.

A 250 gram batch of ammonium perchlorate with a 1%w coating of 100,000 molecular weight polyethyleneimine was prepared by adsorption from n-butanol. In order to minimize the amount of solvent employed, the treatment was conducted in two steps with addition of the polymer in two increments, each being close to the solubility limit of the polymer in n-butanol at room temperature. A coating of 1.01%w was produced and the product (LR 9950-111) was utilized in a propellant formulation. In view of our prior findings concerning chemical reactivity of AP coated with 1% polyethyleneimine, a second large preparation at the 2% coating level was also prepared for use in propellant testing.

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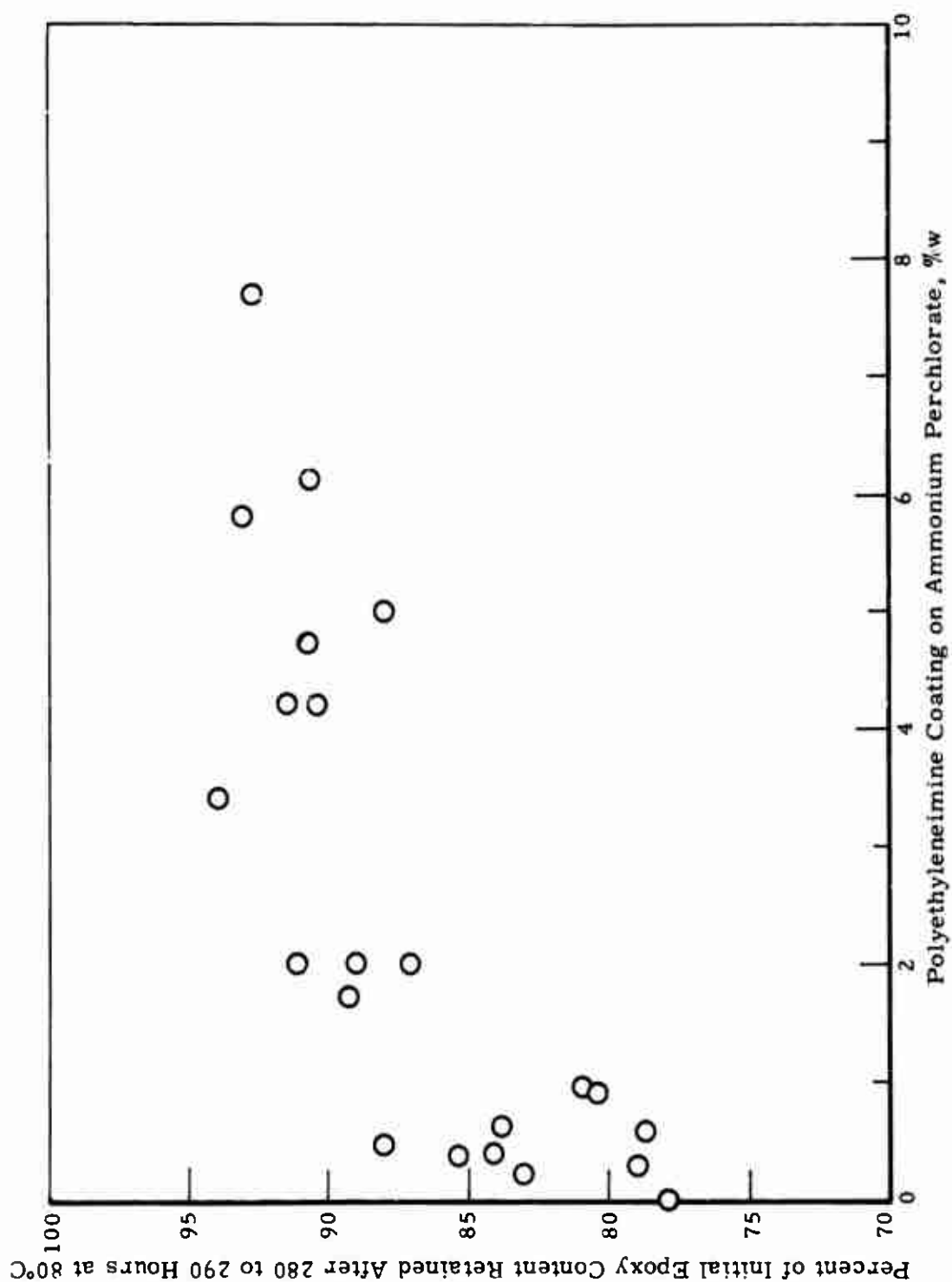
Figure 28. EVALUATION OF CHEMICAL REACTIVITY OF POLYETHYLENEIMINE-COATED AP IN EPON H-825 AT 80°C

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B. Polyethyleneimine-Epoxy Coating

A few experiments established the fact that polyethyleneimines will act as curing agents for epoxy resins. In the event that the polyethylene-imine adsorbed by or reacted with the AP still contains some reactive hydrogens, they should also be capable of curing epoxy resins. A sample of AP which had a polyethyleneimine coating of about 8.5% (LR 9950-43) was mixed with a 3.2% solution of polyallylglycidyl ether (PAGE) in n-butanol at 70°C for 30 minutes, cooled to room temperature and filtered. The treated AP was vacuum dried at 60°C and the filtrate was evaporated to dryness. The residue from the filtrate slightly exceeded the amount of PAGE in the original solution, indicating a lack of any appreciable amount of reaction with the treated AP and possibly some removal of polyethyleneimine from the AP. This may be an indication that the polyethyleneimine is largely reacted with the AP (possibly as an amine perchlorate) rather than physically adsorbed. Comparison of chemical reactivity tests of specimens with and without the PAGE treatment showed that the AP treated with polyethyleneimine alone attacked EPON H-825 at 80°C to a leaser degree than the specimen which had also been treated with PAGE, the percent of initial epoxy content retained efter 280 hours at 80°C being 92.5 and 90.4% respectively.

C. Polyalkylene-polyamine Coatings

In view of the encouraging results obtained with polyethyleneimines it appeared likely that the linear polyalkylene polyamines which are commonly used as curing agents for epoxy resins might also interact with ammonium perchlorate and produce a durable surface coating. One percent solutions of three polyalkylene polyamines in n-butanol were used to treat 10 g batches of AP. The systems were mixed for 5 minutes at room temperature and for 15 minutes at 70°C after which they were cooled to room temperature and filtered. The treated AP was vacuum dried at 60°C and the filtrates were evaporated to dryness for determination of the amount of polyalkylene polyamine taken up.

The coated AP had a yellow color similar to that of the polyethyleneimine-coated specimens. Chemical reactivity tests of these coated AP specimens in EPON H-825 at 80°C for a period of 263 hours gave the following results:

	% Adsorbed	Coating, % on AP	% of Initial Epoxy Content Retained
Tetraethylenepentamine (LR 9950-51)	51.6	5.2	93.4
Diethylenetriamine (LR 9950-55)	84.4	8.4	60.7
Ethylenediamine (LR 9950-53)	62.0	6.2	<40, gelled

The highest molecular weight linear polyalkylene polyamine is the most effective coating for AP.

A portion of the AP which had been treated with tetraethylene-pentamine was mixed with a 1% solution of polyalkylglycidyl ether in n-butanol and heated to 70°C for 30 minutes. The treated AP was filtered off and the filtrate was evaporated to dryness. The residue from the filtrate was approximately equivalent in weight to the PAGE used. It appears that no

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reactive hydrogens are available on the tetraethylenepentamine adsorbed on or reacted with the AP as in the case of the polyethyleneimine. The percent of initial epoxy content retained when mixed with EPON H-825 for 263 hours at 80°C was 93.4% in the case of the parent product and this was reduced to 88.1% by the PAGE treatment.

D. Alkylamine Coatings

In view of the results with polyamines, two coating experiments with C_{22} alkyl mono amines produced by the Humko Division of National Dairy Products Corporation were tried. Coatings of Kemamine Q-1902-C and Kemamine T-1902-D were applied by mixing of 1% solutions in toluene with AP followed by filtration. Analysis of the filtrates indicated that a coating of 7.9% of T-1902-D was formed on AP while a coating of 1.4% of Q-1902-C was formed.

In a similar manner, octadecyl, hexadecyl and dodecyl amines were adsorbed from n-butanol solutions onto bimodal ammonium perchlorate in an attempt to evaluate the possible effect of chain length on coating effectiveness. The concentration of the amines were sufficient to produce coatings amounting to 5%w on the AP. A similar treatment with methyl amine was made with a coating of 2%w on AP resulting.

The results of the chemical reactivity tests are summarized in Table XI where it can be seen that there is no evidence of a trend in effectiveness attributable to chain length. The data indicate that the Kemamine Q-1902-C coating at a level of 1.4% is the most effective in preventing the attack of AP on the epoxy resin.

Table XI. COMPARING EFFECTIVENESS OF ALKYL AMINES OF
VARIOUS CHAIN LENGTHS AS COATINGS
FOR AMMONIUM PERCHLORATE

Amine Coating	Hours at 80°C in EPON H-825	% of Initial Epoxy Content Retained	Evaluation No.
Q-1902-C (C_{22})	281	87.4	30
T-1902-D (C_{22})	263	82.9	31
Octadecylamine	234	77.7	61
Hexadecylamine	233	82.7	65
Dodecylamine	233	80.1	63, 88
Methylamine	288	79.4	66

E. Diamine Coatings

Two cyclic diamines, metaphenylenediamine and menthanediamine were employed in the form of 100 cc of 1% solutions in n-butanol to coat 10 g of AP. About 43% of the metaphenylenediamine was adsorbed and none of the menthanediamine was adsorbed. The evaluation of these coating operations is described in a later section where the metaphenylenediamine is the more

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effective as expected, with 81.1% of the initial epoxy content retained after 283 hours in EPON H-825 at 80°C (evaluation number 47).

Polyoxypropylenediamine-400 (Jefferson Chemical Company) which is believed to contain about 6 propyleneoxide units terminated with amine groups was used in the form of 100 cc of a 1% solution in n-butanol to coat 10 g of AP. The analysis of the filtrate indicated that very little had been adsorbed but the evaluation of the coating reported in a later section indicates some effectiveness of the coating, 90.8% of the initial epoxy content being retained after 216 hours in EPON H-825 at 80°C (evaluation number 59).

Hexamethylenediamine proved to be an ineffective coating for AP, the activity evaluation (number 95) showing only 73% of the initial epoxy content retained after 186 hours in EPON H-825 at 80°C.

F. Amide Coatings

A 1% solution of urea in n-butanol was mixed with AP (20 g/100 cc of solution) at room temperature for 5 minutes followed by filtration and drying of the solid at 60°C. Analysis of the filtrate indicated that no urea was adsorbed and essentially no change in the chemical activity of the AP toward epoxy resin was observed (evaluation number 72).

AP was treated in a similar way with 1% solution of formamide in n-butanol. Analysis of the filtrate indicated that about 85% of the formamide had been adsorbed. Little influence on the reactivity of the AP toward epoxy resin was observed (evaluation number 71).

G. Polyamide Coatings

The polyamides, Versamid 125 and Versamid 140, produced by reaction of diethylenetriamine with polymers (dimer and some trimer) of linoleic acid were investigated as coatings for AP. They were applied as 1% solutions in n-butanol (100 cc/10 g AP) by mixing for five minutes at room temperature, followed by filtration, drying of the AP at 60°C and evaporation of the filtrate. About 33% of the Versamid 125 was adsorbed and about 46% of the lower moleculer weight Versamid 140 was adsorbed. The Versamid 125 proved to be the more effective of the two coatings as with 90.8% of initial epoxy content retained after 285 hours at 80°C as compared with 88.7% for the V Versamid 140 (evaluations 55 and 56).

H. Diethylenetriamine-Epoxy Resin Adduct Coating

An addition product of diethylenetriamine (112 parts) with the diglycidylether of Bisphenol-A (100 parts) plus phenol (4 parts) was employed as a coating for AP. A one-percent solution of this material in n-butanol (100 cc/10 g of AP) was mixed at room temperature for five minutes with AP and filtered. About 2/3 of the coating material was taken up by the AP. The evaluation of this coating described later indicates that the disappearance of epoxy groups in EPON H-825 is accelerated rather than retarded by this coating (evaluation number 48).

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I. Cationic Surface Coatings

It was proposed that the ammonium ions in the surface of the ammonium perchlorate crystal might be exchanged with the ions of long-chain quatenary ammonium salts. Because the quatenary ammonium salts are stronger bases, they should replace the ammonium ion on the surface and because these salts have long paraffin tails, it was hoped that this treatment would provide a surface barrier of hydrocarbon chains which might prevent inter-action of AP with epoxy resins or other binder components.

The quatenary ammonium compounds which were used in the adsorption experiments included:

Arquad 2HT-75   (Dioctadecyldimethyl ammonium chloride)

Arquad 2C-75   (Dicoco Dimethyl ammonium chloride, 75% active)

Arquad 12-50   (Dodecyltrimethyl ammonium chloride, 50% active)

Arquad 16-50   (Hexadecyltrimethyl ammonium chloride, 50% active)

Arquad 18-50   (Octadecyltrimethyl ammonium chloride)

Tetra-n-propyl ammonium iodide.

The compounds were applied as solutions in n-butanol and Arquad 18-50 was also applied as a benzene solution. The amounts adsorbed were not determined, but the amounts of these compounds available in the solutions exceeded 10%w of the AP with which they were mixed for 20 hours at room temperature. After filtration, the AP was dried at 80°C.

The results of evaluations of chemical reactivity of these tested AP specimens with EPON H-8 5 at 80°C are summarized in Table XII. A result from an earlier treatment with octadecyl trimethyl ammonium bromide (OCTAB) is included. Comparison of the results with the performance of uncoated AP indicates that the quatenary ammonium compounds did not provide any protection of the epoxy resin from attack by AP and in some cases, slightly accelerated the loss of epoxy groups.

Table XII.   EVALUATION OF CATIONIC
SURFACTANT COATINGS ON AP

Coating Material	Evaluation Number	Hours at 80°C	% Initial Epoxy Content Retained
Arquad 2HT-75	199	263	77.0
Arquad 2C -75	37	263	82.7
Arquad 12 -50	62	233	gelled
Arquad 16 -50	200	114	77.1
Arquad 18 -50	38	263	gelled
Arquad 18 -50(ex-benzene)	25	187	61.1
Tetra-n-propylammonium iodide	53	285	58.8
OCTAB	8	215	85.5
No Coating	-	241	84.5

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J.   Fatty Acid and Polymerized Acid Coatings

The possibility of adsorbing fatty acids (lauric or stearic acid) with the AP surface thus forming a hydrophobic surface was explored. The AP was mixed for 20 hours with solutions of these two acids in n-butanol containing sufficient acid to produce a coating amounting to 20% basis AP if all adsorbed. The amounts adsorbed were not determined. The evaluations (numbers 51 and 64) of chemical reactivity of the treated AP indicated that neither acid produced a protective coating on the AP, the percent of initial epoxy content after 233 hours of mixing with EPON H-825 at 80°C being 85.7 in the case of the lauric acid-treated AP and 76.8% in the case of the stearic acid-treated AP.

The trimer of linoleic acid produced by Emery Industries was used in the form of a 1% solution in n-butanol to coat AP (100 cc/10 g AP). Analysis of the filtrate indicated that only about 1% of the trimer acid was adsorbed (aabout 0.1% basis AP) and the evaluation of this coating described in a subsequent section indicated very little influence on the interaction of the AP and epoxy resin at 80°C, the percent of initial epoxy content retained after 238 hours being 88.8% as compared with about 84% for uncoated AP.

K.   Alkyl Halide Coating

The possibility of reacting an alkyl halide, iodooctane, with the AP surface thus forming a hydrophobic surface was explored. AP was dispersed by mixing for 20 hours in twelve times its weight of iodooctane at room temperature followed by filtration and drying at 80°C. The effectiveness of this treatment in reducing the interaction of AP and epoxy resin at 80°C was very small as indicated by an 85.5% retention of initial epoxy content after 263 hours at 80°C as compared with about 85% for the uncoated AP.

L.   Alkavinol Coatings

It was therorized that a compound which contains hydroxyl groups may hydrogen bond with any water adsorbed on the AP surface. To test this idea, a proprietary dispersant, Alkavinol (e copolymer of vinyl acetate and C_{12}-C_{18} alpha olefins (3.5 to 1) hydrolyzed to the alcohol form), was used to coat the AP. The Alkavinol was applied to the AP by evaporation from two different solvents. A 1.5%w coating was deposited from benzene and a 2%w coating was deposited on AP from n-heptane. The evaluations of the effectiveness of the coatings (number 15 and 16) showed respectively 89.7% and 88.5% of initial epoxy content retained when these two coated AP specimens were mixed for 190 hours with EPON H-825 at 80°C. These coatings represent a small improvement over the uncoated AP.

Alkavinol was also applied to AP by mixing a 10% solution in benzene with the AP powder for 20 hours at room temperature to allow for adsorption to take place. This was followed by filtration and drying at 80°C. The amount adsorbed was not determined. Evaluation of the coating (number 24) indicates that a fair amount of protection was obtained, the percent of initial epoxy content retained after 187 hours being 91.8% as compared with 89.4% for uncoated AP during the same period.

M.   Condensation Polymerization (Nylon) Coatings

Condensation polymerization was used as a method of coating AP particles with a polyamide, nylon by the following reaction:

$$NH_2-(CH_2)_6-NH_2$$
(hexamethylenediamine)

+

$$ClC-(CH_2)_8-CCl$$
(with O above each C)

Sebacylchloride

$$\xrightarrow[\text{or NaOH}]{\text{excess diamine}}$$

$$H\left[\begin{array}{c}H \\ N-(CH_2)_6-N-C-(CH_2)_8-C\end{array}\right]_x Cl$$

6-10 Polyamide

+

diamine hydrochlorides

or

2 x NaCl
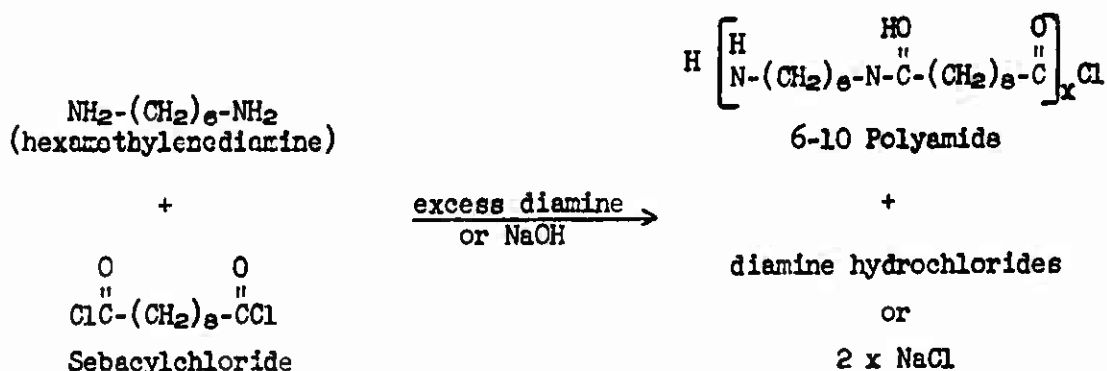
First, the individual diamine and acid chloride compounds were used to coat the AP particles. To a series of n-butanol solutions of hexamethylenediamine (1.6 g of HMDA in 90 ml of n-butanol), sebacylchloride (1.2 g of sebacylchlordie in 90 ml of n-butanol) and sodium hydroxide (0.13 g dissolved in 90 ml of n-butanol), 6 g of AP particles (70/30 bimodal) were added. These dispersions were stirred with a magnetic stirrer for approximately 20 hours; then, the AP particles were filtered off and dried at 80°C. The amounts of these compounds which adsorbed onto the AP particles is now being determined. Evaluation of the effectiveness of these compounds alone to coat the AP particles is given in another section. None of the above coatings were effective in reducing the attack of AP on epoxy groups (see evaluations numbers 92 and 95'. The sebacylchloride accelerated the attack of AP on the epoxy resin as shown in evaluation 92.

To another n-butanol solution containing 1.2 g of sebacylchloride in 90 ml of n-butanol, 7.5 g of AP (70/30 bimodal) was added and stirred magnetically for approximately 20 hours. Then the AP particles were removed by filtration and were added to 10 g of hexamethylenediamine dissolved in 90 ml of n-butanol. This dispersion was stirred for approximately 20 hours; then, the AP particles were removed by filtration and dried at 80°C. The nylon coating which should have formed was not effective in reducing the attack of the **treated** AP on **epoxy** resins (evaluation 96) but actually accelerated the attack slightly (74.2% of initial epoxy content retained after 186 hours as compared to 90.9% for uncoated AP in the same period).

N.   Hydrocarbon Polymer Coatings

A polyorthoxylene (about monomer 8 units) was deposited on AP by evaporation from solution giving a coating amounting to 10% by weight of the AP. The product was so dark that the normal titration for epoxy groups with visual end point could not be made on the system. Evaluation of the coating after 312 hours at 80°C, in contact with EPON H-825 by an electrometric titration, showed that about 82% of the inital epoxy content remained as compared with 60% for a control   with no coating.

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Two hydrocarbon polymer coatings were applied to AP by polymerization of the monomer in solution in a stirred system containing AP powder. In separate experiments, methylmethacrylate and styrene were polymerized from 2% solutions of the monomers in n-butanol in the presence of AP powder at 60°C with azobisisobutyronitrile (0.1% in solution) as initiator. The polymerization was carried out for 45 minutes after which the temperature was lowered to room temperature, while stirring. About 1.9% of each of the polymers was deposited on the AP. These coatings provided some protection of the epoxy resin from attack by AP as indicated by evaluations numbers 57 and 58 in which the percent of initial epoxy content retained was 90.1% after 216 hours at 80°C for the polystyrene-coated AP and 89.5% after 239 hours for the polymethylmethacrylate-coated AP as compared with about 84% for uncoated AP.

O. NEODOL 25-3P Coating

A product proprietary to Shell, the potassium salt of a sulfated, ethoxylated long-chain alcohol plus a sodium xylene sulfonate was adsorbed from solution in n-butyl alcohol on AP. A coating amounting to 0.58% based on the AP resulted. The evaluation of the chemical reactivity of the coated AP (evaluation 154) shows that after 288 hours of mixing with EPON H-825 at 80°C only 77.8% of the initial epoxy content remained, a result essentially identical with that obtained with uncoated AP.

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SECTION VIII

SURFACE COATING OF AMMONIUM PERCHLORATE IN A FLUIDIZED BED

A vapor phase coating technique was developed for application of potential coatings to AP while fluidized in the form of an expanded bed by a stream of nitrogen. The experimental arrangement is shown in Figure 29. Ten grams of AP powder is placed in the column and expanded to twice its initial bed height by passing a stream of nitrogen through the apparatus. The nitrogen picks up vapors of the heated liquid which is to be used as the coating and passes them into the expanded AP bed. This method of coating AP has the obvious advantage over adsorption from solution that filtration and drying steps are not required. It has the potential disadvantage that if high boiling liquids are to be applied they must be converted into a finely divided aerosol which is introduced into the fluid bed. So far, only relatively low boiling liquids have been applied to the fluid bed of AP. These include diethylenetriamine, methylamine, Dri-Film SC-77 and ethyleneimine.

A. Ethyleneimine Coatings

Ethyleneimine was adsorbed from a 1% solution in n-butanol on AP to produce a coating amounting to 5.99% basis AP. Its chemical activity in EPON H-825 at 80°C was investigated for comparison with other coatings as discussed below.

Ethyleneimine was applied to a fluidized bed of AP using a stream of N_2 to carry the vapor from the liquid heated to 45°C into the fluidized bed. The coating amounted to 9.5% basis AP. The specimen was used in chemical reactivity tests at 80°C.

The results of chemical reactivity tests of a mixture of 20% of the coated AP in EPON H-825 at 80°C are summarized in Table XIII. The coating adsorbed from solution was ineffective in changing the reactivity of AP, but the coating applied from the vapor phase gave a small improvement in retention of epoxy groups.

Table XIII. EVALUATION OF ETHYLENEIMINE COATINGS APPLIED FROM
THE VAPOR PHASE AND ADSORBED FROM n-BUTANOL SOLUTION

LR 9950-	Evaluation No.	Method of Application	Coating, %w	Time at 80°C, hr					
				77	124	168	216	239	293
				Epoxy, eq/100 g					
92	123	vapor	9.5	-	0.551	-	0.520	-	0.482
94	129	solution	6.0	0.556	-	0.526	-	0.461	-
← No coating on AP →			0	0.557	0.544	0.527	0.494	0.479	0.441

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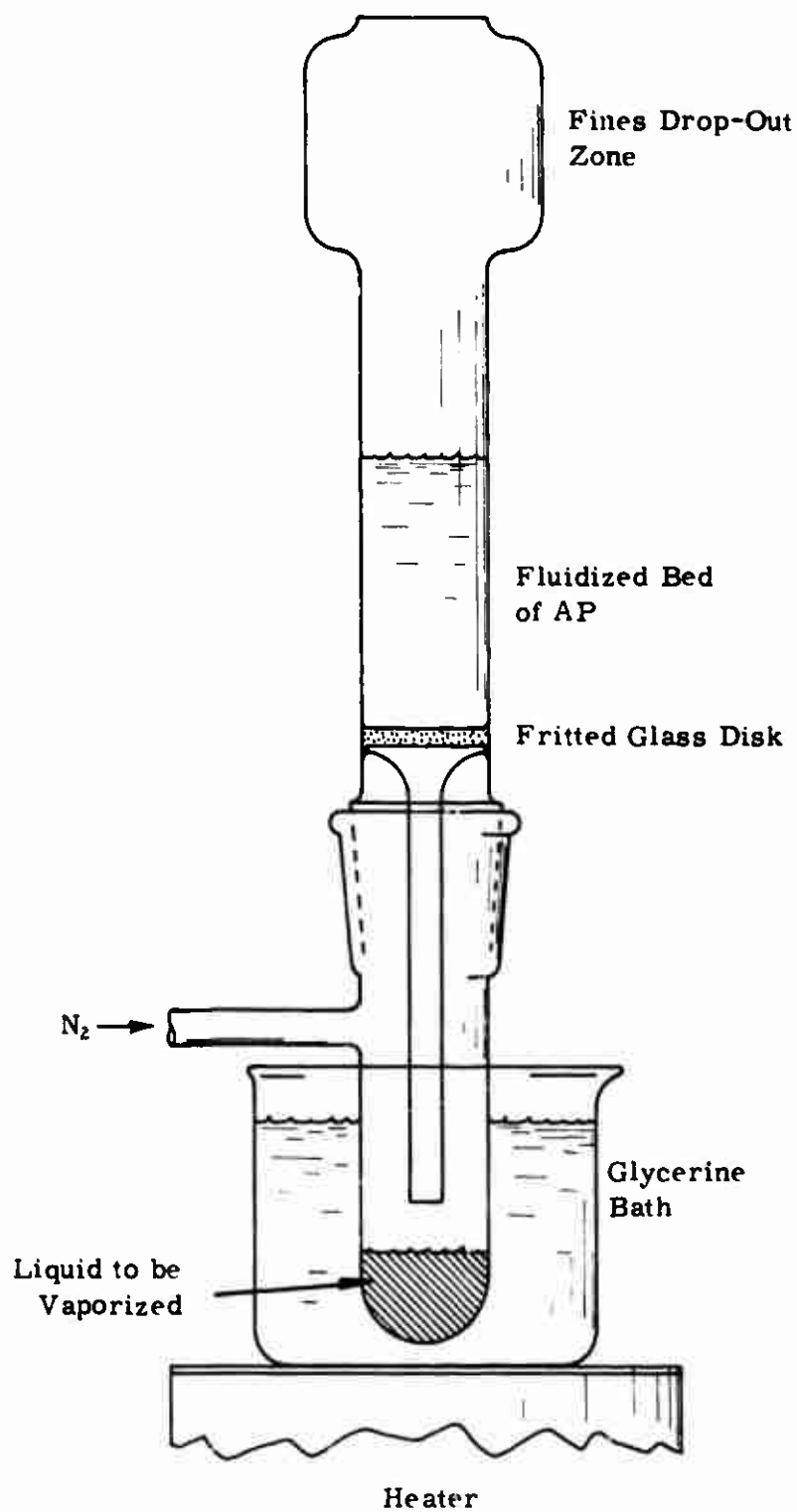
Figure 29. EXPERIMENTAL ARRANGEMENT FOR
VAPOR PHASE TREATMENT OF FLUIDIZED AP

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B. Methylamine Coatings

Two treatments with methylamine were made, one from solution of 0.4% methylamine in butanol and one by vaporization of 0.4 g of methylamine into a stream of nitrogen passing through a fluidized bed of powdered AP. In each case 0.4 g of methylamine was applied to 20 g of AP and all of the methylamine was adsorbed or reacted. The evaluation of the chemical reactivity of these specimens described in detail in evaluation 66 and 67 showed that the vapor phase treatment with methylamine increased the reactivity toward epoxy resin while the liquid phase treatment produced a slight reduction in reactivity relative to uncoated AP. In the case of the fluid bed treatment it appeared that the major part of the amine was concentrated in the lower part of the bed and was not evenly distributed. A slower vaporization rate might give better distribution.

C. Diethylenetriamine Coatings

Diethylenetriamine (1 g) was placed in the liquid reservoir and heated to 155°C while nitrogen swept out the vapors into a 10 g fluidized bed of AP. About 50% of the diethylenetriamine was deposited on the AP, the remainder forming a yellow residue (polymer) in the reservoir. The evaluation of this vapor-phase AP treatment (evaluation number 49) indicates that the coating protects epoxy resins from attack by AP, the percent of initial epoxy content remaining after 238 hours at 80°C in EPON H-825 being 90.8%. By contrast, a treatment of AP with diethylenetriamine by adsorption from n-butanol solution gave a product which was shown by evaluation number 40 to accelerate the attack of the AP on epoxy resins (60.7% of initial epoxy content remaining after 263 hours at 80°C.

D. Dri-Film SC-77 Coating

A fluidized bed of 10 g of AP was treated with 1 g of Dri-Film SC-77, a mixture of monomethyl trichlorosilane and dimethyl dichlorosilane, vaporized into a stream of nitrogen. The treated powder was then heated at 60°C in a water vapor-saturated atmosphere for two hours and dried in a dry atmosphere at 60°C for 16 hours. From the hydrophobic nature of the fluidized bed column acquired during the treatment, it was apparent that a portion of the Dri-Film was deposited on the glass. The evaluation of this coating (evaluation number 82) indicates a small protective action after 235 hours in EPON H-825 at 80°C relative to uncoated AP (86.7% initial epoxy content retained as compared with 84.3% for uncoated AP).

SECTION IX

INERT POWDER COATINGS

The use of finely divided SiO_2 having particle sizes ranging between 10 and 500 A to prevent caking of hydroscopic materials is common in the chemical industry. These anticaking silicon oxides may insulate the AP particles from their immediate environment. Two silicon oxides-Cab-O-Sil M-5 (obtained from the Cabot Corporation) and Aerosil R-972 (hydrophobic surface, obtained from Degussa Incorporated) - were used to treat AP (70/30 bimodal).

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To 2.1 g of AP 0.04 g of Cab-O-Sil was added then mixed well in a mortar. This mixture was shaken overnight and then dried at 80°C. We also treated 4.1 g of AP and with 0.04 g of Aerosil R-972 using the same mixing procedure described for the Cab-O-Sil treated AP. The effectiveness of these coatings as evaluated in a later section (evaluations 28 and 201) was shown to be nil relative to untreated AP.

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SECTION X

SURFACE TREATMENT OF AMMONIUM PERCHLORATE WITH POTASSIUM, RUBIDIUM AND CESIUM IONS

A survey of the solubility of a large number of perchlorates shows the K, Rb and Cs compounds to be the most insoluble in water as well as in organic liquids. Data from Willard and Smith and from Isben and Kohe summarized in Table XIV illustrate this point particularly in comparison with ammonium perchlorate. For some time we have felt that the consumption of the epoxy groups in epoxy resins containing ammonium perchlorate was related more closely to the solubility of the AP in the resin than to the amount of AP surface presented to the resin. This point was supported by the finding that the rate of epoxy disappearance at $80°C$ is about the same whether the amount of AP in the resin is 0.5% or 30% (see Figure 5). The treatment of AP with K, Rb and Cs was designed to place an insoluble surface layer of perchlorate salt on the AP particles in an attempt to reduce the release of NH_4^+ and ClO_4^- into solution.

Table XIV. SOLUBILITY OF PERCHLORATES IN WATER AND ORGANIC LIQUIDS

g/100 g of solvent at 25°C: from Willard and Smith[a]) and Isben and Kohe[b])

	H_2O	Ethyl Alcohol	n-Propyl Alcohol	n-Butyl Alcohol	i-Butyl Alcohol	Acetone	Ethyl Acetate
NH_4ClO_4	23.922	1.907	0.387	0.017	0.127	2.260	0.032
$KClO_4$	2.062	0.012	0.010	0.005	0.005	0.155	0.002
$RbClO_4$	1.338	0.009	0.006	0.002	0.004	0.095	0.016
$CsClO_4$	2.000	0.011	0.006	0.006	0.007	0.150	"Insol."

a) Willard, H. H. and Smith, G. F., JACS 44, 2255 (1922).
b) Isben, H. W. and Kohe, K. A., JACS 67, 464 (1945).

Two methods of treatment of AP powder were used. In the first method the AP powder was dropped through a column of aqueous solution of K, Rb or Cs chloride having an underlying reservoir of CCl_4 into which the treated solid particles passed. Twenty grams of AP powder was dropped through a 30 cm column of saturated aqueous solution of RbCl or KCl at room temperature, the travel time through the column being about 5 seconds. Not all of the solid passed cleanly through the aqueous solution -CCl_4 interface so that mechanical agitation was required. The solid was filtered off and dried at $60°C$. The results of treatment using potassium and rubidium chlorides are given in Table XV. The exchange was more effective than expected in view of the short contact time and a very large fraction of the AP was converted into K and Rb perchlorates. The evaluation of chemical stability of epoxy resin in contact with these treated AP specimens is described in evaluations 68 and 73. The Rb treated specimen showed very little attack on epoxy resin, 92.1% of the initial epoxy content being retained after 288 hours of mixing with EPON H-825 at 80°C (evaluation 68). resin while the K-treated specimen caused very rapid loss of the epoxy group and gelation of the resin. This latter result with the K-treated AP

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(evaluation 73) was unexpected and appears spurious in view of later findings with K-treated systems.

Table XV. COLUMN TREATMENT OF AP WITH SATURATED
RbCl and KCl SOLUTIONS

LR 9950-	Treating Solution	Initial Conc, $\%w$	Dry Solids Analysis
70	RbCl	74.2	19.9% Rb = 43.1% $RbClO_4$
76	KCl	25.9	15.8% K = 56.0% $KClO_3$

The second method of treatment of AP with K, Rb and Cs chlorides consisted of mixing 20 g of AP with 100 cc of $4\%w$ solutions of the chlorides for 5 minutes followed by filtration and drying of the solids at 60°C. The dry solids were analyzed for K, Rb and Cs, respectively, with the results shown in Table XVI. Again the recorded solids contained a rather high level of K, Rb and Cs and it was evident that additional treatments at much lower levels were in order. The evaluation of the chemical activity of these specimens in epoxy resin, reported in Section XVIII, showed the effectiveness to be in the order K > Rb >> Cs, the % of epoxy content retained after 283 hours at 80°C being 94.9, 93.7 and 78.9, respectively.

Table XV. COLUMN TREATMENT OF AP WITH SATURATED
OF K, Rb AND Cs CHLORIDES

20 g AP, 100 cc of the $4\%w$ solution

LR 9950-	Treating Solution	Initial Concentration, $\%w$	Final Concentration, $\%w$	Solids Analysis	
79	KCl	2.1 K	0.14 K	8.2% K	= 29.2% $KClO_4$
80	RbCl	2.8 Rb	0.18 Rb	12.5%w Rb	= 27.0% $RbClO_4$
81	CsCl	3.2 Cs	0.027 Cs	23.5%w Cs	= 41.1% $CsClO_4$

In addition to these treated AP specimens some $KClO_4$ was prepared by precipitation and submitted for evaluation. It proved to be completely inert in epoxy resin over a period of 288 hours at 80°C. The K, Rb and Cs chlorides were also submitted for chemical activity tests. The appear to be effective when simply added to the AP-resin mixture. The results obtained when 10% of K, Rb or Cs chloride were added at a level of 10% basis AP to and AP-EPON H-825 mixture containing 20% HP were as shown in Table XVII. The K, Rb and Cs chlorides when mixed with EPON H-825 for 318 hours at 80°C proved to be completely inert as shown in evaluations 98, 99 and 100.

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Table XVII. ADDITION OF K, Rb OR Cs CHLORIDES TO
AP - "EPON" H-825 MIXTURES AT A LEVEL OF
10% BASIS AP

20% AP in EPON H-825

Salt Added	Evaluation No.	% Initial Epoxy Content Retained	Hours at 80°C
CsCl	81	92.7	288
RbCl	70	92.1	285
KCl	76	90.6	283

SECTION XI

INFLUENCE OF COATED AMMONIUM PERCHLORATES ON EPOXY-ACID REACTION KINETICS

In view of the reduced reactivity of the Montrek 1000, rubidium chloride and potassium chloride treated AP toward EPON H-825 at 80°C, the influence of these samples on the kinetics of our model epoxy-acid system at 80°C was tested. Acid and epoxide consumption rate was determined for the base system [EPON H-825-hexanoic acid - 0.10% $Cc(Oct)_3$ (on EPON resin)] under the following conditions:

a) Neat

b) Plus 20%w untreated AP

c) Plus 1%w Montrek 1000 treated AP (LR 9950-46)

d) Plus 20%w Montrek 1000 treated AP (LR 9950-46)

e) Plus 20% RbCl treated AP (LR 9950-70)

f) Plus 20%w untreated AP and 2% (10% on AP) KCl

Our data, see Figures 30 and 31, indicate that these treatments do moderate the effect of AP on the reaction rate but do not eliminate the reaction stoichiometry perturbation effects of ammonium perchlorate on the epoxy-carboxyl reaction.

SECTION XII

SOME PROPOSED MECHANISMS FOR THE INTEREFERENCE OF AP WITH THE EPOXY-ACID REACTION

In our attempt to understand the mechanism by which ammonium perchlorate interferes with the epoxy-acid curing reaction, we have proposed and tested several hypotheses. Our first hypothesis was that one or more of

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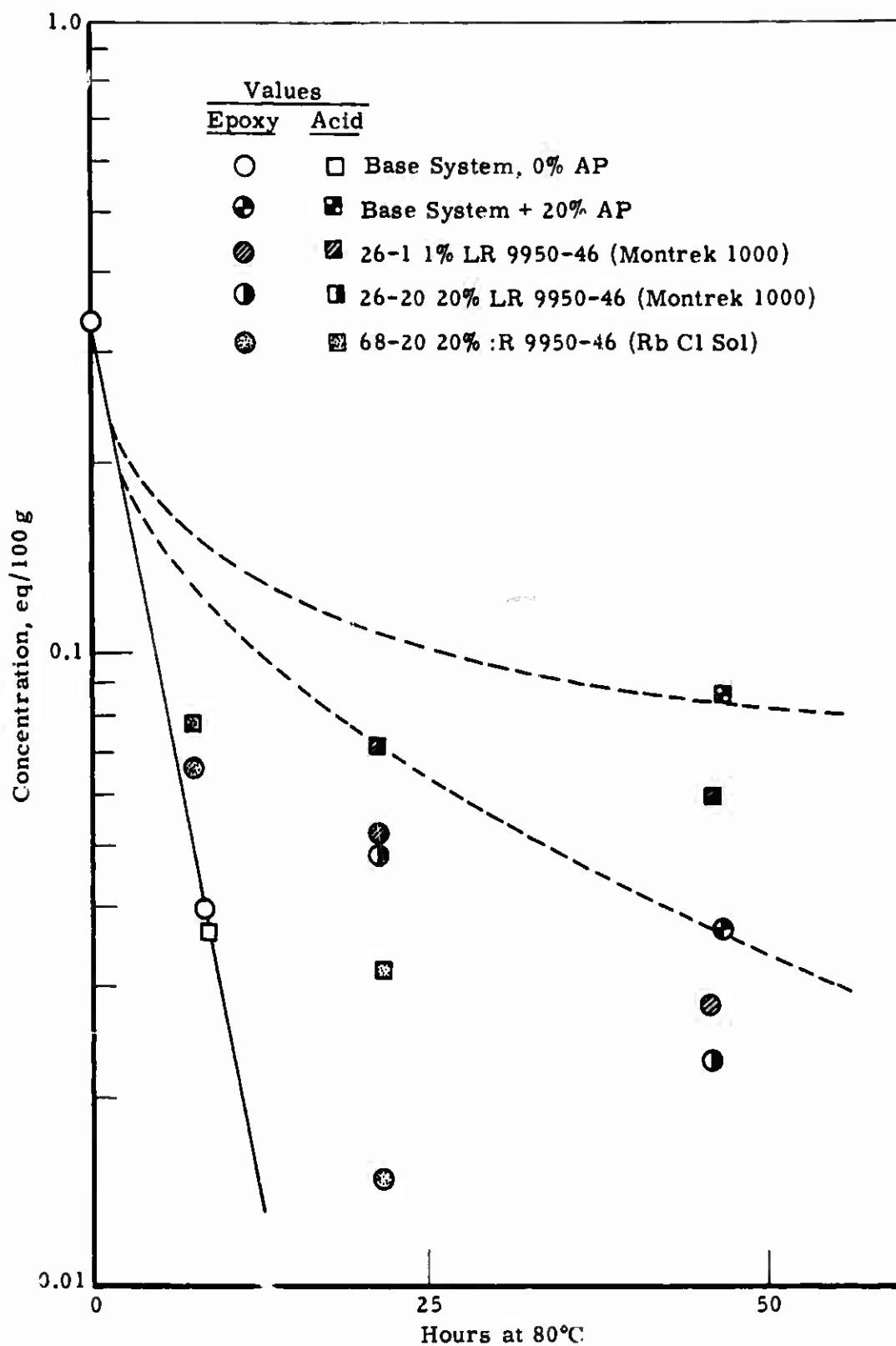
Figure 30. INFLUENCE OF SELECTED COATED AP SAMPLES
ON KINETICS OF EPON H-825-HEXANOIC ACID-
Cr (OCT)₃ AT 80°C
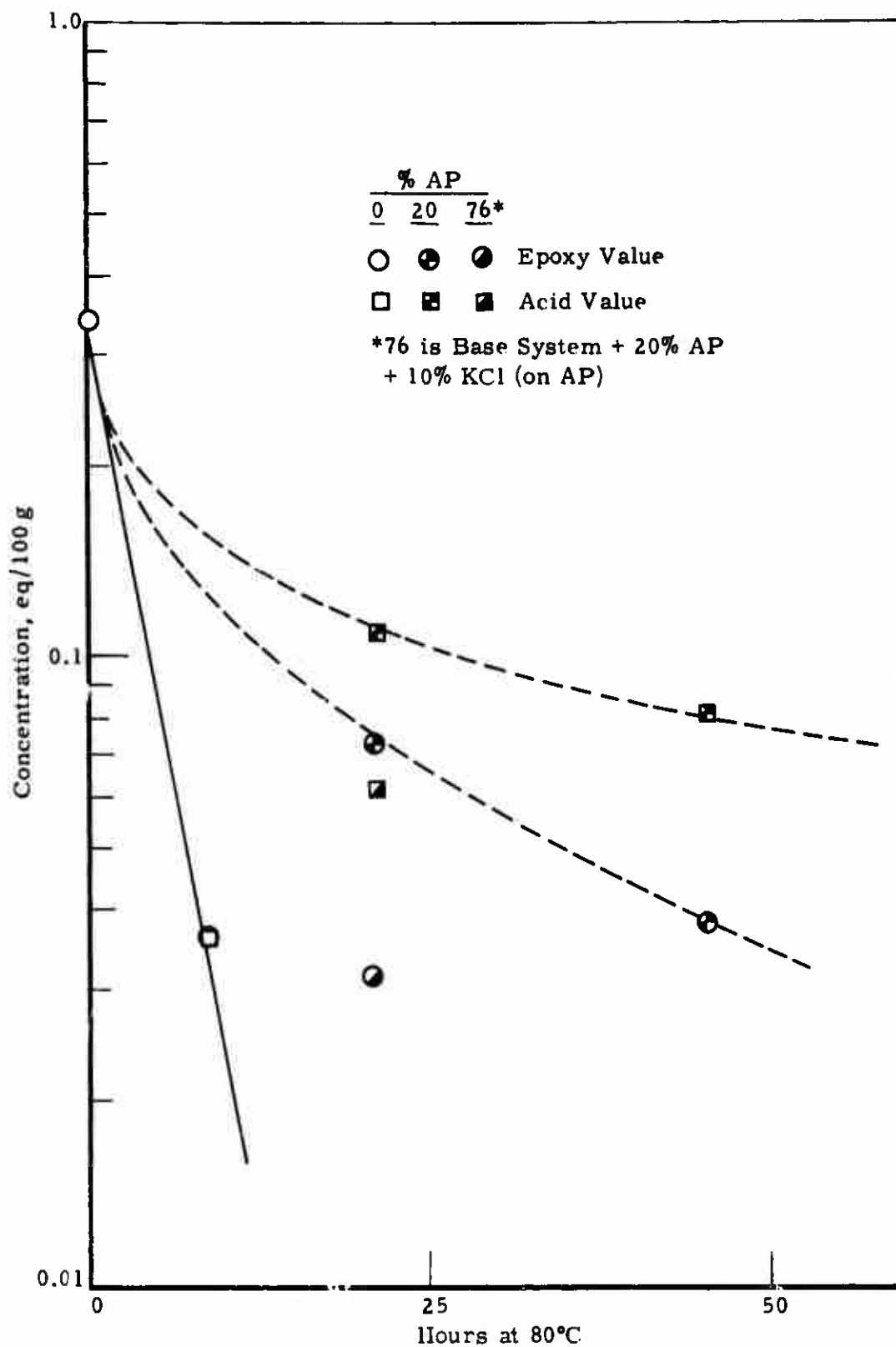
Figure 31. INFLUENCE OF KCl ON KINETICS OF EPON H-825-
HEXANOIC ACID-0.1% Cr (OCT)₃ OVER AP AT 80°C

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the binder components reacts with the surface of AP particles and is removed from the liquid phase binder system. This notion was discarded when it was shown that the rate and stoichiometry of the epoxy-acid reaction in the presence of AP was essentially independent of the amount of AP surface in the system (see Figures 3 and 4).

A second hypothesis was that the solubility of AP in the binder system is the controlling factor, the interaction between binder components and ammonium perchlorate taking place in the liquid phase. This idea is supported by our finding that the addition of K, Rb and Cs halides to the AP-epoxy-acid system reduces the interference of AP presumably by precipitating dissolved NH_4ClO_4 as the much less soluble K, Rb or Cs perchlorates plus the ammonium halides. Since the ammonium halides may not be chemically inert in the binder system, we propose to add K, Rb or Cs salts whose anions form insoluble ammonium compounds as discussed in another section of this report.

A third hypothesis is that AP decomposes by proton transfer to produce NH_3 and $HClO_4$, the latter reacting with epoxy groups in the binder system. The effectiveness of polyethyleneimines and polyalkylenepolyamines in reducing the interference of AP with binder reactions might be attributed to a reaction of the amine groups with $HClO_4$ thus removing it from the system. It has been shown that polyethyleneimines react with AP to produce a polyethyleneimine perchlorate plus NH_3. The proposed decomposition of AP to gaseous NH_3 and $HClO_4$ was investigated by following weight changes in AP 60, 80 and 100°C for a period of 260 hours. At all three temperatures, the weight losses after the first few hours were negligible and the total weight changes were of the order of 0.05% in all three cases. Thus, there appears to be no evidence that thermal decomposition of AP, to yield gaseous products, occurs at temperature levels of interest in propellant binder curing operation.

Our present opinion is that AP, or its adsorbed decomposition products, are dissolved in the binder system and are responsible for interference with the binder curing rate and stoichiometry. The addition to the propellant formulation of chemicals which will react with the dissolved AP or its decomposition products and prevent its interference with binder reactions seems the most promising approach.

SECTION XIII

SOLUBILITY OF AMMONIUM PERCHLORATE IN "EPON" H-825

Since it was proposed that the ammonium perchlorate (AP) or its adsorbed decomposition products dissolved in the binder system are responsible for interference with binder cure rate and stoichiometry the solubility of AP in EPON H-825 was determined to enable us to assess the above hypothesis.

The AP solubility in EPON H-825 at 40°C and 60°C was determined in the following manner. An excess of AP was added to EPON H-825 and to a dried sample of EPON H-825. These samples were thoroughly mixed and then placed in a 40°C or 60°C oven. Then these samples were allowed to stand for ~4 days

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at 40°C or 60°C and were thoroughly mixed at least three times a day. The samples were then centrifuged for one hour at 6,000 rpm and then replaced in the 40°C or 60°C oven for ~7 days. Two controls, EPON H-825 and EPON H-825 (dried), were treated in the same manner. The Shell Development Analytical Department determined the total nitrogen in these samples using the Kjeldahl method. Total nitrogen content and AP solubility in the EPONS are given in Table XVIII. (Also note that there was no evidence of reaction of epoxy resin with the AP or of homopolymerization cure since the epoxide content determined by titration remainded unchanged.) The concentration of AP dissolved in the EPON at 40°C and 60°C was 0.034% in both cases. The lack of influence of temperature on solubility is puzzling but the values are so low that the differences could be within the accuracy of the measurements. Solubility at 80°C could not be determined because of the reaction which takes place between AP and epoxy resins at that temperature.

Table XVIII. SOLUBILITY OF AP IN "EPON" H-825 AT 40° AND 60°C

Sample Designation	% Nitrogen		Epoxide Content, eq/100 gms		AP. %w in EPON	
	40°C	60°C	40°C	60°C	40°C	60°C
EPON H-875 (as recieved)	0.003	0.003	0.569	0.569	0	0
EPON H-875 (dried)	0.002	0.003	0.570	0.570	0	0
AP + EPON H-825 (as recieved)	0.007	0.007	0.569	0.569	0.034	0.034
AP + EPON H-825 (dried)	0.006	0.007	0.570	0.570	0.034	0.034

SECTION XIV

PRECIPITATING AP FROM SOLUTION IN BINDER SYSTEMS

On the basis of the encouraging results obtained with the addition of K, Rb and Cs salts to AP-epoxy-acid systems, we reasoned that in order to remove ammonium perchlorate from a binder system as it dissolves, a cation such as K should be present which forms an insoluble perchlorate and an anion should be present which forms an insoluble ammonium salt. Although not much information is readily available regarding solubility of ammonium salts in organic systems, a number of compounds were selected on the basis of handbook information as being likely candidates for precipitating AP from solution. Table XIX lists potassium salts whose corresponding ammonium salts are insoluble or have very low solubility in water and in organic solvents. A number of these compounds were on hand and several others were easily obtainable. Many of them were not readily available.

The compounds listed in Table XX were added to an AP-EPON H-825 system at a level of 1% basis AP and the chemical reactivity at 80°C was followed. KBH_4, $KMnO_4$, KCNO, $K_4Fe(CN)_6$ and K_2PdCl_6 are effective in reducing the attack of AP on EPON H-825 and K_2PdCl_6 in the most effective of these salts at the 1% level based on AP.

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Table XIX. SALTS WHICH SHOULD PRECIPITATE BOTH NH_4^+ AND ClO_4^- FROM AQUEOUS AND ORGANIC SOLUTIONS

Corresponding NH_4 Salt Has Low Water Solubility	Corresponding NH_4 Salt Has Low Solubility in Organic Solvents
KBH_4	$K_2H_2Sb_2O_7 \cdot 4H_2O$
$K_3A_2O_4$	K_2HAsO_4
KB_5O_8	$KBO_3 \cdot 1/2H_2O$
$KBO_3 \cdot 1/2H_2O$	$K_2B_4O_7 \cdot 8H_2O$
$K_2B_4O_7 \cdot 8H_2O$	$KHCO_3$
K_2PtBr_6	$KClO_3$
K_4IrCl_8	KCl
K_2PtCl_6	$KAuCl$
K_2PbCl_6	$KAuCl_4 \cdot 2H_2O$
K_3CrO_8	K_4IrCl_8
KBF_4	K_2PtCl_6
$KzZrF_8$	K_3CrO_8
KIO_3	$K_2SO_4 \cdot CoSO_4 \cdot 6H_2O$
$KMgPO_4 \cdot 6H_2O$	$KOCN$
$KSeO_4 \cdot MgSeO_4 \cdot 6H_2O$	$K_4Fe(CN)_6 \cdot 3H_2O$
$KMnO_4$	K_2GeF_8
$KC_{14}H_{27}O_2 \cdot C_{14}H_{28}O_2$	KHF_2
$K_2C_2O_4$	K_2SiF_6
$KC_{16}H_{31}O_2 \cdot C_{16}H_{32}O_2$	$K_2TiF_6 \cdot H_2O$
$KC_6H_2N_3O_7$	$KGa(SO_4)_2 \cdot 12H_2O$
$(K_2SO_4)_3Pr_2(SO_4)_3 \cdot H_2O$	K_2PtI_8
$KReO_4$	$K_2SO_4 \cdot FeSO_4 \cdot 6H_2O$
$KHC_8H_8O_8$	$KC_{12}H_{22}O_2 \cdot C_{12}H_{24}O_2$
$KHC_4H_4O_6$	$K_2O \cdot 3MoO_4 \cdot 3H_2O$
$(K_2CO_3)_2 \cdot UO_2CO_3$	$KC_{14}H_{27}O_2 \cdot C_{14}H_{28}O_2$
KVO_3	$KC_{16}H_{31}O_2 \cdot C_{16}H_{32}O_2$
$KSb(OH)_6 \cdot 1/2H_2O$	$KC_6H_2N_3O_7$
KIO_4	K_2S_5
	$KCNS$
	$K_2S_2O_3$

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Table XX. SALTS TESTED FOR REDUCING ATTACK
OF AP ON "EPON" H-825

Sample No.	Salts		%w Added to AP	Hours at 80°C	Epoxy Retained, %
86-A	Potassium iodate	KIO_3	10	261	81.2
B	Potassium metaperiodate	KIO_4	10	261	67.2
C	Potassium permanganate	$KMnO_4$	10	261	87.3
E	Potassium borohydride	KBH_4	1	238	88.5
F	Potassium tetrafluoroborate	KBF_4	1	236	83.4
G	Potassium cyanate	KCNO	1	236	88.1
H	Potassium chlorate	$KClO_3$	1	238	77.3
I	Potassium ferrocyanide	$K_4Fe(CN)_6 \cdot 3H_2O$	1	238	86.9
J	Potassium iridic chloride	K_4IrCl_6	1	240	81.0
K	Potassium chloropalladate	K_2PdCl_6	1	240	92.8
L	Potassium pyroantimonate	$K_2H_2Sb_2O_7 \cdot 4H_2O$	1	-	-
	No coating on AP	-	-	236	83.8
				240	83.2
				261	80.7

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SECTION XV

ATTEMPT TO REDUCE DECOMPOSITION OF AP WITH UNSTABLE AMMONIUM COMPOUNDS

If the ammonium perchlorate which dissolves in epoxy-acid binder system undergoes proton transfer to produce HN_3 and $HClO_4$ then it may be possible to drive the reaction in the reverse direction by adding to the system an ammonium compound which is thermally unstable and decomposes to produce NH_3. This idea has its basis in a finding of Jacobs and Russell-Jones[13] that the low temperature ($230°C$) decomposition and sublimation of ammonium perchlorate are suppressed by moderate pressures of ammonia as might be expected from the following equations:

$$NH_4ClO_4 \longrightarrow \underset{\substack{\text{(adsorbed on}\\ \text{AP crystals)}}}{NH_3 + HClO_4} \rightleftharpoons \underset{\text{(gas, gas)}}{NH_3 + HClO_4} \rightleftharpoons \underset{\text{(sublimate)}}{HClO_4}$$
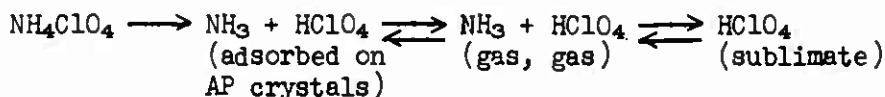
A brief survey of ammonium compounds which decompose at relatively low temperatures turned up the list given in Table XXI. A vew of these compounds which were readily available were tested for their influence on the chemical reactivity of AP in EPON H-825 at $80°C$. The compounds tested and the results obtained are summarized in Table XXII. Ammonium fluoride is the most effective of this group of compounds tested.

Table XXI. AMMONIUM COMPOUNDS WHICH DECOMPOSE AT LOW TEMPERATURES

$NH_4C_2H_3O_2$	NH_4F
$(NH_4)_2HAsO_4$	NH_4I
NH_4AsO_2	NH_4MnO_4
$(NH_4)_2Br_6Se$	$(NH_4)_2MoO_4$
$NH_4CaPO_4 \cdot 7H_2O$	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$
$NH_4NH_2CO_2$	NH_4NO_2
NH_4HCO_3	$(NH_4)_2OsCl_6$
$(NH_4)_2CO_3 \cdot H_2O$	NH_4HSO_4
$(NH_4)_2PbCl_6$	$(NH_4)_2S$
$(NH_4)_2CrO_4$	NH_4HS
$(NH_4)_3CrO_8$	$(NH_4)_3SbS_4 \cdot 4H_2O$
$NH_4CoPO_4 \cdot H_2O$	$(NH_4)_2CS_3$
$NH_4I \cdot CuI \cdot H_2O$	$2(NH_4)_2CO_3 \cdot UO_2CO_3 \cdot 2H_2O$
NH_4CNO	NH_4VO_3

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Table XXII INFLUENCE OF THERMALLY UNSTABLE AMMONIUM COMPOUNDS
ON CHEMICAL REACTIVITY OF AP IN "EPON" H-825 AT 80°C

Sample No.	Compounds		Basis AP, %w	Hours at 80°C	Epoxy Retained, %
91-A	Ammonium acetate	$NH_4C_2H_3O_2$	1	286	Gelled (<70)
B	Ammonium chromate	$(NH_4)_2CrO_4$	1	218	Gelled (<70)
C	Ammonium fluoride	NH_4F	1	286	87.1
D	Ammonium paramolybdate	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	1	286	77.0
E	Ammonium iodide	NH_4I	1	286	81.2
	No coating on AP	-	-	286	77.8

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SECTION XVI

PROPRIETARY SHELL PRODUCTS FOR AMMONIUM PERCHLORATE TREATMENT

Our earlier studies showing the effectiveness of a variety of potassium compounds in preventing the reaction of ammonium perchlorate with epoxy groups in resins at 80°C led to the conversion of 11 miscellaneous Shell products into potassium salts for evaluation. Seven more proprietary compounds from our family of phosphonic acid derivatives were converted to mono and dipotassium salts for evaluation. The structures and identification of the first group of eleven products are given in Table XXIII. The structures of the phosphonic acid derivatives are given in Table XXIV. These compounds were expected to perform two functi ns: 1) to provide a source of potassium ion which has been shown to be effective in removing ClO_4 ions from solution in binder systems and 2) to provide a surface active anion which may be expected to reduce the viscosity of propellant mixes at high loadings of solids. This latter expectation is based on earlier experience with the monobutyl ester of 2-triododecylphosphonic acid which is known to be an effective viscosity-reducing additive in propellant mixes containing aluminum and ammonium perchlorate.

The effectiveness of these 18 proprietary compounds in preventing the attack of AP on epoxy groups in EPON H-825 was evaluated in a system containing 20% AP based on the epoxy resin and 1% of the additive based on the AP. These were aged with continuous mixing at 80°C and samples were periodically withdrawn for epoxy content determination by titration. The results of the evaluations are given in Table XXV and in Figure 32. All except three of the additives display some ability to reduce the loss of epoxy groups from the resin in the presence of ammonium perchlorate. On the basis of these evaluation the most effective additives include the following:
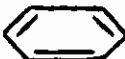
> potassium salt of Shell paraffin acid i-C_{12} (184)
> potassium salt of monobutyl ester of eicosylphosphonic acid (193)
> potassium salt of eicosylphosphonic acid (191)
> potassium salt of VERSATIC 911 (180)
> potassium salt of NEODOL 25 sulfate (167)
> potassium salt of NEODOL 25 3EO sulfate (166)
> potassium salt of Shell paraffin acid, n-C_{12} (182)

The potential effectiveness of these compounds for viscosity reduction in propellant mixes was evaluated in other studies.

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Table XXIII. PROPRIETARY SHELL PRODUCTS FOR INERTING
OF AP IN EPOXY RESINS

LR 9950 No.	Name	Structure
104	NEODOL 25-3-P	C_{12} to C_{15}-(O-CH$_2$CH$_2$)$_3$-O-$\overset{\overset{O}{\|\|}}{\underset{\underset{O}{\|\|}}{S}}$-OK
106	NEODOL 25-P	C_{12} to C_{15}-O-$\overset{\overset{O}{\|\|}}{\underset{\underset{O}{\|\|}}{S}}$-OK
108	VERSATIC 911-P	Cyclo C_8 to C_{10}-$\overset{\overset{O}{\|\|}}{C}$-OK
110-A	SPAKN-C_{15}	n-C_{14}-$\overset{\overset{O}{\|\|}}{C}$-OK
110-B	SPAKN-C_{12}	n-C_{11}-$\overset{\overset{O}{\|\|}}{C}$-OK
110-C	SPAKI-C_{12}	i-C_{11}-$\overset{\overset{O}{\|\|}}{C}$-OK
110-D	SPAKI-C_{15}	i-C_{14}-$\overset{\overset{O}{\|\|}}{C}$-OK
112	KNABL	potassium salt of naphthenic acid bottoms - lube crude
113	K-Pivalate	CH_3-$\overset{\overset{CH_3}{\|}}{\underset{\underset{CH_3}{\|}}{C}}$-$\overset{\overset{O}{\|\|}}{C}$-OK
114	K-PTBBA	CH_3-$\overset{\overset{CH_3}{\|}}{\underset{\underset{CH_3}{\|}}{C}}$⟨ ⟩-$\overset{\overset{O}{\|\|}}{C}$-OK
105-8	K-SPS	potassium salt of Shell petroleum sulfonate

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Table XXIV. STRUCTURES OF POTASSIUM SALTS OF PHOSPHONIC ACID DERIVATIVES PRODUCED FOR EVALUATION AS ADDITIVES TO PREVENT INTERACTION OF AMMONIUM PERCHLORATE WITH EPOXY RESINS

LR 9950 No.	Name	Structure
116-A	Potassium salt of eicosylphosphonic acid	$KO-\overset{\overset{O}{\parallel}}{\underset{\underset{KO}{\mid}}{P}}-C_{20}H_{41}$
116-B	Potassium salt of monobutyl ester of eicosyl-phosphonic acid	$KO-\overset{\overset{O}{\parallel}}{\underset{\underset{O-C_4H_9}{\mid}}{P}}-C_{20}H_{41}$
117-A	Potassium salt of monbutyl ester of 2-thiadodecylphosphonic acid	$KO-\overset{\overset{O}{\parallel}}{\underset{\underset{O-C_4H_9}{\mid}}{P}}-CH_2-S-C_{10}H_{21}$
117-B	Potassium salt of 4,7,10,13,16-pentaoxa-18-hydroxyoctadecylphosphonic acid	$KO-\overset{\overset{O}{\parallel}}{\underset{\underset{KO}{\mid}}{P}}-CH_2-CH_2-CH_2-O-(CH_2-CH_2-O)_5H$
118-A	Potassium salt of monomethyl ester of 4,7,10,13,16-pentaoxa-18-hydroxyoctadecylphosphonic acid	$KO-\overset{\overset{O}{\parallel}}{\underset{\underset{O-CH_3}{\mid}}{P}}-CH_2-CH_2-CH_2-O-(CH_2-CH_2-O)_5H$
118-B	Potassium salt of 4,7,10,13,16,19,22,25,28,31-decaoxa-33-hydroxytriatriacontylphosphonic acid	$KO-\overset{\overset{O}{\parallel}}{\underset{\underset{KO}{\mid}}{P}}-CH_2-CH_2-CH_2-O-(CH_2-CH_2-O)_{10}H$

(Continued)

Table XXIV (Contd). STRUCTURES OF POTASSIUM SALTS OF PHOSPHONIC ACID DERIVATIVES
PRODUCED FOR EVALUATION AS ADDITIVES TO PREVENT INTERACTION OF
AMMONIUM PERCHLORATE WITH EPOXY RESINS

LR 9950 No.	Name	Structure
119	Potassium salt of monomethyl ester of 4,7,10,13,16,19, 22,25,28,31-decoxahydroxytriatriaconty1-phosphonic acid	$$\text{KO-}\overset{\displaystyle\overset{O}{\Vert}}{P}\text{-CH}_2\text{-CH}_2\text{-O-(CH}_2\text{-CH}_2\text{-O)}_{10}\text{H}$$ $$\text{O-CH}_3$$

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Table XXV. EVALUATION OF PROPRIETARY COMPOUNDS AS ADDITIVES FOR
REDUCTION OF ATTACK OF AMMONIUM PERCHLORATE ON
EPOXY GROUPS IN "EPON" H-825

(10% AP Basis Epoxy Resin, 1% Additive Basis AP)

Initial epoxy value: 0.573 eq/100 g

Additive, 1% Basis AP	Run No.	% of Initial Epoxy Retained After (Hrs) at 80°C
NEODOL 25-3-P LR 9950-104	166	(265) 89.9
Potassium Petroleum Sulfonate LR 9950-105-8	178-2	(328) 78.1
NEODOL 25-P LR 9950-106	167	(280) 90.8
VERSATIC 911-P LR 9950-108	180	(265) 90.8
SPAK N-C_{15} LR 9950-110-A	181	(262) 90.4
SPAKN-C_{12} LR 9950-110-B	182	(262) 90.8
SPAKI-C_{12} LR 9950-110-C	184	(262) 93.2
SPAKI-C_{15} LR 9950-110-D	183	(262) 87.1
KNABL - Potassium salt of naphthenic acid bottoms of lube crude LR 9950-112	185	(282) 84.0
K-Pivalate LR 9950-113	186	(282) 89.4
K-TBBA LR 9950-114	187	(282) 88.4
K salt of eicosyl phosphonic acid LR 9950-115-A	191	(264) 91.8
K salt of monobutyl ester of eicosyl phosphonic acid LR 9950-116-B	193	(264) 91.5

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Table XXV (Contd). EVALUATION OF PROPRIETARY COMPOUNDS AS
ADDITIVES FOR REDUCTION OF ATTACK OF AMMONIUM PERCHLORATE
EPOXY GROUPS IN "EPON" H-825

Additive, 1% Basis AP	Run No.	% of Initial Epoxy Retained After (Hrs) at 80°C
K salt of monobutyl ester of 2-thiadodecylphosphonic acid LR 9950-117-A)	194	(264) 86.4
Di K salt of 4,7,10,13,16-pentaoxa- 18-hydroxyoctadecylphosphonic acid LR 9950-117-B	195	(290) 85.8
K salt of monomethyl ester of 4,7,10,13,16-pentaoxa-18-hydroxy- octadecylphosphonic acid LR 9950-118-A	196	(290) 78.5
Di K salt of 4,7,10,13,16,19,22,25, 28,31-decaoxa-33-hydroxytriatria- contylphosphonic acid LR 9950-118-B	197	(290) 84.3
K salt of monomethyl ester of 4,7,10,13,16,19,22,25,28,31-deca- oxa-33-hydroxytriatraicontyl- phosphonic acid LR 9950-119-A	198	(290) 78.5
Potassium Petroleum Sulfonate, 10% basis AP LR 9950-105-8)	177-2	(328) 93.9
No additive		(330) 76.4

Figure 32. INFLUENCE OF ADDITIVES ON
EPOXY-AMMONIUM PERCHLORATE INTERACTION
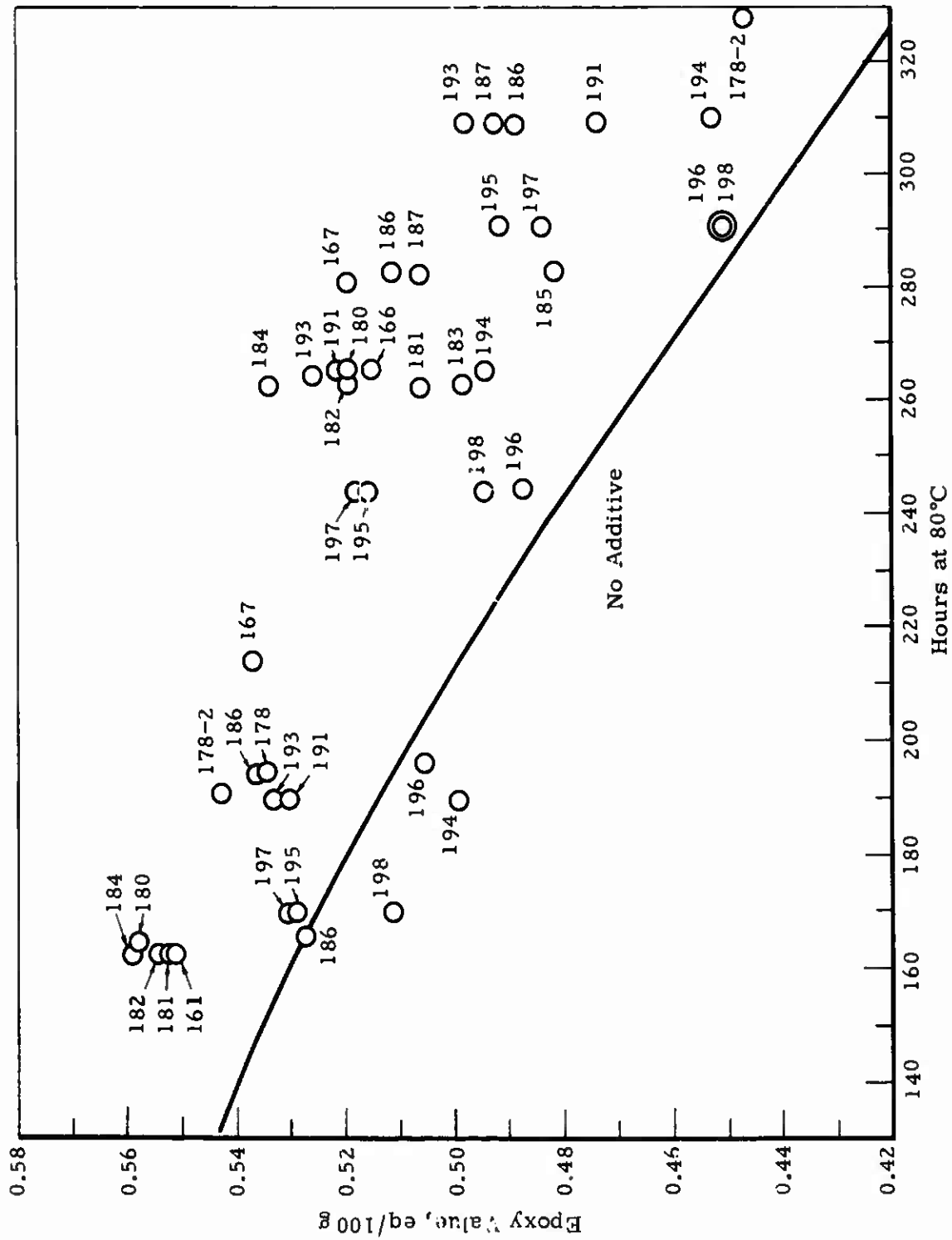
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SECTION XVII

SALTS OF POLYBUTADIENE-ACRYLIC ACID-ACRYLONITRILE (PBAN) COPOLYMERS

On the basis of results of some of the propellant mix work employing additives consisting of potassium salts of various acids, it was reasoned that lack of cure of PBAN-EPON binder systems might be caused by the competition of the anion of the acid for the epoxy group. Since these anions are monofunctional they would tend to terminate polymerizing chains and prevent cure. We then reasoned that the anion of the additive containing K, Rb or Cs should be the anion which we want to react with the epoxy group in the resin. Thus, the general idea evolved of producing the K, Rb and Cs salts of PBAN by reactions of the acid groups (0.065 equivalents/100 g) in the terpolymer. The function of the K, Rb or Cs ions would be to capture and precipitate any ClO_4^- ions in the binder system produced by NH_4ClO_4 thus preventing their attack on epoxy groups in the binder. The K, Rb and Cs salts of PBAN-703, a polybutadiene-acrylic acid-acrylonitrile tepolymer, were made.

A test of the curability of the K salt of PBAN with EPON H-825 in the presence of ammonium perchlorate was made using the Ball Pentration (see Section XIX) measurement as an indication of cure. Chemically equivalent quantities of EPON H-825 and the product PBAN-K (LR 9950-122) were blended and 20% AP basis binder was added. A similar blend of EPON H-825, PBAN and AP was made as a control. These were stored in an 80°C oven and the Ball Penetration values were determined periodically. The results are shown in **Figure 33**. The potassium derivative of the PBAN-703 used in this experiment cured much more rapidly in the presence of AP than the control sample. By only partial conversion of the acid groups in PBAN to the potassium form it should be possible to obtain cure rates intermediate to those shown in the figure. This encouraging result led us to produce a propellant mix based on this binder which is discussed in a later section (see Section XXI).

SECTION XVIII

EVALUATION OF TREATED AMMONIUM PERCHLORATE WITH "EPON" H-825

Our procedure for determining rate and extent on reaction of various treated AP samples with EPON H-825 at 80°C was: Ten grams of EPON H-825 plus two grams of treated AP, together with a 1 x 4 cm glass rod, were added to a one-ounce wide mouth screw cap (Teflon liner) bottle and attached to the rotating disc in our 80°C oven (see **Figures 7 and 8**). At specified intervals the sample containers were removed from the disc and left standing in the oven for at least thirty minutes. Samples for duplicate epoxide determination (ca 0.3 gram each) were taken from the clear supernatant phase with a medicine dropper and the bottle re-sealed and returned to the rotating disc for additional contact time.

The initial series of coatings, selected to cover a spectrum of surface active compounds of varying functionality, were:

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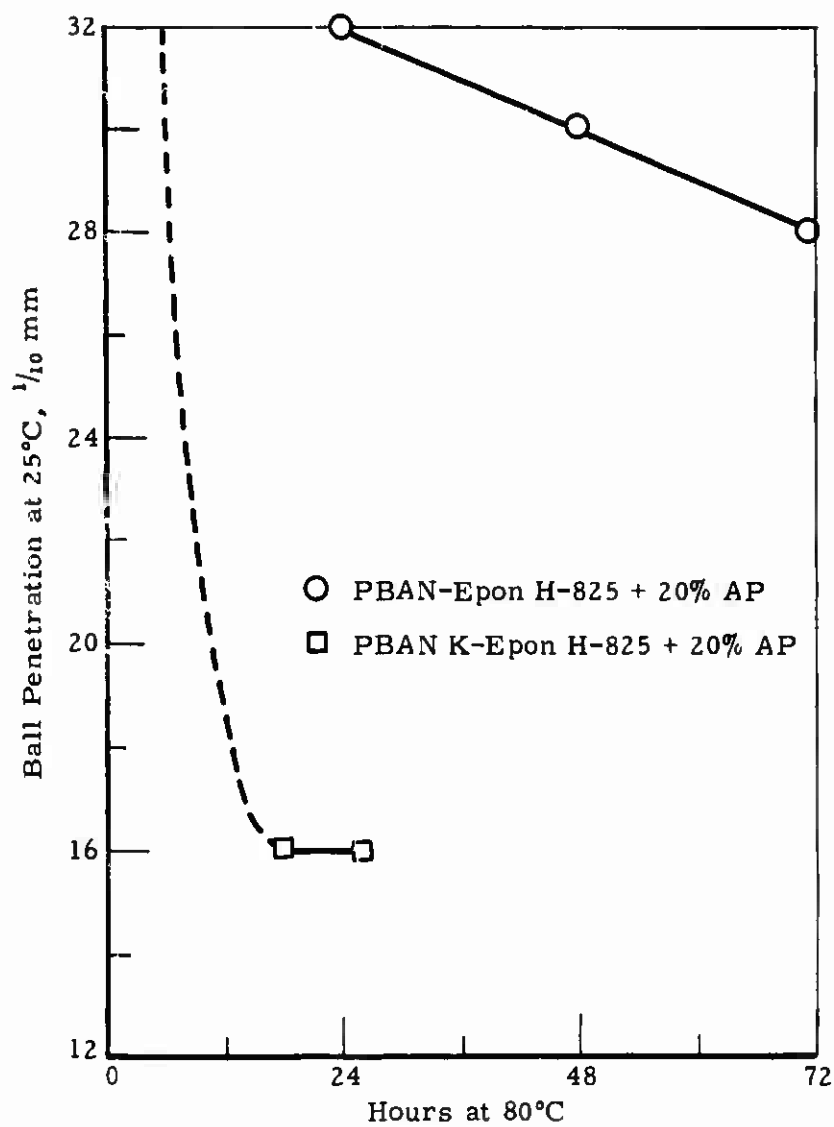
Figure 33. BENEFICIAL EFFECT OF CONVERSION
OF PBAN TO POTASSIUM SALT

a) A mixed methylchlorosilane, Dri Film SC-77.

b) β-(3,4-Epoxycyclohexyl)ethyltrimethoxysilane

c) γ-Chloropropyltrimethoxysilane.

d) γ-Glycidoxypropyltrimethoxysilane.

e) Butylglycidyl ether.

f) Phenylglycidyl ether.

g) Shell MB2TDDP.

h) Octadecylbenzyldimethylammonium chloride (OCTAB).

i) Shell LR 5880-136.

j) Shell LR 5880-17.

One-half percent weight of coating was applied to the AP by adding one gram of a 1%w coating solution in n-pentane (benzene solvent for OCTAB and the Shell LR 5880-17) to two grams of AP. AP plus solution were left in a sealed vial overnight. The solvent was then evaporated off and the coating cured by aging the coated AP for 90 hours at 80°C.

EPON H-825 samples plus 20%w coated AP were aged, with mxing, at 80°C and the epoxy disappearance followed. These data are given in Table XXVI, and the range of epoxy values versis time is illustrated by Figure 34. Our data indicate these coatings had little or no effect on AP/epoxy reactivity when subjected to intimate mixing at 80°C.
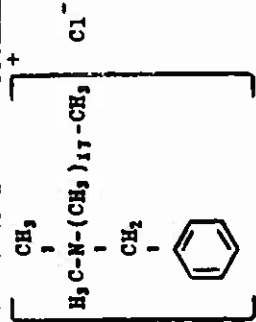
In order to determine whether the coating film was effective but too weak to withstand the shearing forces involved in our test set-up we also tested the Dri-Film SC-77 coated AP in static contact with the resin. The results, see Figure 35, show that in static contact the epcxide consumption rate is lower but still significant.

All epoxide values determined in our evaluation of the treated AP samples discussed in Sections VII, VIII, IX and X are listed in numerical order in Table XXVII and plotted in Figures 34 and 36 to 41 inclusive. Epoxide data on system treated with Shell proprietary compounds discussed in Section XVI are shown in Table XXVIII.

Table XXVI. EFFECT OF VARIOUS COATINGS ON REACTIVITY OF AMMONIUM PERCHLORATE - "EPON" H-825

Run No.	Treating Agent	Structure	Average Epoxide Value After Indicated Hours at 80°C					
			38	120	168	160	183	215
1	General Electric "DRI-FILM" SC 77 (0.35%w)	75% CH_3-Si-Cl_3 25% $(CH_3)_2$-Si-Cl_2	0.555			0.521	0.512	
2	Union Carbide A-186 Silane β-(3,4-Epoxycyclohexyl)ethyl-trimethoxysilane	CH_2-CH_2-Si-$(OCH_3)_3$ (epoxycyclohexyl)	0.550			0.521	0.503	
3	Union Carbide Y-4351 Silane γ-Chloropropyltrimethoxysilane	Cl-CH_2-CH_2-CH_2-Si$(OCH_3)_3$	0.551			0.527	0.513	
4	Dow Corning Z-6040 γ-Glycidoxypropyltrimethoxysilane	CH_2-CH-CH_2-O-$(CH_2)_3$Si$(OCH_3)_3$	0.553			0.530	0.500	
5	Butylglycidyl Ether	CH_2-CH-CH_2-O-$(CH_2)_3$-CH_3				0.526	0.496	
6	Phenylglycidyl Ether	CH_2-CH-CH_2-O- (phenyl)				0.522		
7	Shell MB2	-		0.533	0.526			0.506
8	OCTAB Octadecylbenzyldimethyl-ammonium Chloride	$[H_3C$-N-$(CH_3)_{17}$-$CH_3]^+$ CH_3 / CH_2 (phenyl) Cl^-		0.538	0.519			0.490
9	Shell LR 5880-136	-		0.533	0.527			0.493
10	Shell LR 5080-17	-		0.525	0.514			-
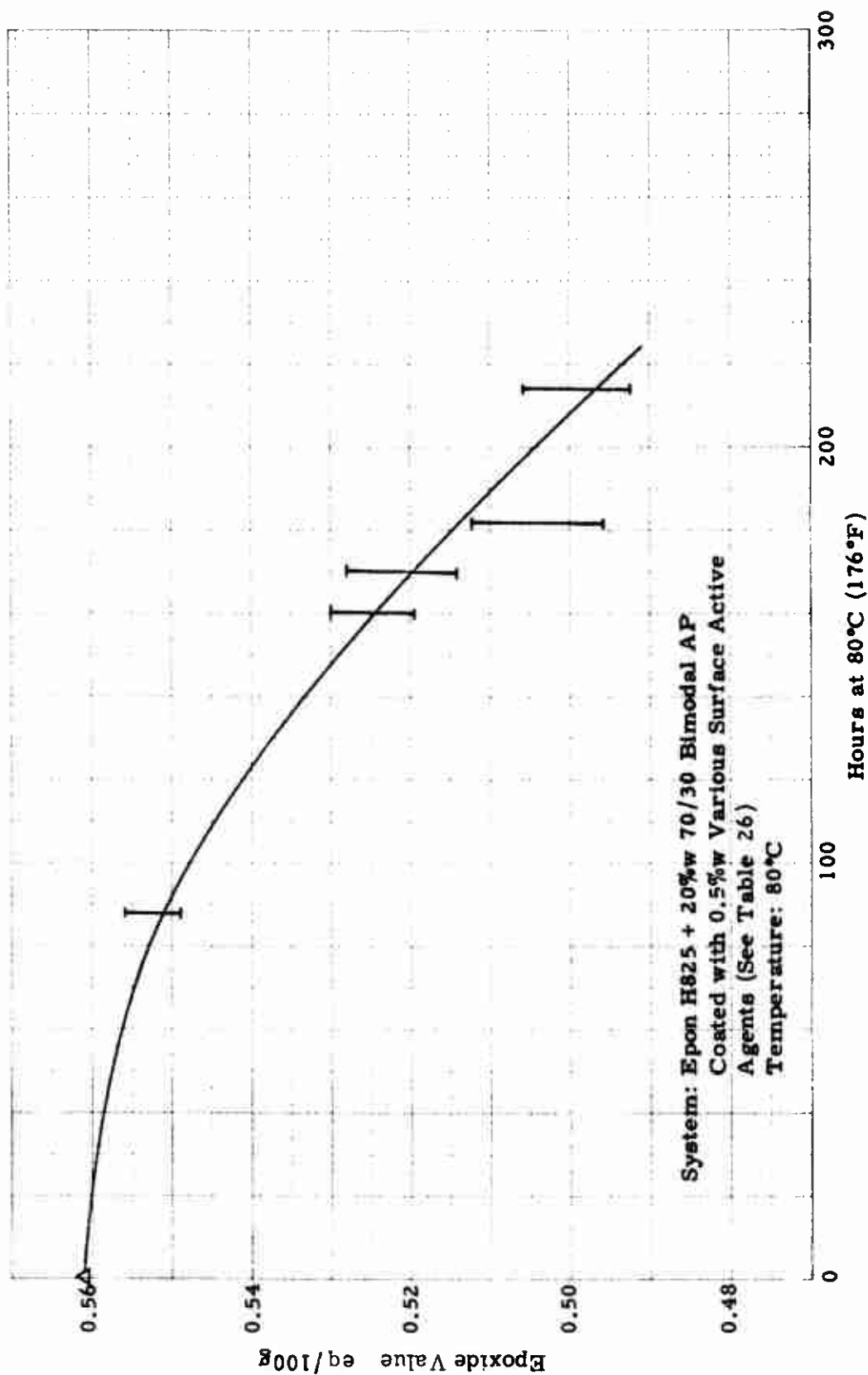
Figure 34. TREATED AMMONIUM PERCHLORATE - EPOXIDE REACTIVITY

System: Epon H825 + 20%w 70/30 Bimodal AP
Coated with 0.5%w Various Surface Active
Agents (See Table 26)
Temperature: 80°C

Hours at 80°C (176°F)

Epoxide Value eq/100g

63641
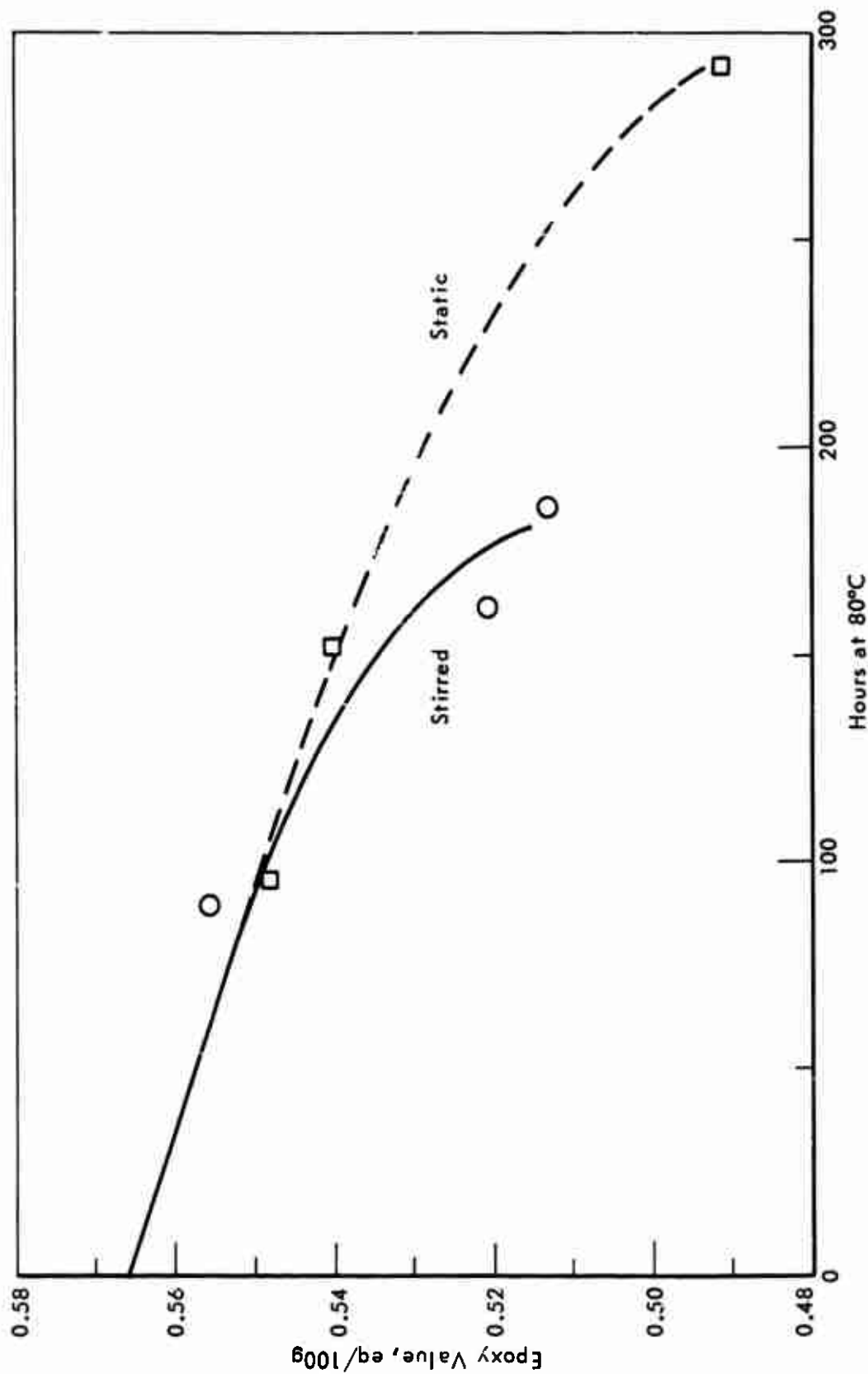
Figure 35. REACTIVITY OF "DRI FILM" 77 TREATED AMMONIUM PERCHLORATE WITH EPON H-825 AT 80°C
Stirred vs Static Contact
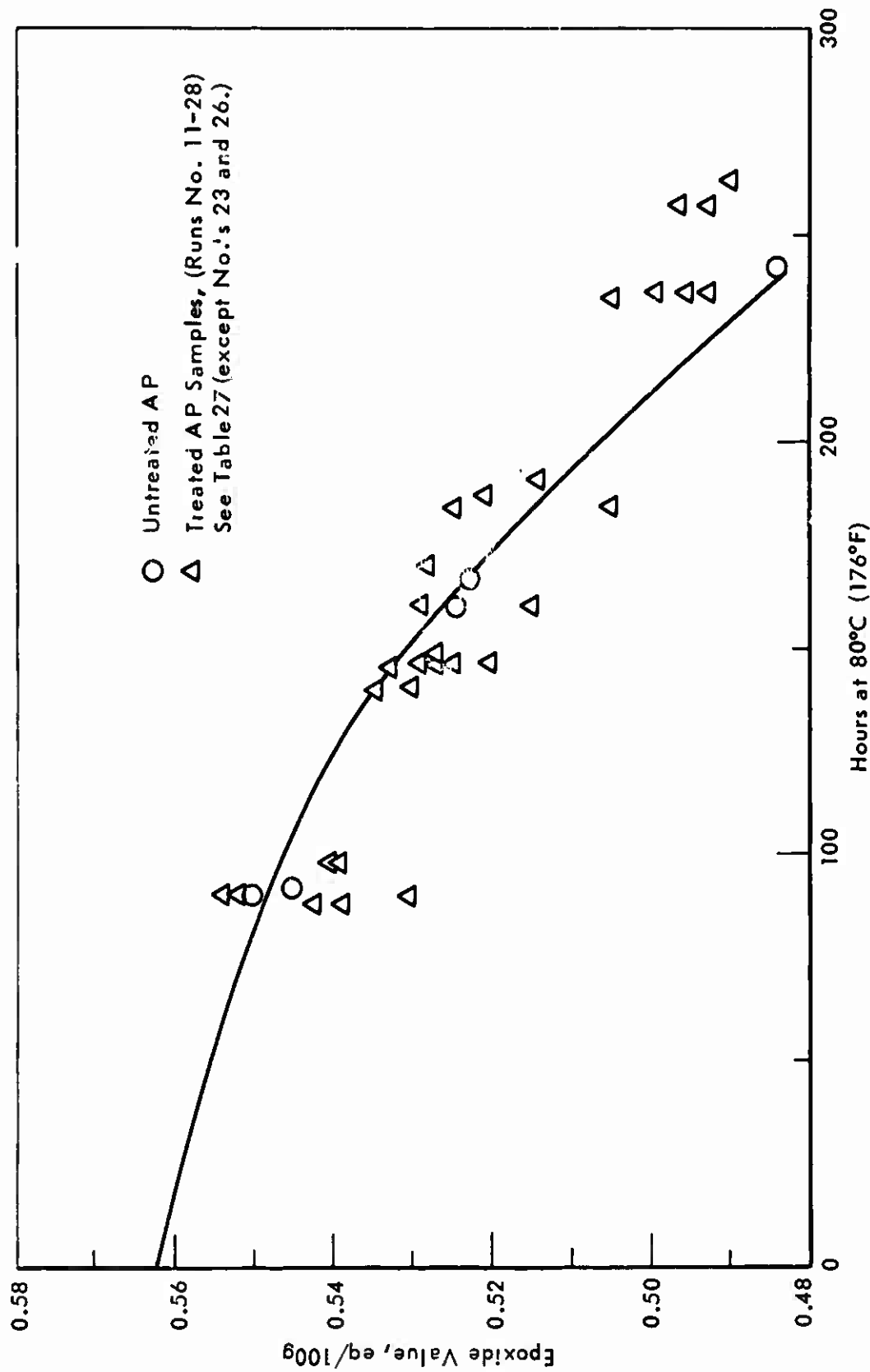
Figure 36. REACTIVITY OF TREATED AMMONIUM PERCHLORATE WITH EPON H-825 AT 80°C

63911
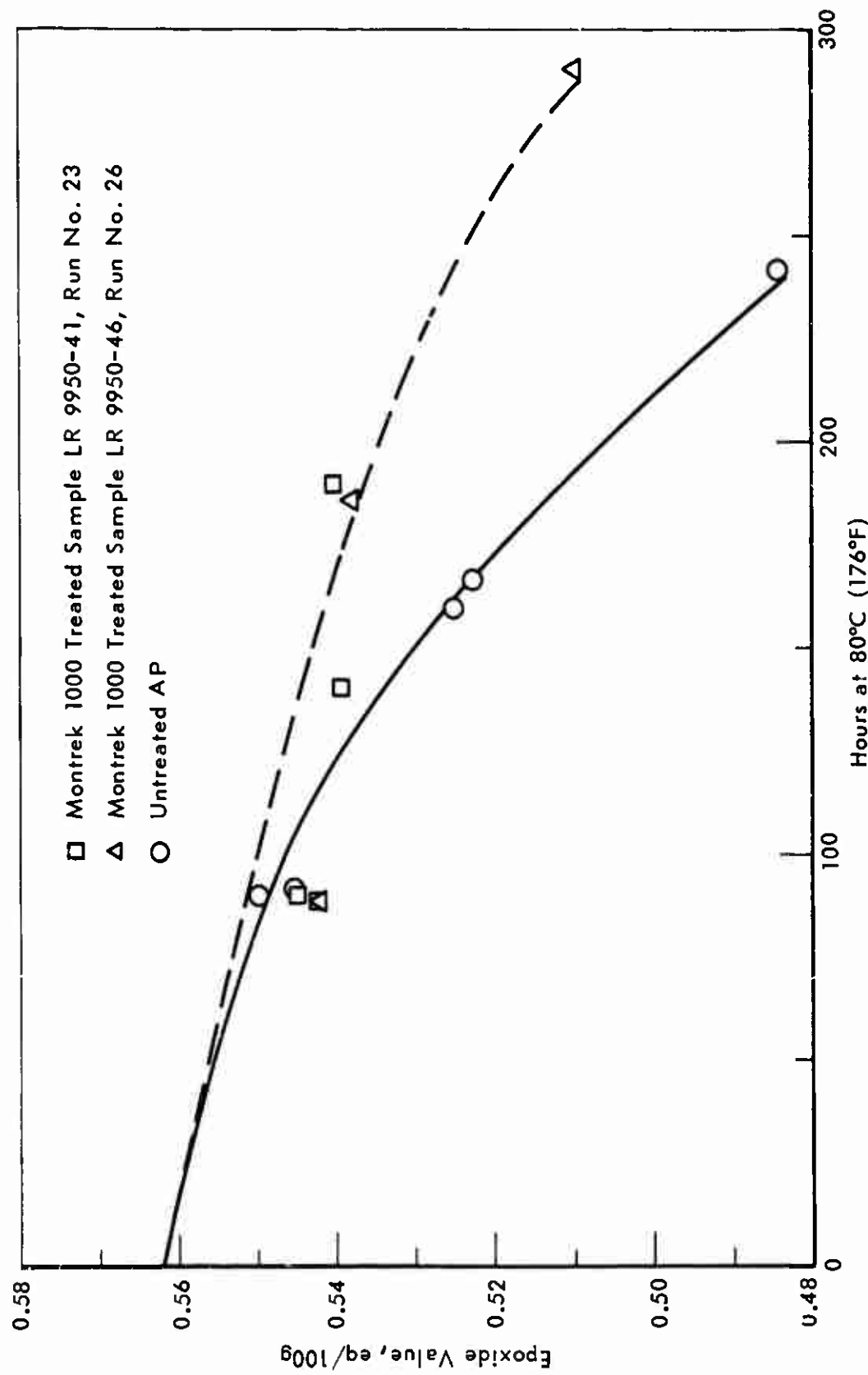
Figure 37. REACTIVITY OF MONTREK 1000 COATED AMMONIUM PERCHLORATE
WITH EPON H-825 AT 80°C

63711
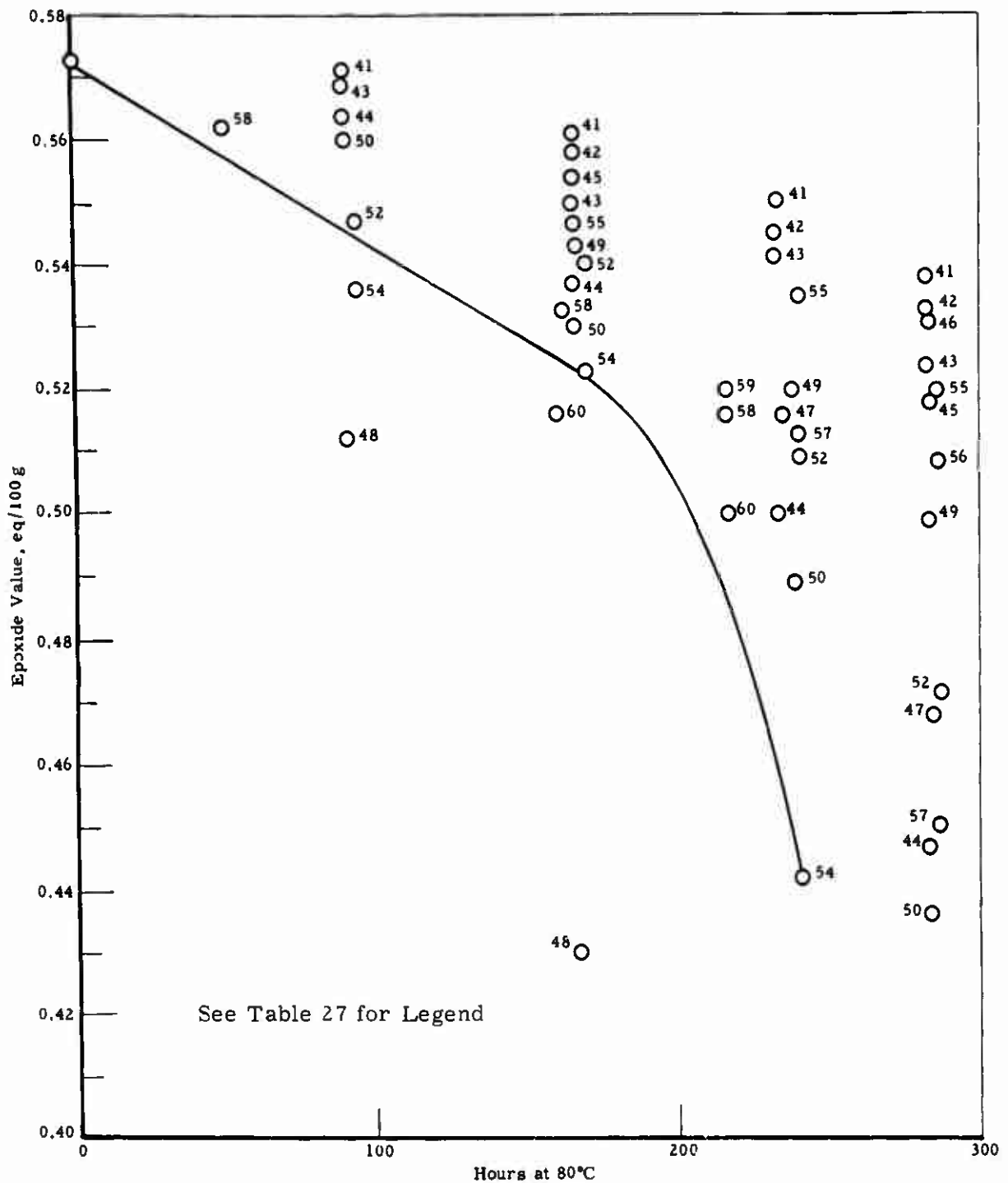
Figure 38. REACTIVITY OF VARIOUS COATED AMMONIUM PERCHLORATE SAMPLES WITH EPON H-825 AT 80°C

63280
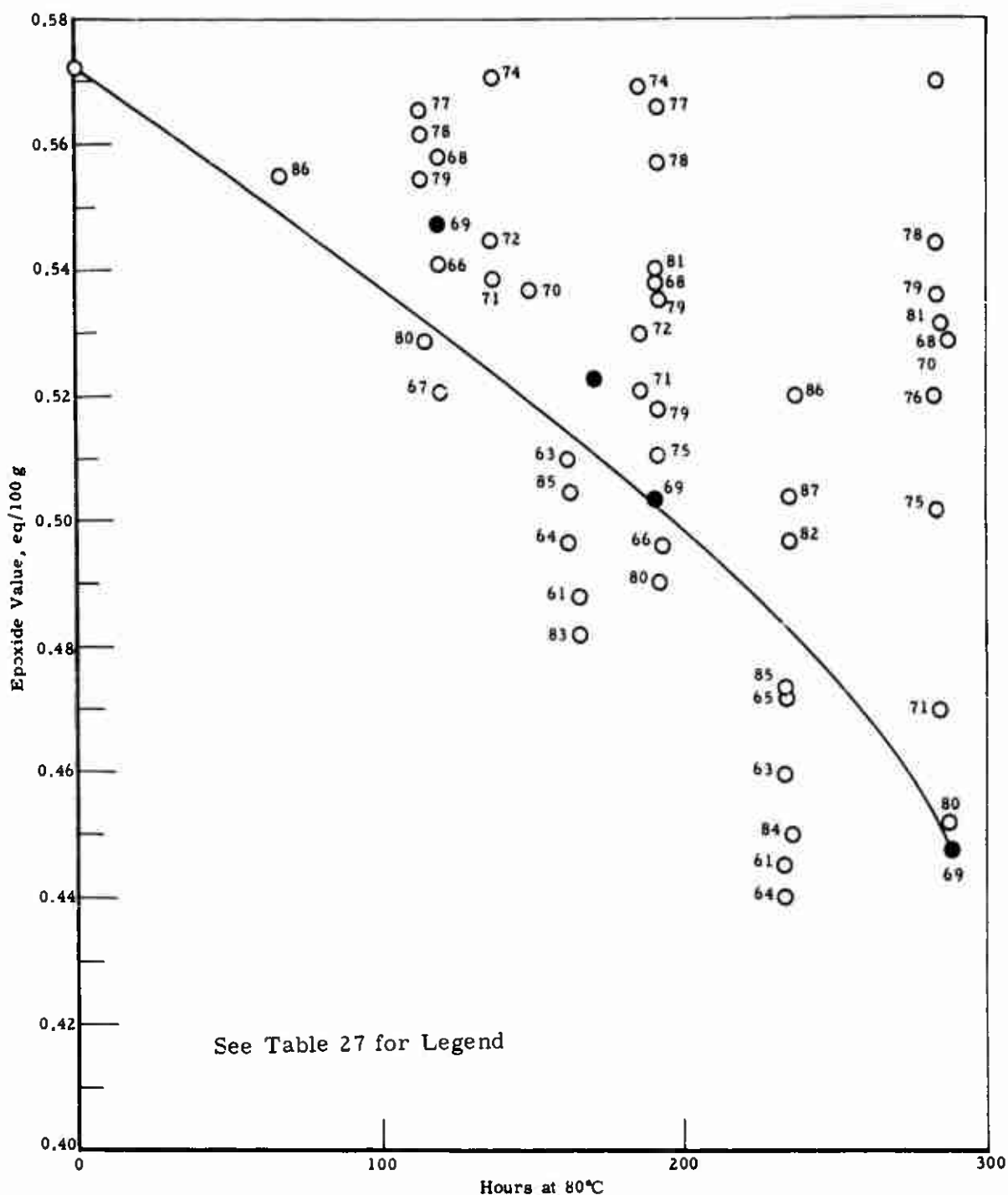
Figure 39. REACTIVITY OF VARIOUS COATED AMMONIUM PERCHLORATE
SAMPLES WITH EPON H-825 AT 80°C

63280
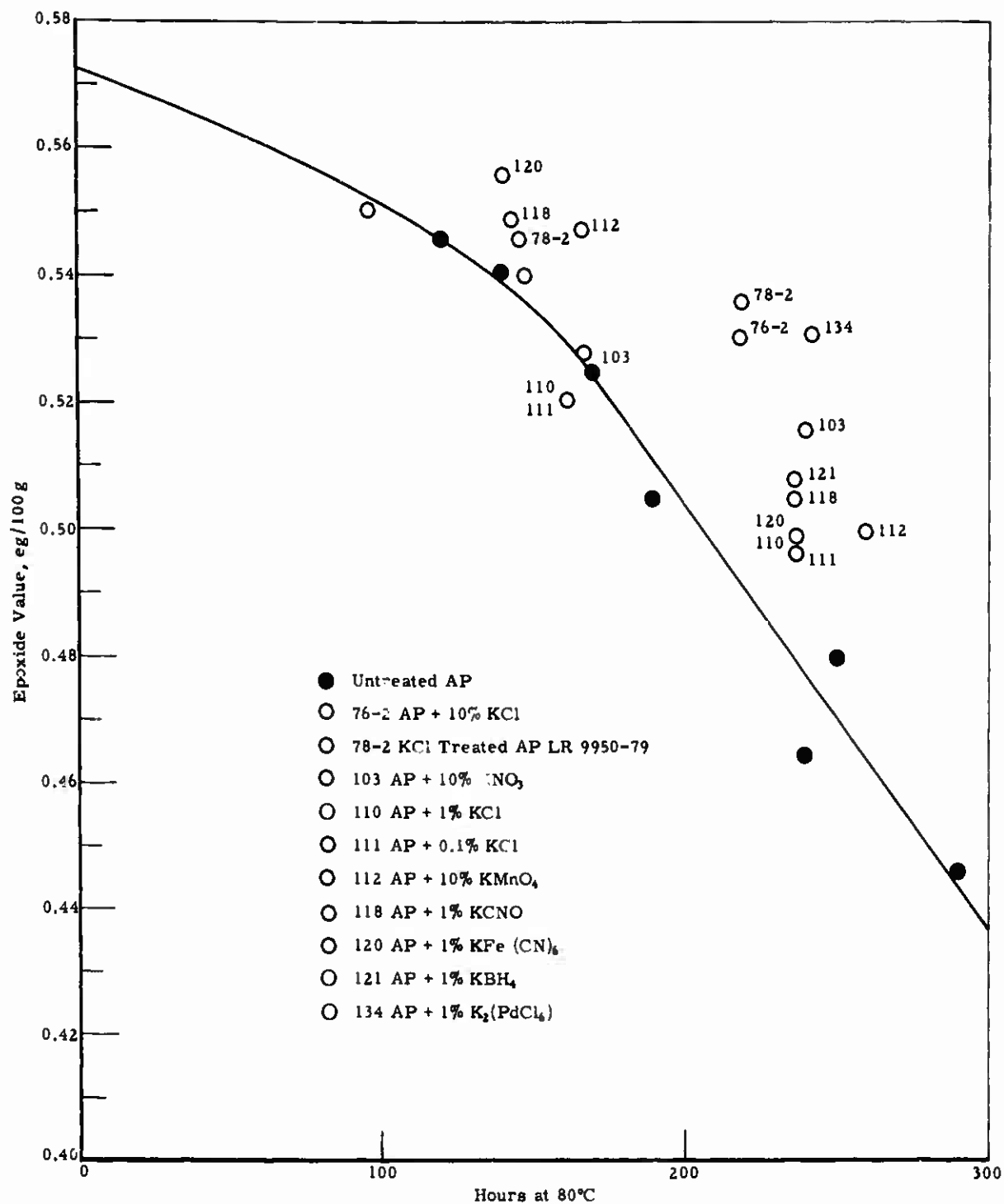
Figure 40. REACTIVITY OF VARIOUS COATED AMMONIUM PERCHLORATE
SAMPLES WITH EPON H-825 AT 80°C

63280
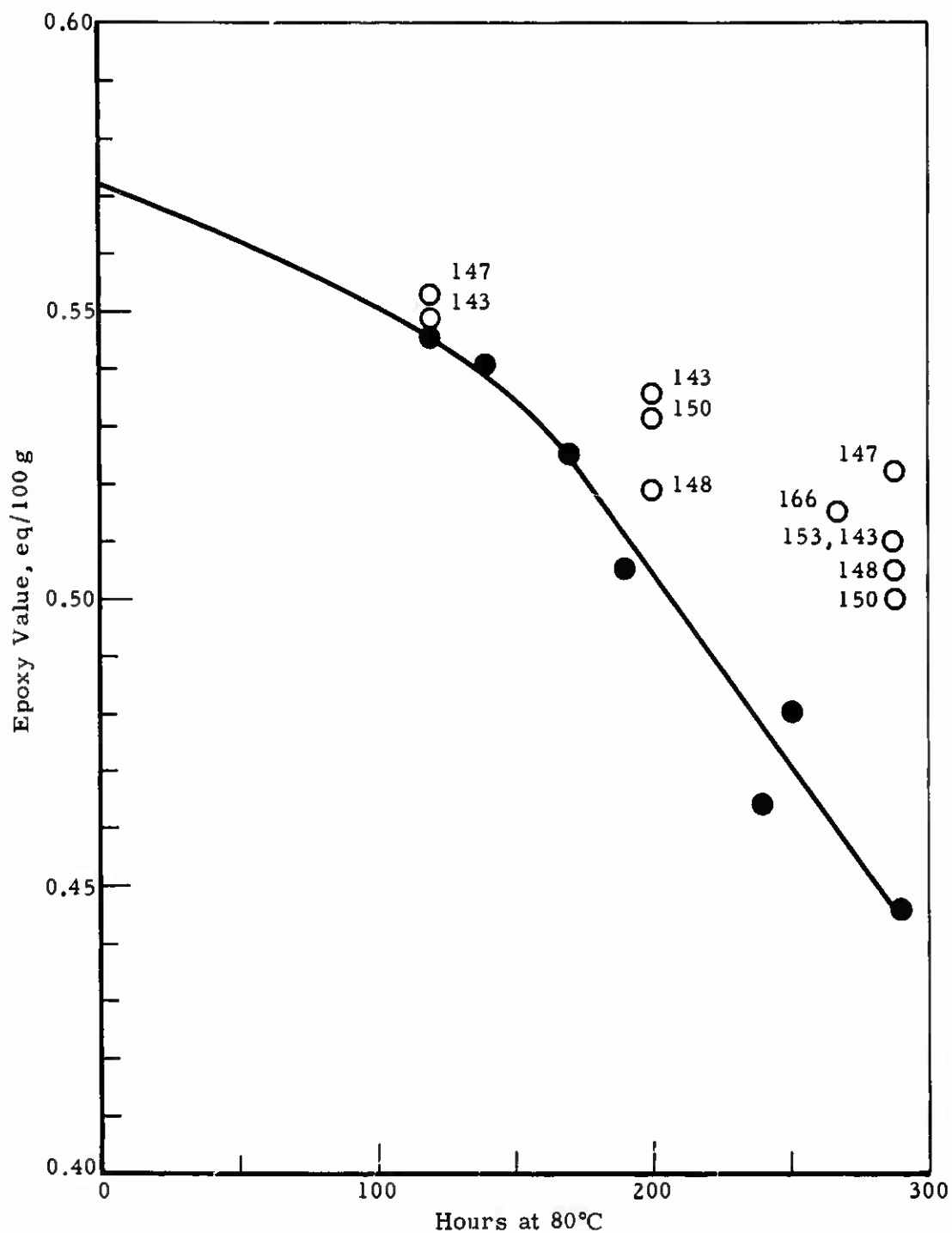
Figure 41. TREATED AP SYSTEMS HAVING REDUCED ACTIVITY
RELATIVE TO UNTREATED CONTROL

63680

Table XXVII. REACTIVITY OF TREATED AMMONIUM PERCHLORATE WITH
"EPON" H-825 AT 80°C (176°F)

SYSTEM: EPON H-825 + 20%w Treated AP, Continuous
agitation.

Coating on AP	Run No.	Epoxy Value, eq/100 g, After (Hours) at 80°C				
Aluminum salt of monobutyl ester of C_{20} phosphonic acid (AlMBE)	11	(89) 0.554	(160) 0.515	(257) 0.497		
Aluminum salt of monobutyl ester of 2-thiadodecycl phosphinic acid (alMB2)	12	(89) 0.553	(160) 0.529	(257) 0.493		
Eicosyl phosphonic acid (EPA)	13	(89) 0.552	(257) 0.432			
Monobutyl ester of eicosyl phosphonic acid (MBE)	14	(89) 0.547	(257) 0.494			
1.5% Alkavinol TK 926 from benzene solution	15	(142) 0.532	(143) 0.530	(190) 0.514		
2.0% Alkavinol TK 926 from heptane	16	(92) 0.530	(142) 0.530	(190) 0.507		
EPON 828 ca 1.5μ. Triple coating from benzene solution. Cured 24 hours at 80°C after each coat.	17	(98) 0.541	(146) 0.529	(235) 0.499		
Diclycidyl ether of hydrogenated bisphenol A ca 1.5μ. Triple coat from n-heptane. Cured 24 hours at 80°C between coats.	18	(98) 0.541	(146) 0.527	(235) 0.495		
Al salt of 2-thiadodecyl phosphonic acid ca 1.5μ. Three coats from benzene solution. Cured 24 hours at 80°C after each coat.	19	(98) 0.539	(146) 0.525	(235) 0.493		
Al salt of eicosyl phosphonic acid ca 1.5%. Three coats from benzene solution. Cured 24 hours at 80°C between each coat.	20	(98) 0.535	(146) 0.533	(235) 0.505		
Montrek 18 from n-butanol solution followed by HCHO vapor treat at 60°C (LR 9950-39F)	21	(88) 0.452	(146) 0.527	(184) 0.525		
Montrek 18 from n-butanol solution	22	(88) 0.539	(146) 0.520	(184) 0.505		

(Continued)

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Table XXVII (Contd-1). REACTIVITY OF TREATED AMMONIUM PERCHLORATE
WITH "EPON" H-825 AT 80°C (176°F)

Coating on AP	Run No.	Epoxy Value, eq/100 g, After (Hours) at 80°C				
Montrek 1000 ex n-butanol LR 9950-41	23	(90) 0.545	(139) 0.540	(187) 0.539		
Alkavinol TK 926 adsorbed from benzene solution	24	(90) 0.547	(139) 0.535	(187) 0.526		
Arquad 18-50 ex benzene	25	(90) 0.464	(139) 0.461	(187) 0.350		
Montrek 1000 (LR 9950-46)	26	(89) 0.542	(185) 0.538	(288) 0.510		
Iodooctane	27	(71) 0.547	(167) 0.528	(263) 0.490		
Cab-O-Sil, 1%	28	(64) 0.554	(160) 0.525			
None	-	(89) 0.550	(92) 0.545	(160) 0.525	(167) 0.523	(241) 0.484
Montrek 1000 + PAGE LR 9950-49	29	(66) 0.559	(168) 0.543	(281) 0.518		
Kemamine Q 1902C	30	(66) 0.555	(168) 0.529	(281) 0.501		
Kemamine T 1902D	31	(101) 0.552	(195) 0.525	(263) 0.475		
Tetraethylpentamine + PAGE	32	(99) 0.546	(195) 0.530	(263) 0.505		
Tetraethylpentamine (adsorbed) LR 9950-51	33	(99) 0.551	(197) 0.543	(263) 0.535		
Ethylenediamine ex n-BuOH	34	(95) Gelled	-	-		
Montrek 1000 ex 0.1% sol. in n-BuOH LR 9950-46C	35	(96) 0.541	(194) 0.515	(263) 0.451		
Montrek 1000 ex 0.5% sol. in n-BuOH	36	(96) 0.533	(194) 0.496	(263) 0.417		

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Table XXVII (Contd-2). REACTIVITY OF TREATED AMMONIUM PERCHLORATE
WITH "EPON" H-825 AT 80°C (176°F)

Coating on AP	Run No.	Epoxy Value, eq/100 g, After (Hours) at 80°C			
Arquad 2C-75	37	(101) 0.532	(195) 0.521	(263) 0.474	
Arquad D18-50	38	(101) 0.524	(195) 0.434	(263) Gelled	
Arquad D12-50	39	(96) 0.551	(195) 0.537	(263) 0.524	
Diethylenetriamine absorbed from 1% BuOH solution LR 9950-55	40	(98) 0.532	(196) 0.474	(263) 0.348	
Montrek-600 ex 1% solution in n-butanol, LR 9950-61C	41	(90) 0.571	(166) 0.561	(233) 0.550	(282) 0.538
Montrek-1000 ex 1% solution in butanol, LR 9950-61E	42	(90) 0.572	(166) 0.558	(233) 0.547	(282) 0.533
Montrek-600 E ex 1% solution in n-butanol, LR 9950-61D	43	(90) 0.569	(166) 0.550	(233) 0.543	(282) 0.524
Montrek-18 ex 1% solution in n-butanol, LR 9950-61B	45	(90) 0.569	(166) 0.554	(234) 0.544	(283) 0.518
Montrek-12 ex 1% solution in n-butanol, LR 9950-61A	46	(90) 0.567	(166) 0.553	(235) 0.543	(283) 0.531
Metaphenylenediamine ex 1% solution in n-butanol, LR 9950-60	47	(90) 0.566	(167) 0.552	(235) 0.516	(283) 0.468
Curing agent U ex 1% solution in n-butanol, LR 9950-58	48	(90) 0.512	(167) 0.430	(238) Gelled	-
Diethylenetriamine ex vapor phase on fluid bed, LR 9950-54	49	(90) 0.564	(167) 0.543	(238) 0.520	(283 0.498

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Table XXVII (Contd-3). REACTIVITY OF TREATED AMMONIUM PERCHLORATE
WITH "EPON" H-825 AT 80°C (176°F)

Coated AP Sample	Run No.	Epoxy Value, eq/100 g, After (Hours) at 80°C			
Menthanediamine ex 1% solution in n-butanol, LR 9950-59	50	(90) 0.560	(167) 0.530	(238) 0.489	(283) 0.436
Lauric acid	51	(94) 0.487	(168) 0.527	(238) 0.491	(285) 0.383
Trimer acid ex 1% solution in n-butanol, LR 9950-62	52	(94) 0.547	(168) 0.541	(239) 0.509	(285) 0.471
Tetra-n-propylammonium iodide	53	(94) 0.465	(168) 0.515	(239) 0.452	(285) 0.337
Uncoated AP control	54	(94) 0.536	(168) 0.523	(239) 0.442	(285) Gelled
Versamid 125 ex 1% solution in n-butanol, LR 9950-66	55	(95) 0.563	(167) 0.547	(239) 0.535	(285) 0.520
Versamid 140 ex 1% solution in n-butanol, LR 9950-67	56	(94) 0.561	(167) 0.546	(239) 0.520	(285) 0.508
Polymethylmethacrylate polymerized in n-butanol, LR 9950-65	57	(95) 0.563	(167) 0.541	(239) 0.513	(285) 0.450
Polystyrene polymerized in n-butanol, LR 9950-64	58	(48) 0.562	(162) 0.533	(216 0.516	-
Polyoxypropylenediamine ex 1% solution in n-butanol, LR 9950-68	59	(48) 0.565	(162) 0.532	(216) 0.520	-
Direction addition of Montrek-1000 (10% on AP) to EPON H-825/AP mix	60	(47) 0.560	(160) 0.516	(216) 0.500	-
Octadecylamine, LR 10139-33	61	(91) 0.545	(162) 0.488	(233) 0.445	(306) 0.349
Dodecyltrimethylammonium chloride, 50% active, LR 10139-29(Arquad 12-50)	62	(91) 0.475	(162) 0.390	(233) Gelled	-
Dodecylamine, LR 10139-30	63	(91 0.553	(162) 0.510	(233) 0.459	(307) 0.352
Stearic acid, LR 10139-31	64	(91) 0.558	(162) 0.497	(233) 0.440	(307) 0.362

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Table XXVII (Contd-4). REACTIVITY OF TREATED AMMONIUM PERCHLORATE
WITH "EPON" H-825 AT 80°C (176°F)

Coated AP Sample	Run No.	Epoxy Value, eq/100 g, After (Hours) at 80°C			
Hexadecylamine, LR 10139-31	65	(92) 0.559	(162) 0.522	(234) 0.474	(307) 0.390
Methylamine ex 0.4% sol. in n-BuOH, LR 9950-71	66	(120) 0.541	(191) 0.496	(288) 0.455	-
Methylamine ex vapor phase on fluid bed, LR 9950-72	67	(120) 0.520	(191) 0.464	(288) Gelled	-
Rubidium chloride, AP passed through RbCl sol., LR 9950-70	68	(120) 0.558	(191) 0.538	(288) 0.528	-
Control uncoated AP	69	(120) 0.547	(191) 0.503	(288) 0.447	-
"In situ" RbCl, 10 g EPON H-825, 2 g AP, 0.2 g RbCl	70	(120) 0.554	(143) 0.535	(288) 0.528	-
Formamide treated AP, LR 9950-75	71	(138) 0.538	(186) 0.521	(284) 0.470	-
Urea treated AP, LR 9950-74	72	(138) 0.544	(186) 0.529	(0.284) 0.479	-
AP passed through KCl LR 9950-70	73	(138) 0.467	(185) 0.430	(284) Gelled	-
KClO$_4$, LR 9950-77	74	(138) 0.570	(186) 0.569	(284) 0.571	-
10 g EPON H-825, 2 g untreated AP, 1 g KCl	75	(138) 0.524	(192) 0.510	(283) 0.503	-
10 g EPON H-825, 2 g untreated AP, 0.2 g KCl	76	(138) 0.530	(192) 0.506	(283) 0.519	-
No ammonium perchlorate EPON H-825 + 20% KClO$_4$	77	(114) 0.566	(192) 0.566	(283) 0.571	-
KCl treated AP, LR 9950-79	78	(114) 0.562	(192) 0.556	(283) 0.544	-
AP treated with RbCl, LR 9950-80	79	(115) 0.555	(192) 0.535	(283) 0.536	-

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Table XXVII (Contd-5). REACTIVITY OF TREATED AMMONIUM PERCHLORATE
WITH "EPON" H-825 AT 80°C (176°F)

Coated AP Sample	Run No.	Epoxy Value, eq/100 g, After (Hours) at 80°C			
AP treated with CsCl, LR 9950-81	80	(115) 0.527	(192) 0.490	(283) 0.452	-
"In situ" CsCl, 10 g EPON H-825, 2 g untreated AP, 0.2 g CsCl	81	(115) 0.558	(192) 0.539	(285) 0.531	-
Dri-film SC 77 ex vapor phase, LR 9950-73	82	(67) 0.561	(163) 0.519	(235) 0.497	-
AP + Montrek 12 ex 0.5% sol. in n-BuOH, LR 9950-82A	83	(67) 0.544	(163) 0.482	(235) 0.443	-
AP + Montrek 18 ex 0.5% sol. in n-BuOH, LR 9950-82B	84	(67) 0.547	(163) 0.483	(237) 0.450	-
AP + Montrek 600 ex 0.5% sol. in n-BuOH, LR 9950-82C	85	(67) 0.556	(163) 0.505	(237) 0.472	-
AP + Montrek 600 E ex 0.5% sol. in n-BuOH, LR 9950-82D	86	(67) 0.555	-	(237) 0.520	-
AP + Montrek 1000 ex 0.5% sol. in n-BuOH	87	(67) 0.558	(163) 0.535	(237) 0.504	-
Dodecylamine ex n-octanol	88	(67) 0.515	(163) 0.435	(237) 0.425	-
Montrek 600 E ex 0.25% sol. in n-BuOH, LR 9950-85D	89	(66) 0.510	(138) 0.410	(186) Gelled	-
Montrek 600 ex 0.25% sol. in n-BuOH, LR 9950-85C	90	(66) 0.519	(138) 0.410	(186) Gelled	-
Montrek 18 ex 0.25% sol. in n-BuOH, LR 9950-85B	91	(66) 0.470	(138) Gelled	-	-
Sebacylchloride	92	(66) 0.407	(138) Gelled	-	-
Montrek 100 ex 0.25% sol. in n-BuOH, LR 9950-85E	93	(66) 0.495	(138) 0.457	(186) Gelled	-
Montrek 12 ex 0.25% sol. in n-BuOH, LR 9950-85A	94	(66) 0.488	(138) Gelled	-	-

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Table XXVII (Contd-6). REACTIVITY OF TREATED AMMONIUM PERCHLORATE
WITH "EPON" H-825 AT 80°C (176°F)

Coated AP Sample	Run No.	Epoxy value, eq/100 g, After (Hours) at 80°C			
Hexamethylenediamine treated	95	(90) 0.475	(138) 0.433	(186) 0.418	-
Nylon coated	96	(90) 0.453	(138) 0.434	(186) 0.425	-
NaCH treated	97	(90) 0.518	(138) 0.458	(186) 0.443	-
No ammonium perchlorate EPON H-825 + 20%w KCl	98	(90) 0.574	-	(233) 0.573	-
No ammonium perchlorate EPON H-825 + 20%w CsCl	99	(72) 0.573	(144) 0.573	(318) 0.567	-
No ammonium perchlorate EPON H-825 + 20%w RbCl	100	(72) 0.573	(144) 0.573	(318) 0.571	-
AP + K$_2$SO$_4$ (10%)	101	(96.5) 0.533	(163) 0.500	(236) 0.480	-
AP passed through KCl solution, LR 9950-76	73-2	(90) 0.544	(161) 0.506	(233) 0.438	-
AP + K acetate (10%)	102	(96.5) Gelled	-	-	-
AP + K nitrate (10%)	103	(96.5) 0.551	(163) 0.527	(236) 0.516	-
AP + Na phenoxide (10%)	104	(96.5) Gelled	-	-	-
AP + K oxalate (10%)	105	(96.5) 0.547	(163) 0.523	(236) 0.501	-
AP + K$_2$ Cr$_2$O$_7$ (10%)	106	(96.5) 0.492	(163) 0.418	(236) Gelled	-
AP + K phthalimide (10%)	107	(96.5) 0.450	(163) Gelled	-	-
AP + KMnO$_4$ (10%)	108	(96.5) 0.540	(163) 0.520	(236) 0.502	-
AP + K oleate	109	(96.5) 0.413	(163) Gelled	-	-

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Table XXVII (Contd-7). REACTIVITY OF TREATED AMMONIUM PERCHLORATE
WITH "EPON" H-825 AT 80°C (176°F)

Coated AP Sample	Run No.	Epoxy Value, eq/100 g, After (Hours) at 80°C			
AP + KCl (1%)	110	(98.5) 0.566	(163) 0.521	(236) 0.499	-
AP + KCl (0.1%)	111	(98.5) 0.568	(163) 0.521	(236) 0.496	-
KCl treated AP, LR 9950-79	78-2	(77.5) 0.550	(145.5) 0.546	(218) 0.536	-
AP + KCl (10%)	76-2	(77.5) 0.516	(146) 0.540	(218) 0.530	-
AP + KMnO$_4$, <60 mesh (10%, LR 9950-86C	112	(95.5) 0.560	(165.5) 0.547	(261) 0.600	-
AP + KIO$_4$ (10%), LR 9950-86B	113	(95.5) 0.533	(165.5) 0.497	(261) 0.385	-
AP + KIO$_3$ (10%)	114	(95.5) 0.557	(170) 0.505	(261) 0.465	-
AP + NH$_4$BF$_4$ (10%)	115	(95.5) 0.500	(166) 0.426	(261) Gelled	-
AP + guanidine carbonate (10%), LR 9950-87A	116	(95.5) Gelled	-	-	-
AP + KBF$_4$ (1%)	117	(71) 0.560	(141) 0.529	(236) 0.478	-
AP + KCNO (1%)	118	(71) 0.555	(142) 0.548	(236) 0.505	-
AP + KClO$_3$ (1%)	119	(71) 0.560	(142) 0.536	(238) 0.443	-
AP + K$_4$Fe(CN)$_6$ (1%)	120	(71) 0.568	(14.2) 0.556	(238) 0.498	-
AP + KBH$_4$ (1%)	121	(72) 0.564	(144) 0.547	(238) 0.507	-
AP + KClO$_4$ (1%)	122	(122) 0.535	(216) 0.504	(292) 0.475	-

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Table XXVII (Contd-8). REACTIVITY OF TREATED AMMONIUM PERCHLORATE
WITH "EPON" H-825 AT 80°C (176°F)

Coated AP Sample	Run No.	Epoxy Value, eq/100 g, After (Hours) at 80°C			
AP + KNO$_3$ (10%)	103-2	(73.5) 0.564	(145) 0.539	(240) 0.457	-
AP + KCl (0.1%)	111-2	(73.5) 0.565	(145) 0.543	(240) 0.463	-
Ethyleneimine treated AP (vapor phase), LR 9950-92	123	(124) 0.551	(216) 0.520	(293) 0.482	-
AP + NH$_4$Ac (1%), LR 9950-91A	124	(124) 0.443	(218) 0.431	(286) Gelled	-
AP + (NH$_4$)$_2$CrO$_4$ (1%), LR 9950-91B	125	(124) 0.421	(219) Gelled	-	-
AP + NH$_4$F (1%), LR 9950-91C	126	(124) 0.547	(218) 0.519	(286) 0.499	-
AP + (NH$_4$)$_2$MoO$_4$ (1%), LR 9950-91D	127	(124) 0.545	(218) 0.501	(286) 0.441	-
AP + NH$_4$I (1%), LR 9950-91E	128	(124) 0.534	(218 0.497	(286) 0.465	-
Ethyleneimine treated AP LR 9950-94	129	(77) 0.556	(168) 0.526	(239) 0.461	-
Montrek 12 treated AP, dried at room temperature, LR 9950-93A	130	(77) 0.540	(168) 0.482	(239) Gelled	-
Montrek 12 treated AP, dried at 60°C, LR 9950-93B	131	(94) 0.517	(168) 0.485	(239) 0.380	-
Montrek 12 treated AP, dried at 100°C, LR 9950-93C	132	(94) 0.435	(168) Gelled	-	-
AP + K$_4$IrCl$_6$ (1%), LR 9950-86J	133	(77) 0.556	(167) 0.518	(240) 0.464	-
AP + K$_2$PdCl$_6$ (1%)	134	(77) 0.560	(167) 0.528	(240) 0.532	-
Control, uncoated AP	C-1	(144) 0.541	(331) 0.425	-	-

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Table XXVII (Contd-9). REACTIVITY OF TREATED AMMONIUM PERCHLORATE
WITH "EPON" H-825 AT 80°C (176°F)

Coated AP Samples	Run No.	Epoxy Value, eq/100 g, After (Hours) at 80°C		
AP + K Naphthenate (1%)	135	(67) 0.541	(140) 0.511	(212) 0.490
AP + K pyroantimonate K Sb(OH)$_6$ 1/2 H$_2$O (1%)	136	(116) 0.533	(188) 0.540	(288) 0.491
AP + KOH (1%)	137	(115) 0.518	(188) 0.508	(288) 0.454
AP + Montrek 600 ex 0.1% sol. in BuOH LR 9950-97B	142	(120) 0.529	(197) 0.516	(288) 0.481
AP + Montrek 600 ex 0.2% sol. in BuOH LR 9950-98B	143	(120) 0.547	(197) 0.536	(288) 0.510
AP + Montrek 600 ex 0.05% sol. in BuOH LR 9950-96B	144	(120) 0.536	(197) 0.523	(288) 0.482
AP + Montrek 1000 ex 0.05% sol. in BuOH LR 9950-96D	145	(120) 0.539	(197) 0.522	(288) 0.476
AP + Montrek 1000 ex 0.1% sol. in BuOH LR 9950-97D	146	(120) 0.536	(197) 0.515	(288) 0.464
AP + Montrek 1000 ex BuOH Sol. LR 9950-98D	147	(120) 0.553	(197) 0.541	(288) 0.522
AP + Montrek 600 E ex 0.05% sol. in BuOH LR 9950-96C	148	(120) 0.544	(197) 0.519	(288) 0.505
AP + Montrek 600 E ex 0.2% sol. in BuOH LR 9950-97C	149	(120) 0.517	(197) 0.468	(288) gelled
AP + Montrek 600 E ex 0.2% sol. in BuOH LR 9950-98C	150	(121) 0.549	(197) 0.532	(288) 0.500
AP + Montrek 12 ex 0.05% sol. in BuOH LR 9950-96A	151	(121) 0.554	(197) 0.532	(288) 0.490

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Table XXVII (Contd-10).   REACTIVITY OF TREATED AMMONIUM PERCHLORATE
WITH "EPON" H-825 AT 80°C (176°F)

Coated AP Samples	Run No.	Epoxy Value, eq/100 g, After (Hours) at 80°C		
AP + Montrek 12 ex 0.10% sol. in BuOH LR 9950-97A	152	(121) 0.537	(197) 0.449	(289) 0.445
AP + Montrek 12 ex 0.2% sol. in BuOH LR 9950-98A	153	(121) 0.554	-	(289) 0.512
AP + NEODOL 3P ex 0.1% sol. in BuOH LR 9950-99	154	(121) 0.544	-	(288) 0.446
AP + KNO$_3$ (1%)	157	(145) 0.529	(216) 0.500	(317) 0.446
AP + KMnO$_4$ (1%)	159	(145) 0.534	(216) 0.508	(317) 0.458
AP + RbCl (1%)	160	(145) 0.536	(216) 0.505	(312) 0.460
AP + CsCl (1%)	161	(148) 0.536	(221) 0.497	(317) 0.440
AP + Versamid 125 ex 0.3% sol in BuOH LR 9950-101A	162	(96) 0.525	(167) 0.501	(265) 0.454
K Salt of disproportionated wood rosin acid resin 731-D LR 9950-103	163	(96) 0.443	(164) 0.430	(265) 0.394
AP + 1% DTA deposited ex vapor on fluid bed	164	(96) 0.545	(164) 0.495	(259) 0.44
AP + Versamid 140 ex 0.2% sol. in BuOH LR 9950-101B	165	(96) 0.534	(164) 0.498	(265) 0.451
AP + NEODOL 25-3P (1%) LR 9950-104	166	(96) 0.549	(167) 0.527	(265) 0.515

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Table XXVII (Contd-11). REACTIVITY OF TREATED AMMONIUM PERCHLORATE
WITH "EPON" H-825 AT 80°C (176°F)

AP Sample	Run No.	Epoxy Value, eq/100 g, After (Hours) at 80°C		
NEODOL 25-P (1% on AP) LR 9950-106	167	(120) 0.554	(213) 0.537	(280) 0.520
Coated AP LR 9950-97D + 1% KFe(CN)$_6$	168	(114) 0.560	(213) 0.554	(280) 0.533
Coated AP LR 9950-97D + 1% KCNO	169	) 0.554	(213) 0.543	(280) 0.527
Coated AP LR 9950-97D + 1% K$_2$(PdCl$_6$)	170	(120) 0.551	(213) 0.548	(280) 0.526
Coated AP LR 9950-97B + 1% KCl	171	(165) 0.554	(232) 0.538	(305) 0.514
Coated AP LR 9950-97B + 1% NH$_4$F	172	(114) 0.555	(213) 0.545	(280) 0.537
Coated AP LR 9950-97B + 1% KBH$_4$	173	(120) 0.560	(213) 0.550	(280) 0.540
Coated AP LR 9950-97C + 1% KFe(CN)$_6$	174	(118) 0.546	(?13) 0.532	(280) 0.513
Coated AP LR 9950-97C + 1% KCl	175	(165) 0.500	(232) 0.458	(305) 0.365
Coated AP LR 9950-97C + 1% NH$_4$F	176	(213) 0.547	(282) 0.535	(353) 0.508
Arquad 2HT-75	199	(96) 0.542	(195) 0.490	(263 0.441
Arquad 16-50	200	(71) 0.543	(114) 0.442	
Aerosil R972	201	(71) 0.567	(114) 0.541	

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Table XXVIII. EVALUATION OF PROPRIETARY COMPOUNDS AS ADDITIVES FOR
REDUCTION OF ATTACK OF AMMONIUM PERCHLORATE ON
EPXOY GROUPS IN "EPON" H-825

System: EPON H-825 + 10 w AP

Additive, 1% Basis AP	Run No.	Epoxide Value After (hrs) at 80°C			% Of Initial Epoxy Retained
NEODOL 25-3-P LR 9950-104	166	(96) 0.549	(167) 0.527	(265) 0.515	(265) 89.9
Potassium Petroleum Sulfonate LR 9950-105-8	178-2		(190) 0.543	(328) 0.447	(328) 78.1
NEODOL 25-P LR 9950-106	167	(120) 0.554	(213) 0.537	(280) 0.520	(280) 90.8
VERSATIC 911-P LR 9950-108	180	(164) 0.558	(265) 0.520	(400) 0.477	(265) 90.8
SPAK N-C_{15} LR 9950-110-A	181	(161) 0.552	(262) 0.517		(262) 90.4
SPAKN-C_{12} LR 9950-110-B	182	(161) 0.554	(262) 0.520	(400) 0.467	(262) 90.8
SPAKI-C_{12} LR 9950-110-C	184	(161) 0.559	(262) 0.534	(400) 0.475	(262) 93.2
SPAKI-C_{15} LR 9950-110-D	183	(161) 0.551	(262) 0.499		(262) 87.1
KNABL-Potassium salt of naphthenic acid bottoms of lube crude LR 9950-112	185	(194) 0.519	(282) 0.482	(308) 0.415	(282) 84.0
K-Pivalate LR 9950-113	186	(194) 0.536	(282) 0.512	(308) 0.489	(282) 89.4
K-TBBA LR 9950-114	187	(194) 0.534	(282) 0.507	(308) 0.493	(282) 88.4
K salt of eicosyl phosphonic acid LR 9950-116-A	191	(189) 0.530	(264) 0.522	(309) 0.474	(264) 9.18

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Table XXVIII (Contd). EVALUATION OF PROPRIETARY COMPOUNDS AS ADDITIVES FOR REDUCTION OF ATTACK OF AMMONIUM PERCHLORATE ON EPOXY GROUPS IN "EPON" H-825

Additive, 1% Basis AP	Run No.	Epoxide Value After (hrs) at 80°C			% Of Initial Epoxy Retained
K salt of monobutyl ester of eicosyl LR 9950-116-A	191	(189) 0.530	(264) 0.522	(309) 0.474	(264) 91.8
K salt of monobutyl ester of 2-thiadodecylphosphonic acid LR 9950-117-A)	194	(189) 0.499	(264) 0.495	(309) 0.453	(264) 86.4
Di K salt of 4,7,10,13,16-pentaoxa-18-hydroxyoctadecylphosphonic acid LR 9950-117-B	195	(169) 0.529	(243) 0.516	(290) 0.492	(290) 85.8
K salt of monomethyl ester of 4,7,10,13,16-pentaoxa-18-hydroxy-octadecylphosphonic acid LR 9950-118-A	196	(169) 0.506	(243) 0.488	(290) 0.45^	(290) 78.5
Di K salt of 4,7,10,13,16,19,22,25 28,31-decaoxa-33-hydroxytriatria-contylphosphonic acid LR 9950-118-B	197	(169) 0.530	(243) 0.518	(290) 0.484	(290) 84.3
K salt of monomethyl ester of 4,7,10,13,16,19,22125,28,31-deca-oxa-33-hydroxytriatraicontyl-phosphonic acid LR 9950-119-A	198	(169) 0.511	(243) 0.495	(290) 0.450	(290) 78.5
Potassium Petroleum Sulfonate, 10% basis AP LR 9950-105-8)	177-2	(190) 0.554	(328) 0.533		(328) 93.9
No Additive		(150) 0.533	(250) 0.473	(300) 0.438	(300) 76.4

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SECTION XIX

EFFECT OF POLYIMINE COATING PLUS K SALT
ADDITION ON AP REACTIVITY TOWARD "EPON" H-825

In order to explore the effect of a combination of polyimine coating and potassium salt addition, three Montrek coated AP samples were tested in combination with 1%w (basis AP) potassium salt. One run using NH_4F with Montrek treated AP was also included.

Coated AP samples used were:

1. LR 9950-97B (0.63%w Montrek 600)

2. LR 9950-97C (0.50%w Montrek 600E)

3. LR 9950-97D (0.95%w Montrek 1000)

Our data from this series of experiments are summarized in Table XXIX where we have tabulated, for comparable times at 80°C, the percent original epoxide retained when the salts were added to the coated AP and the same salt added to untreated AP in dynamic contact with EPON H-825.

Although the over-all percent epoxide retention values are greater for the coating-salt combinations, the relative efficacy of the added salts is essentially equivalent. Addition of these salts to uncoated AP reduces epoxide loss an average of 50% (11 vs 22%). For the polyimine coated AP, the reduction of epoxide loss averages 41% (7 vs 17%).

Table XXIX. EFFECT OF COMBINED POLYIMINE COATING AND POTASSIUM OR AMMONIUM ION ADDITION ON REACTION RATE OF AP WITH "EPON" H-825 AT 80°C

Polyimine Coated AP		Salt Added; 1%w on AP	Uncoated AP	
Run No.	% Original Epoxide Retained After 286 hrs at 80°C		% Original Epoxide Retained After 286 hrs at 80°C	Run No.
168	92	$K_4Fe(CN)_6$	92	120-2
169	92	KCNO	85	118
170	95	$K_2(PdCl_6)$	90	134-2
171	91	KCl	85	110
172	94	NH_4F	97	126
173	94	KBH_4	81	117
142 & 146	84 & 81	None	78	-

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SECTION XX

ASSESSMENT OF CURE BY BALL PENETRATION

A.   PBAN 703-EPON H-825

Since hardness measurements have long been used in thermoset resin technology as a simple, fast and effective indication of rate and extent of cure or crosslinking, we explored the use of Ball hardness as a measure of rate and extent of binder cure both neat and in the presence of AP.

Ball hardness is a test commonly used in sealant technology and is simply the measure of penetration, in 1/10 mm's, of a 0.66" diameter ball into the sample in 5 seconds at 77°F. Total weight of ball and shaft is 125 grams.

For our tests we used the lid from a four ounce seamless tin box as our sample container (60 mm diameter by 11 mm deep). Figure 42 is a photograph of a sample in position for test using a Penetrometer equipped with an automatic timer.

About 20 grams of the thoroughly blended sample (complete dispersion is particularly important with samples containing oxidizers) were poured into the tin lids, placed in an 80°C oven to cure and at selected intervals the samples were removed from the oven, cooled to room temperature, placed in a 25°C bath for thirty minutes and then the penetration value determined. Samples were then dried and returned to the 80°C oven for continued cure. This cycle was repeated until penetration values leveled off.

The influence of ammonium perchlorate on Ball Penetration Values of a PBAN-EPON H-825 system is illustrated in Figure 43. After 50 hours at 80°C the sample containing AP had a Penetration Value of 36 compared to a value of 10 for the neat binder system.

1.   Influence of AP Concentration

The minimum AP concentration to assure an essentially zero slope in the dp/dc curve for the PBAN 703/EPON H-825 trimodel AP system was established by running penetration data in the presence of 1, 2, 5, 10 and 20%w AP. Our data, see Figure 44, show the required minimum concentration to be about 15%w.

2.   Influence of $KClO_4$ on PBAN 703-EPON H-825 Cure

The inertness of $KClO_4$ with respect to the PBAN 703-EPON H-825 curing reaction was demonstrated using the Ball Penetration method. The data (see Figure 45) show that the cure rate of the PBAN 703-EPON H-825 binder containing 26%w dispersed $KClO_4$ (equal in volume to 20%w AP, respective densities are 2.52 and 1.95) is the same as the neat system whereas in the presence of 20%w AP the system is relatively uncured.

3.   Influence of Polyethyleneimine Coated AP

Ball Penetration tests on PBAN 703-EPON H-825 containing Montrek 1000 treated AP (0.5, 1.0 and 2.0%w coating) indicated the inerting effect

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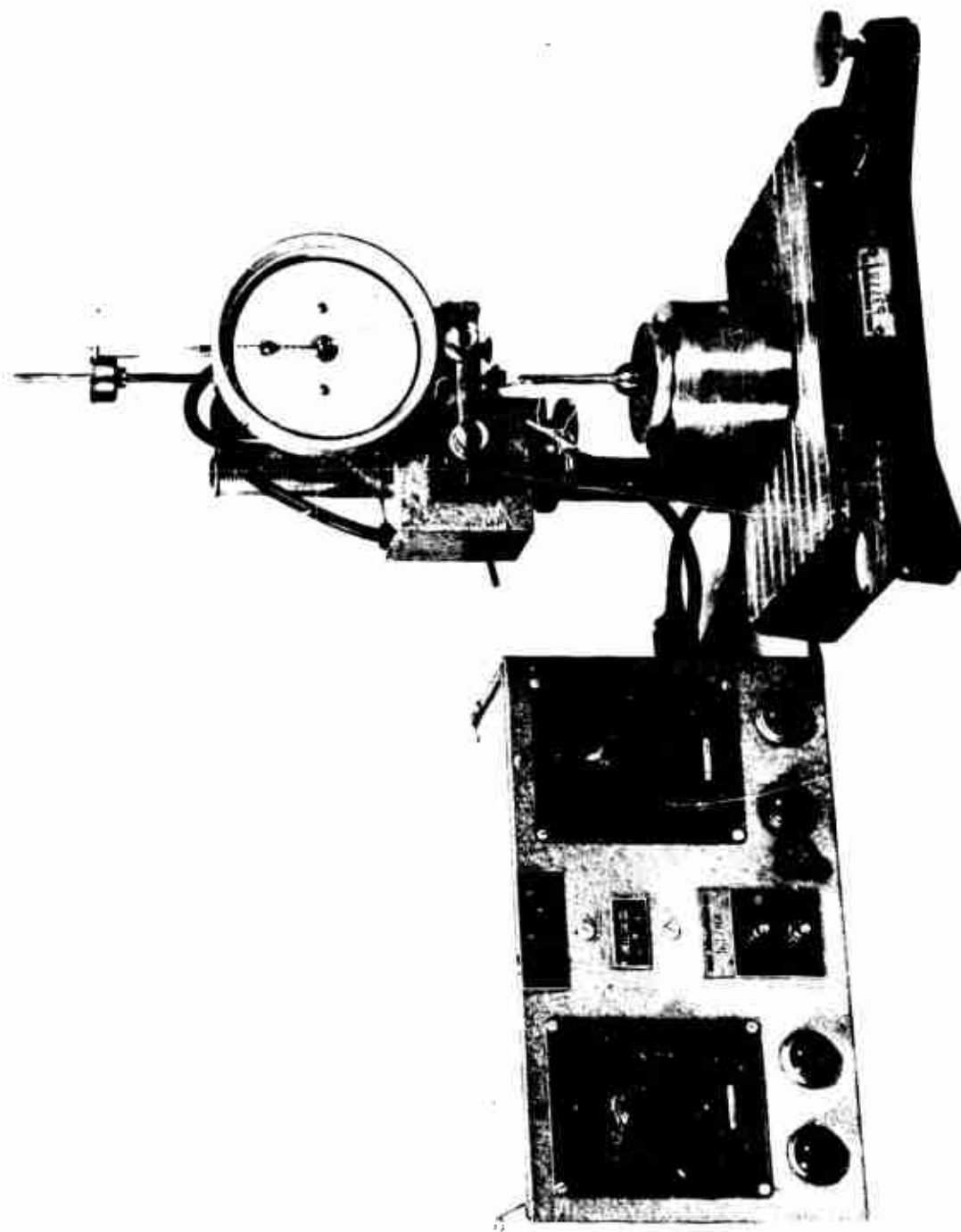Figure 42. BALL PENETRATION APPARATUS EQUIPPED WITH AUTOMATIC TIMER

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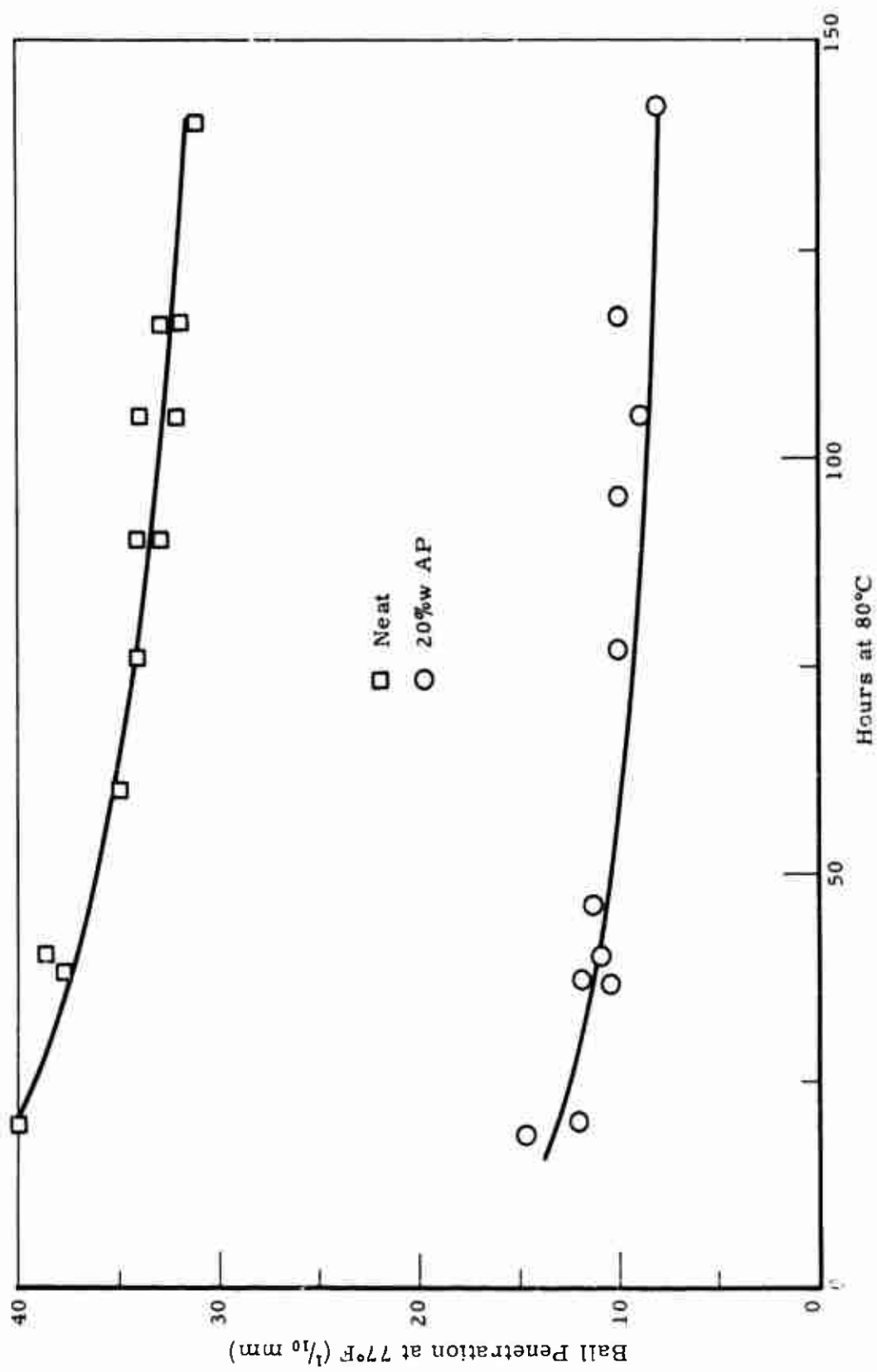
Figure 43. BALL PENETRATION VALUES FOR PBAN 707/EPON H-825 SYSTEM
1:1 COOH:Epoxy

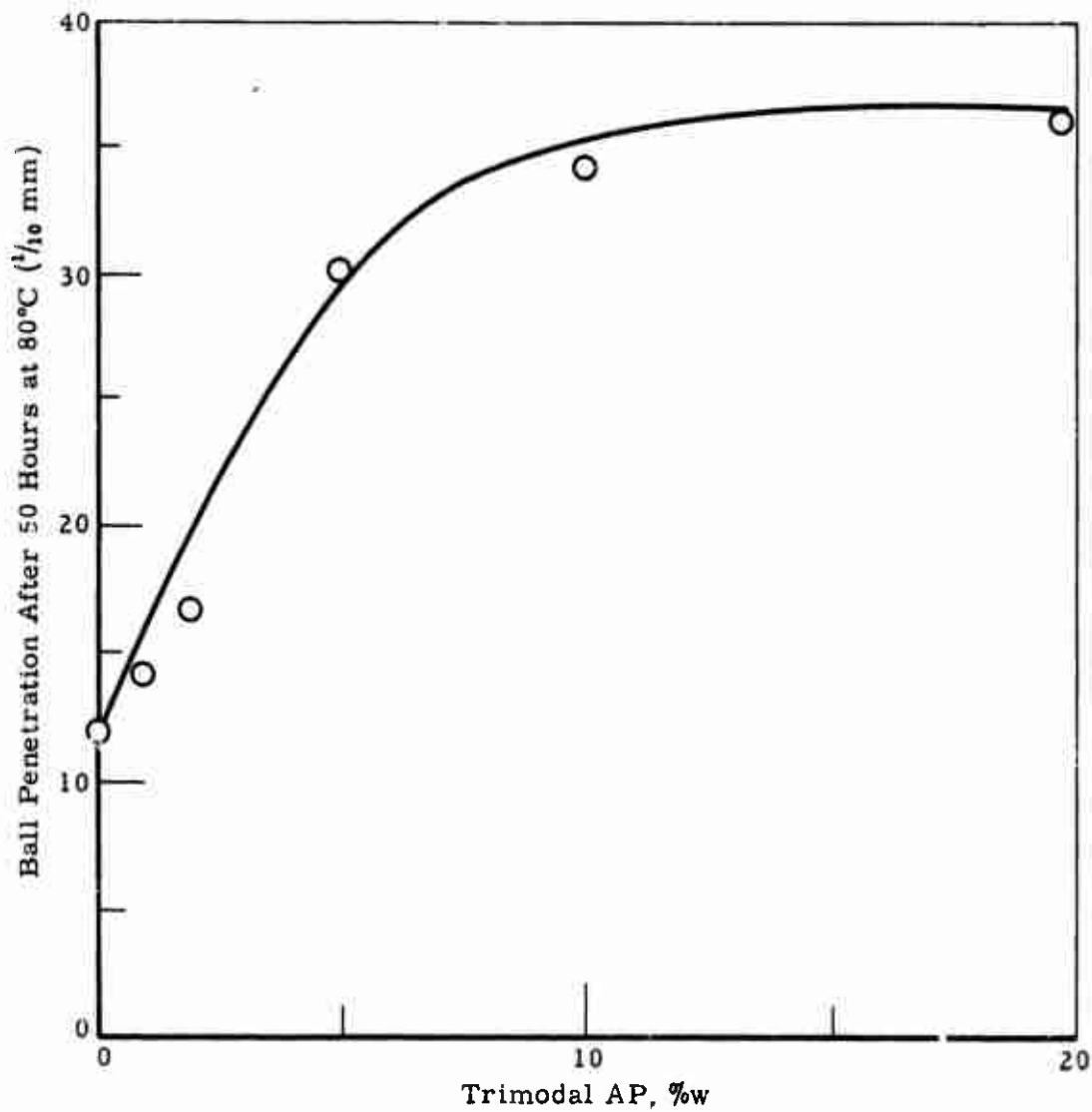Figure 44. INFLUENCE OF AP CONCENTRATION ON CURE RATE
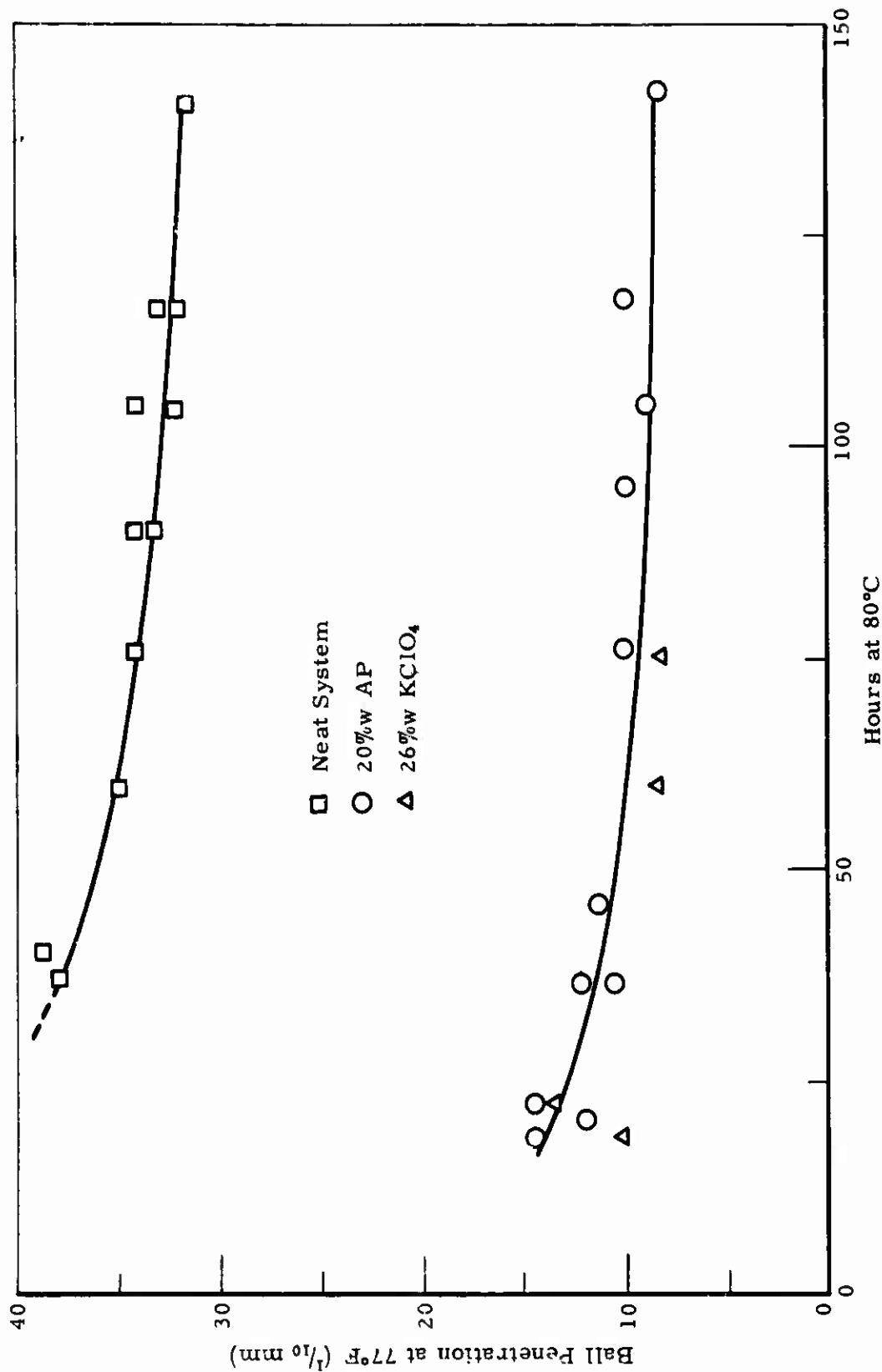OF PBAN-703/EPON 825 AT 80°C

Figure 45. INFLUENCE OF AP AND KClO$_4$ ON CURE RATE OF PBAN 703/EPON H-825 BINDER SYSTEM

on AP to be related to coating weight, see Figure 46, and that about a two percent weight coating should be sufficient to significantly reduce the AP interference with PBAN 703-EPON H-825 cure. However, these data did not correlate with our results when a Montrek 1000 coated AP (2%w coating) was used in an actual propellant mix, see Table XXX, runs A-10 and A-21. This lack of correlation was attributed to the fact that the severe shear forces, compared to hand mixing, during machine mixing at 60°C and reduced pressure were severe enough to rupture a large fraction of the coating film on the AP surface.

4. Effect of Direct K or Rb Salt Addition on Binder Cure in Presence of AP Compared to Pretreatment of AP with Saturated K or Rb Salt Solution

Since the simple addition of potassium or rubidium salts to the EPON H-825-AP system was found to be effective in reducing the rate of epoxide consumption at 80°C, we tested the effect of direct salt addition; KCl, RbCl and K Oxalate, on cure rate of our propellant model system (PBAN 703/EPON H-825/20%w AP) as measured by Ball Penetration.

We also tested, by the same method, two AP samples that had been surface treated by dropping them through saturated aqueous solutions of KCl or RbCl (see Section X).

Our Ball Penetration values, see Figure 47, show that the simple addition of these salts to the system did not improve its cure characteristics. However, the AP that had been pretreated with saturated KCl or RbCl solution was practically inert with respect to interfering with binder cure.

B. Influence of AP and KClO4 on Cure of Thiokol HC 434-EPON H-825/ERL 0510-Chromium Octoate System at 80°C

Ball penetration tests on the carboxy terminated butodiene polymer HC 434 (Thiokol Chemical Company) cured with the epoxy blend EPON H-825/ERL 0510 (70/30 equivalents) and catalyzed with chromium octoate indicate this system to be insensitive to the presence of AP or KClO4 at 80°C, see Figure 48. This insensitivity was confirmed by the tensile properties of the cured propellants based on this system (see Table XXXI).

SECTION XXI

PROPELLANT FORMULATION AND TESTING

The base formulation used in preparing propellant samples for tensile testing was:

14%w binder

16%w aluminum powder

70%w ammonium perchlorate (trimodal mix)
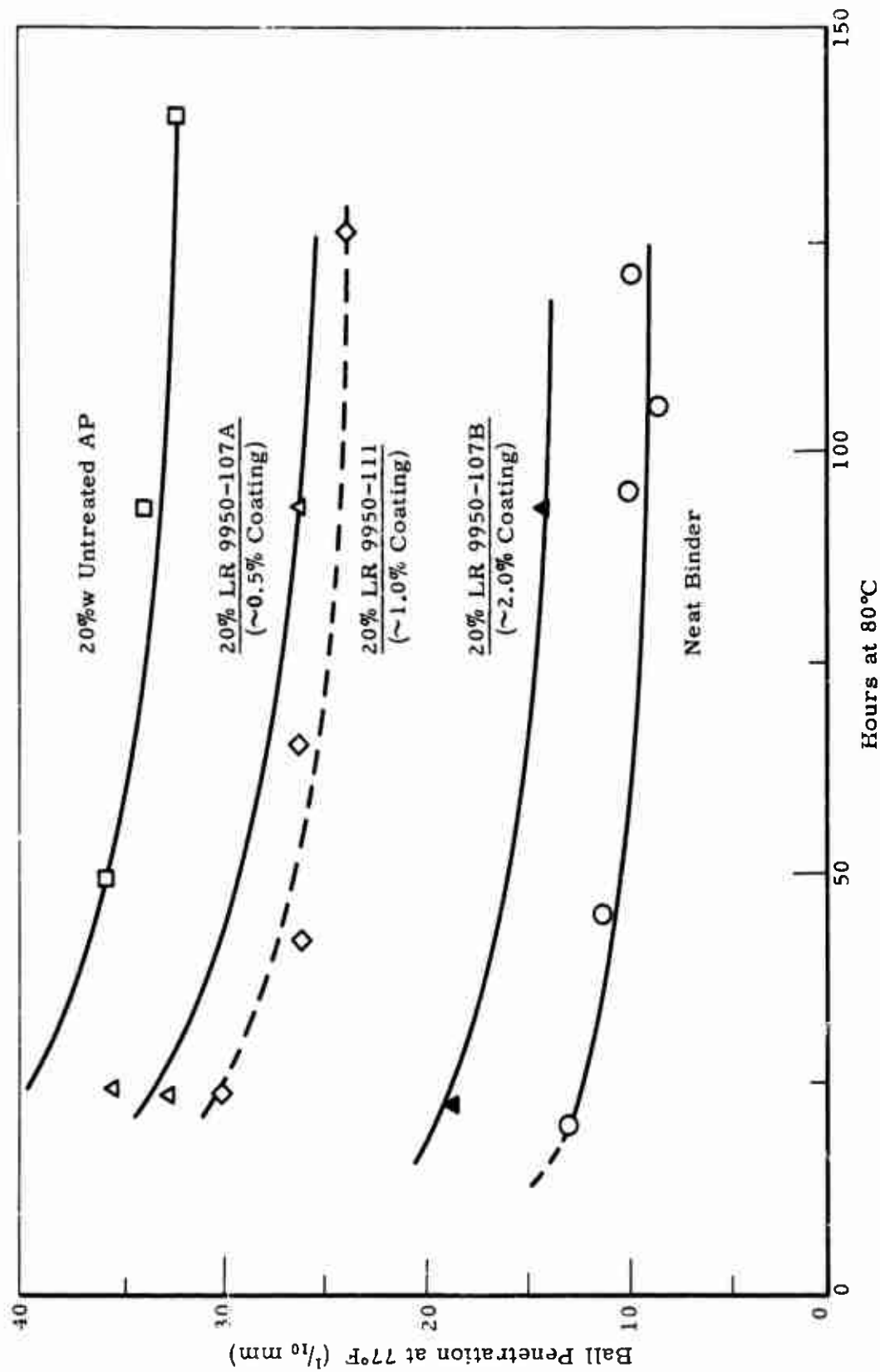
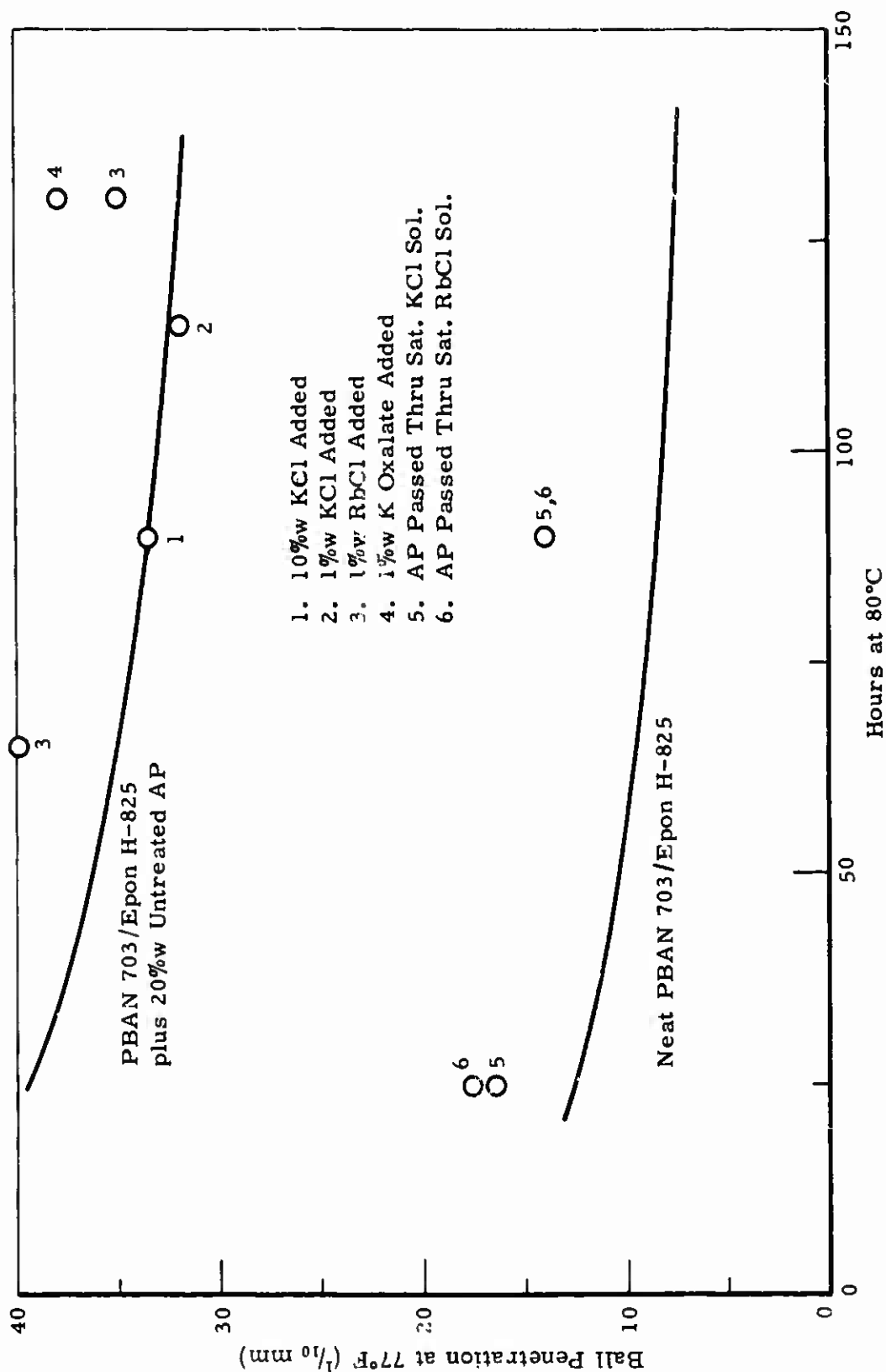Figure 46. EFFECT OF MONTREK 1000 TREATED AP ON CURE RATE OF PBAN 703/EPON H-825 BINDER SYSTEM

Figure 47. EFFECT OF DIRECT POTASSIUM SALT ADDITION ON BINDER CURE IN PRESENCE OF AP COMPARED TO PRETREAT AT AP WITH SATURATED K SALT SOLUTION
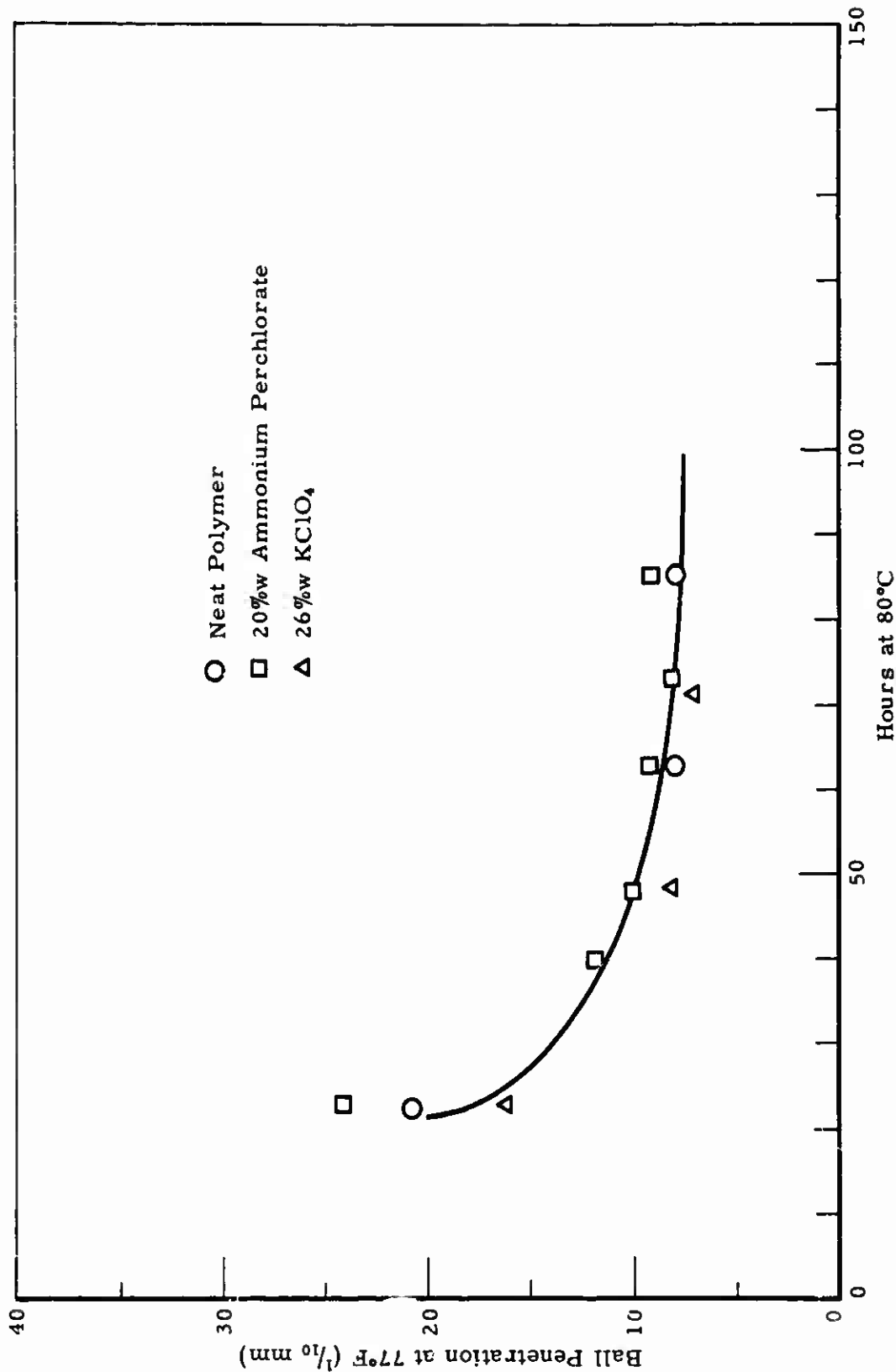
Figure 48. INFLUENCE OF AMMONIUM PERCHLORATE AND POTASSIUM PERCHLORATE ON CURE OF THIOKOL HC 434 -- EPON 825/ERL 0510 - CR (OCT)₃ SYSTEM AT 80°C

Aluminum powder was premixed with the binder system until the aluminum was completely wetted. This mixture was then added to the Atlantic Research Sigma Blade mixer (Model 35-LP) which was held at 80°C by constant temperature water circulated through the jacket provided for this purpose. After fifteen minutes, the first portion of AP, 20% of total to be added, was fed slowly into the mixer. The remaining AP was added in 20% aliquots at fifteen minute intervals. Once all the AP had been added, the vacuum chamber was placed in position and the system mixed under full pump vacuum for thirty minutes. Upon completion of mixing the propellant was scooped and trowled into the preheated (80°C) molds. The filled molds were placed in an 80°C vacuum oven under 25" Hg vacuum for thirty minutes and then transferred to an 80°C oven for the cure cycle.[a]

After cooling to room temperature, the excess propellant was trimmed off the molds with a sharp blade before dismantling the mold to remove the test specimen.

Samples were tested using an Instron tester in a laboratory maintained at 75°F and 50% RH. Cross-head separation rate during test was 2"/minute. Strain was measured by an extensometer with direct feed into an X-Y recorder. Figure 49 is a photograph of the specimen holder with extensometer in position on the Instron.

A. Reference Propellant Systems Based on PBAN-EPON H-825 Binder

In order to test, in a practical system, our hypotheses based on reactivity and kinetics in simple model systems we prepared and tested two reference propellant systems:

Propellant A-2 was our base system containing 70%w untreated AP, 16%w aluminum powder and 14%w PBAN-703/EPON H-825 binder having an acid to epoxy stoichiometry of 1:1.

Propellant AK-1 was comparable to A-2 in all respects except that the AP was replaced with $KClO_4$ and weight adjustments made to yield equivalent volume loading.

System A-2 represents one in which, at 80°C, both the rate and stoichiometry of cure would be perturbed by the oxidizer while in AK-1 the oxidizer is inert at 80°C. The extent of these perturbations would be reflected in the mechanical properties of these systems at equal cure time and serve as references against which we could measure the effectiveness of additives and/or coatings for the AP system.

It should be noted here that these systems were prepared for use as our own reference standards and do not represent the optimum mechanical properties that might be achieved by varying the binder stoichiometry or cure schedules.

a) We are indebted to the Thiokol Corporation, Wasach Division (Dr. Grant Thompson) for providing us with 15 lbs of trimodal mix AP and to the United Technology Center (Dr. Thomas Scortia) for the loan of five JANAF type specimen molds.
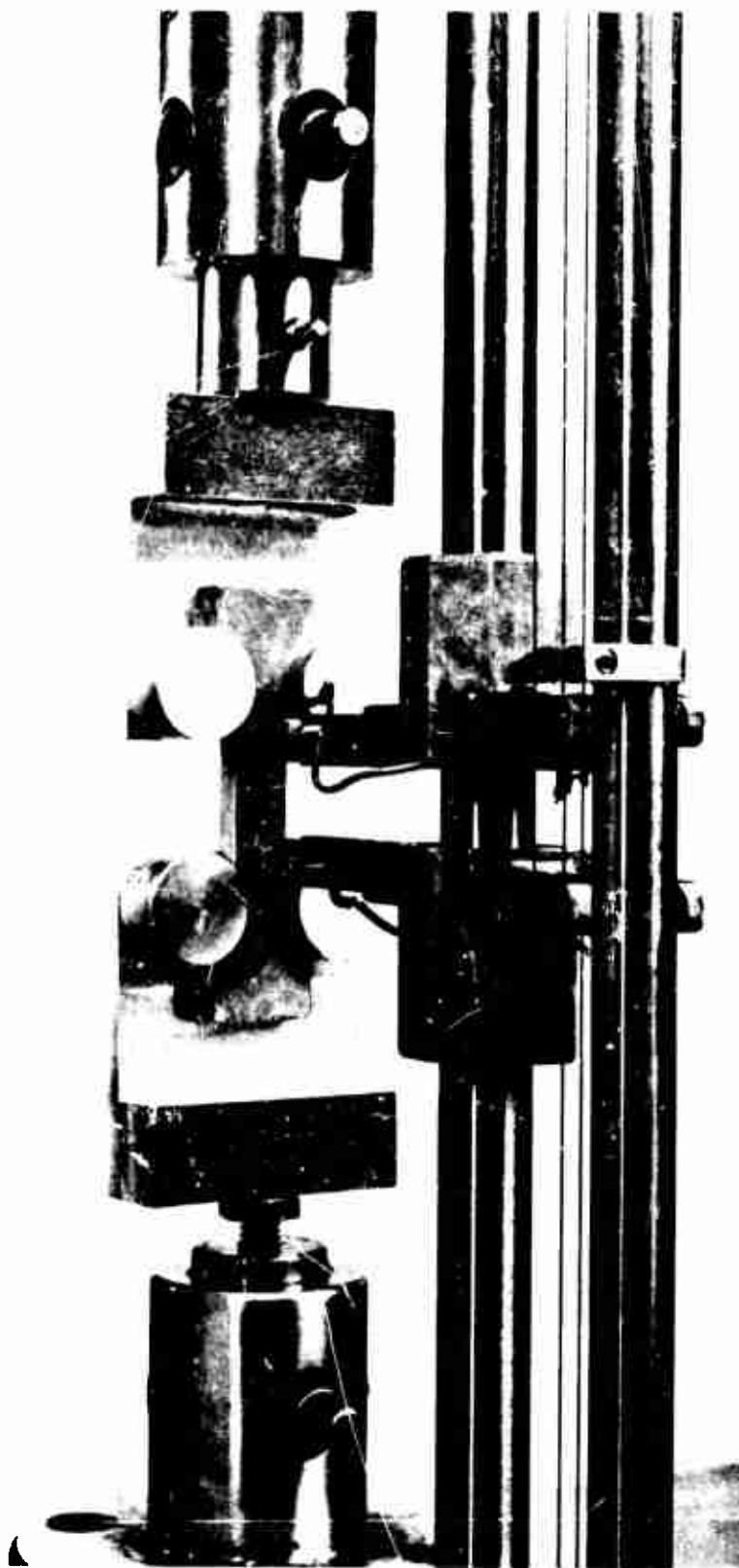
Figure 49. TENSILE TEST SET-UP FOR PROPELLANT SAMPLES

The stress-strain curves for these two reference systems, see Figure 50, illustrates the magnitude of the AP interference with binder cure compared to the inert $KClO_4$.

B. Properties of Modified Propellant Systems (PBAN 703)

In addition to three unmodified reference systems, nineteen modified propellant mixes based on PBAN 703-EPON H-825-Al-AP were prepared and their tensile properties evaluated. The kinds of modifications made, together with the tensile data on the resultant propellants, are shown in Table XXX.

Selection of these modifications for evaluation in finished propellant was based on the relative effectiveness of these additives in reducing AP reactivity toward EPON H-825 in our screening test series. Data obtained in the screening test series suggested the hypothesis that the addition of potassium cation would serve to scavenge and insolubilize any epoxy reactive perchlorate ion, and a potassium salt such as $K_4Fe(CN)_6$ whose anion would form relatively insoluble ammonium salts should be most effective.

The polyimine coating was selected based on its effectiveness in the screening tests and the hypothesis that this polymer was inactivating the AP via amine salt formation on the AP surface.

Replacement of part or all of the PBAN in the binder system with its potassium, rubidium or cesium salt was based on the concept and data discussed in Section XVII.

A review of the data on the effect of these various additives on the cure and tensile properties of the finished propellant shows that when compared to the unmodified AP reference system:

a) Addition of K ion by simple direct addition of 1% potassium salt (basis AP) such as $K_4Fe(CN)_6$ or KCl results in a small but positive improvement.

b) Potassium salts of long chain acids significantly improve physical handling properties of the propellant mix but have a negative effect on cure.

c) Precoating the AP with 1 or 2% polyimine has essentially no effect on cure or properties.

d) Replacement of the PBAN in the binder with its potassium, rubidium or cesium salt had the greatest beneficial effect on cure and properties.

e) None of the modified AP propellants had cure and tensile properties equivalent to the $KClO_4$ reference system.

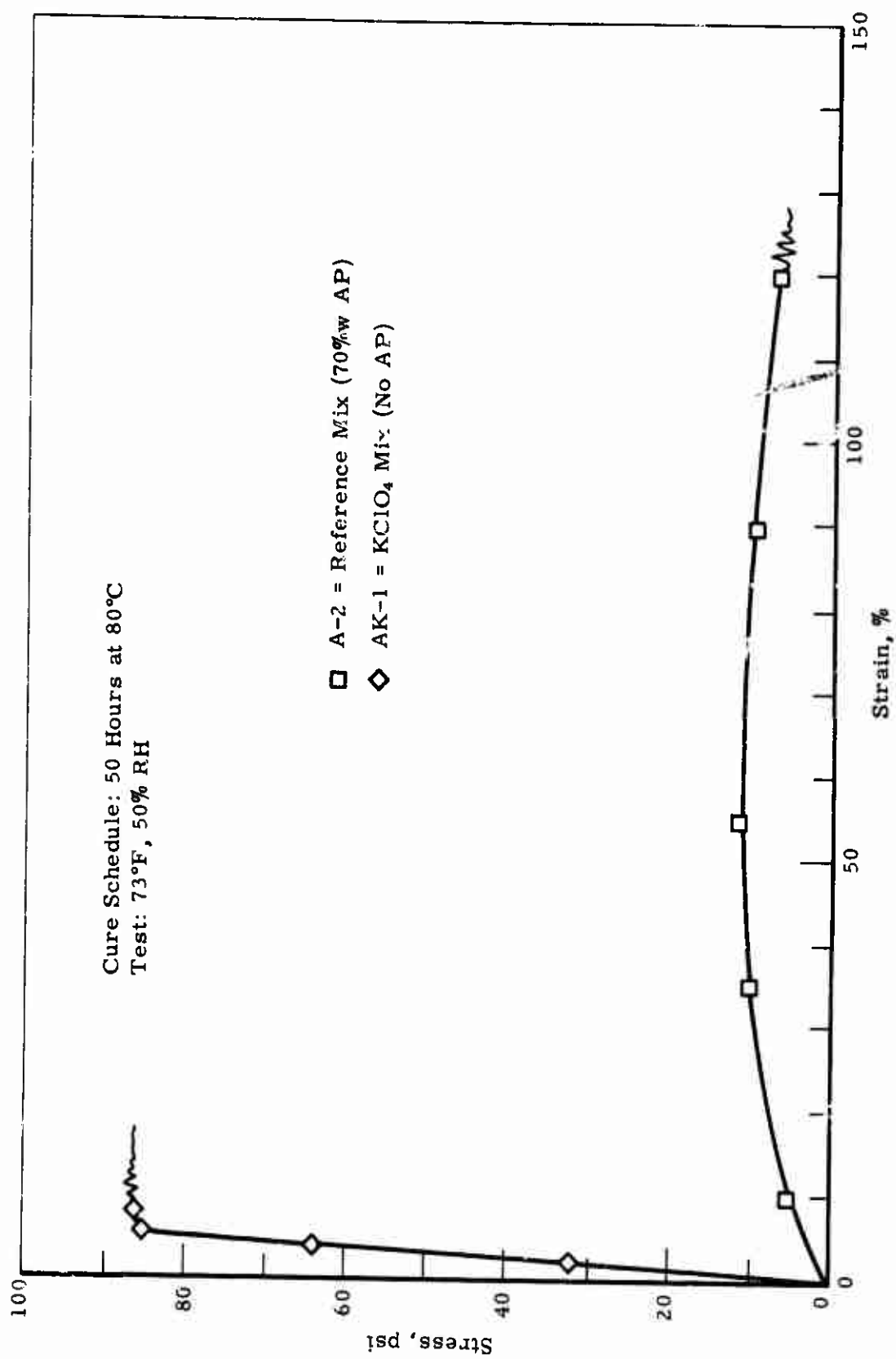Figure 50. STRESS-STRAIN CURVES FOR PBAN 703/EPON H-825 PROPELLANT FORMULATIONS

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Table XXX. TENSILE PROPERTIES OF PROPELLANT SAMPLES (PBAN)

Base System: 14%w Binder, a) 16%w Al Powder, 70%w Oxidizer
Cure Cycle: 50 hrs at 80°C
Test Conditions: 73°F; 50%RH; 2"/min test rate

Mix	Oxidizer	Additive	Concentration and Method of Addition	Maximum Tensile Str., psi	% Strain at Max Tensile	At Break		Secent Modulus, psi
						Stress, psi	Strain, %	
A-2	AP	None	-	11.9	60	Not Clean		20.1
AK-1	KClO4	None	-	86	75	86	7.5	1045
A-3	AP	KCl	1%, Basis AP, added to binder	22	40	20	45	55
A-4	AF	K2(PdCl6)	1%, Basis AP, added to binder		Too Weak to Test			
A-5	AP	K-Petroleum Sulfonate	1%, Basis AP, added to binder		Too weak to Test			
A-6	AP	K4Fe(CN)6	1%, Basis AP, added to binder	18.3	60	11.4	113	30.5
A-7	AP	KCl	1%, Basis AP, added to binder	15.2	60	5.9	160	25.4
A-8	AP	Polyethyleneimine (Montrek 1000)	Ca 1% Montrek 1000 Adsorbed on AP from Solution	12.9	26	6.4	87	50.5
A-9	AP	None	-	12.5	60	6.9	163	20.6
A-10	AP	Polyethyleneimine (Montrek 1000)	Ca 2% Montrek 1000 Adsorbed on AP from Solution	10.6	37	5.8	95	28.7
A-11	AP	Shell NEODOL 25-P	1%, Basis AP, added to binder	2.8	35	0.3	274	8
A-12	AP	SPAK-1 C12	1%, Basis AP, added to binder		Too Weak to Test			
A-13	AP	Shell VERSATIC 911-P	1%, Basis AP, added to binder		Too Weak to Test			
A-14	AP	K Salt of PBAN	100% of PBAN in binder replaced with K-PBAN	43	35	36	44	123
A-15	AP	Rb Salt of PBAN	100% of PBAN in binder replaced with Rb-PBAN	54	39	49	47	138

a) PBAN 703/EPON H-825 1:1 carboxyl:epoxide stoichiometry.

(Continued)

Table XXX (Contd). TENSILE PROPERTIES OF PROPELLANT SAMPLES (PBAN)

Mix	Oxidizer	Additive	Concentration and Method of Addition	Maximum Tensile Str., psi	% Strain at Max Tensile	At Break		Secant Modulus, psi
						Stress, psi	Strain, %	
A-16	AP	K-Salt of PBAN	10% of PBAN in binder replaced with K-PBAN	36	48	32	64	76
A-17	AP	Cs Salt of PBAN	100% of PBAN in binder replaced with Cs-PBAN	18	29	15	39	64
A-18	AP	Cs Salt of PBAN	10% of PBAN in binder replaced with Cs-PBAN	29	57	26	73	51
A-19	AP	Rb Salt of PBAN	10% of PBAN in binder replaced with Rb-PBAN	19	54	13	106	36
A-20	AP	K Salt of Monobutyl Ester of Eicosyl Phosphonic Acid	1%, Basis AP, added to binder	Too Weak to Test				
A-21	AP	Polyethylemeimine (Montrek 1000)	2% Montrek 1000 edsorbored on AP from Solution	9	47	4	159	19
A-17-2	AP	Cs Salt of PBAN	100% of PBAN in binder replaced with Cs-PBAN	34	18	27	33	189

C. Propellant Systems Based on α, ω-Carboxy Terminated Polymer (HC 434)

      Reference propellant systems comparable to the PBAN series were prepared using Thiokol HC 434. Since this polymer is difunctional, we used a mixed difunctional and trifunctional epoxy curing system, EPON H-825/ ERL 0510. ERL 0510 is the trifunctional epoxide, N,N diglycidyl-p-amino phenylglycidyl ether. Ratio of H-825 to ERL 0510 was 70/30 equivalents (80.3/19.7 wt ratio).

      Propellant compositions were corrected for density of AP and $KClO_4$ (1.95 vs 2.54) to yield equal volume concentrations. Reaction catalyst was chromium octoate.

      The tensile properties of these two formulations (see Table XXXI) indicates they are essentially equivalent and that the AP does not inhibit cure. This equivalency was also demonstrated by our Ball Penetration data, see Figure 48.

D. Influence of Various Additives on Propellant Viscosity

      Since the influence of any additive on the handling characteristics of the propellant mix is very important the viscosity of various mixes, at 80°C, was evaluated.

      Initially we attempted to measure viscosity change by incorporating a recording wattmeter in the power supply line to the mixer but this set-up was not sufficiently sensitive due to the highly overpowered motor on the mixer. After some preliminary tests, we found viscosity of our mixes could be determined using a Brookfield Helipath (Brookfield Viscometer Model HBF) and the smallest (TF) spindle.

      Samples of the completed mix, ready for molding, were filled into a 1" x 4" glass test tube and the filled tube placed in an 80°C vacuum oven (25" vac.) for thirty minutes. After the vacuum treatment, the tube was supported in an 80°C constant temperature water bath and the viscosity measured after not less than twenty minutes soak time.

      The viscosity values obtained, see Table XXXII, show that, in all cases, the additives reduced viscosity of the mix and that the extent of reduction was generally proportional to the expected surface activity of the additive.

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Table XXXI. TENSILE PROPERTIES OF PROPELLANT SAMPLES (HC 434)

Base System: (NH₄ClO₄) 14%w binder, a) 16%w Al powder, 70%w oxidizer
                   (KClO₄) 11.6%w binder, 13.3%w Al powder, 75.1%w oxidizer
Cure: 50 hrs at 80°C
Test Conditions: 73°F; 50% RH; 2"/min test rate

Mix No.	Oxidizer	Additive	Max Tensile Str., psi	% Strain at Max Tensile	At Break		Secant Modulus
					Stress, psi	Strain, %	
T-1	Ammonium Perchlorate	None	220	13.6	216	15	1630
TK-2	Potassium Perchlorate	None	209	11.0	199	14	1972

a) Binder composition: 92.5%w Thiokol HC 434, 7.5%w EPON H-825/ERLA 0510
   (70/30 Eq ratio) 0.05% Cr(OCT)₃.

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Table XXXII. VISCOSITY OF PROPELLANT MIXES AT 80°C

Method: Brookfield Helipath, Spindle TF

Mix No.	Composition	Vis, mm cps, at		
		1 rpm	2 rpm	5 rpm
Ref.	70%w AP, 16%w Aluminum Powder 14%w PBAN-EPON H-825 Binder	4.0	3.2	2.6
A-13	70%w AP, 16%w Al Powder 14%w PBAN-EPON H-825 Binder 1% Shell VERSATIC 911-P (Basis AP)	1.6	2.2	0.93
A-14	70%w AP, 16%w Al Powder, 14%w K-PBAN/H-825 Binder	2.8	2.0	1.60
A-15	70%w AP, 16%w Al Powder, 14%w Rb-PBAN/H-825 Binder	2.4	2.0	1.76
A-16	70% AP, 16% Al Powder, 14%w 90/10 PBAN/K-PBAN-EPON H-825 Binder	1.6	1.4	1.2
A-17	70%w AP, 16%w Al Powder, 14%w Cs-PBAN-EPON H-825 Binder	2.4	2.2	1.92
A-18	70%w AP, 16%w Al Powder, 14%w 90/10 PBAN/Cs-PBAN-EPON H-825 Binder	1.8	1.4	0.96
A-20	70%w AP, 16%w Al Powder, 14%w PBAN-EPON H-825 Binder, 1%w (Basis AP) K Salt of Monobutyl Ester of Eicosyl Phosphonic Acid	1.6	1.5	0.91
A-21	70% Montrek 1000 Treated AP (2%), 16% Al Powder, 14% PBAN-EPON H-825 Binder	1.7	1.6	1.4
A-22 Ref.	70%w AP (Shell Trimodal), 16%w Al Powder 14%w PBAN 703-EPON H-825 Binder	4.4	4.0	3.1
A-12	70%w AP, 16%w Aluminum Powder, 14%w Binder, 1% SPAKI-C_{12} LR 9950-C (Basis AP)	1.7	-	-

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SECTION XXII

INERTING HYDROXYLAMINE PERCHLORATE (HAP) TO REDUCE
INTERACTION WITH EPOXY RESINS

A. Reaction of Untreated HAP With EPON H-825

(C)   Our work on rendering solid oxidizers chemically inert in the presence of binder systems was extended to include a more energetic oxidizer, hydroxylamine perchlorate (HAP). The HAP used in these experiments was obtained from the Supply Officer, Naval Propellant Plant, Indian Head, Maryland, stored under carbon tetrachloride. Before using, the CCl_4 was decanted off and the HAP was placed in a vacuum oven at 30°C to remove the remaining CCl_4. Since HAP is extremely hygroscopic, all transferring of this compound was done in an atmosphere of dry nitrogen. The water in the EPON H-825 was removed by azeotropic distillation with toluene and the toluene was removed from the EPON by vacuum distillation. The dried EPON H-825 was mixed with 20%w untreated HAP in the 80°C oven used for evaluations. Within 45 minutes this sample reacted violently and the EPON was cured to a hard insoluble mass. This experiment was repeated with the same result.

(C)   Because of the rapid cure of the dried EPON H-825 in the presence of HAP at 80°C, the interaction of this system at lower temperatures (~22°C and 40°C) was investigated. The extent of reactivity was determined by measuring rate of epoxide consumption using the same titration method employed for the AP system (see Figure 51). It should be noted that these reactivity data are based on simple static conditions. The HAP sample at room temperature cured at a much slower rate. But in both cases the EPON H-825 which was in direct contact with the HAP in this unstirred system was cured and the HAP crystals could not be redispersed. Rapid curing of EPON in the presence of HAP has also been reported by other investigators.[14]

B. Reactivity of HAP Samples Toward EPON H-825 in the Presence of KCl

(C)   Since addition of potassium compounds to the epoxy-AP mixture was shown to be an effective means of reducing AP-epoxy interaction, the reactivity of HAP toward EPON H-825 (dried) in the presence of potassium chloride was examined. Potassium chloride was added directly to HAP. The KCl concentrations were 1%w in one HAP sample and 11%w in the other. The samples were mixed thoroughly under dry nitrogen and then placed in a vacuum oven for approximately 6 hours. To these samples dried EPON H-825 was added so that the mixture contained 20%w HAP. These samples were then placed in a 60°C oven under static conditions. The extent of reactivity was determined by measuring the rate of epoxide consumption in the same manner reported for the curing of the AP-EPON H-825 system. The results are shown in Figure 51. Both samples containing KCl cured at a faster rate than in the absence of KCl. This may be due to an increase in the dissociation of the HAP in the presence of KCl. An increase in the concentration of either hydroxylamine or perchloric acid would increase the curing rate of the epoxy resin.
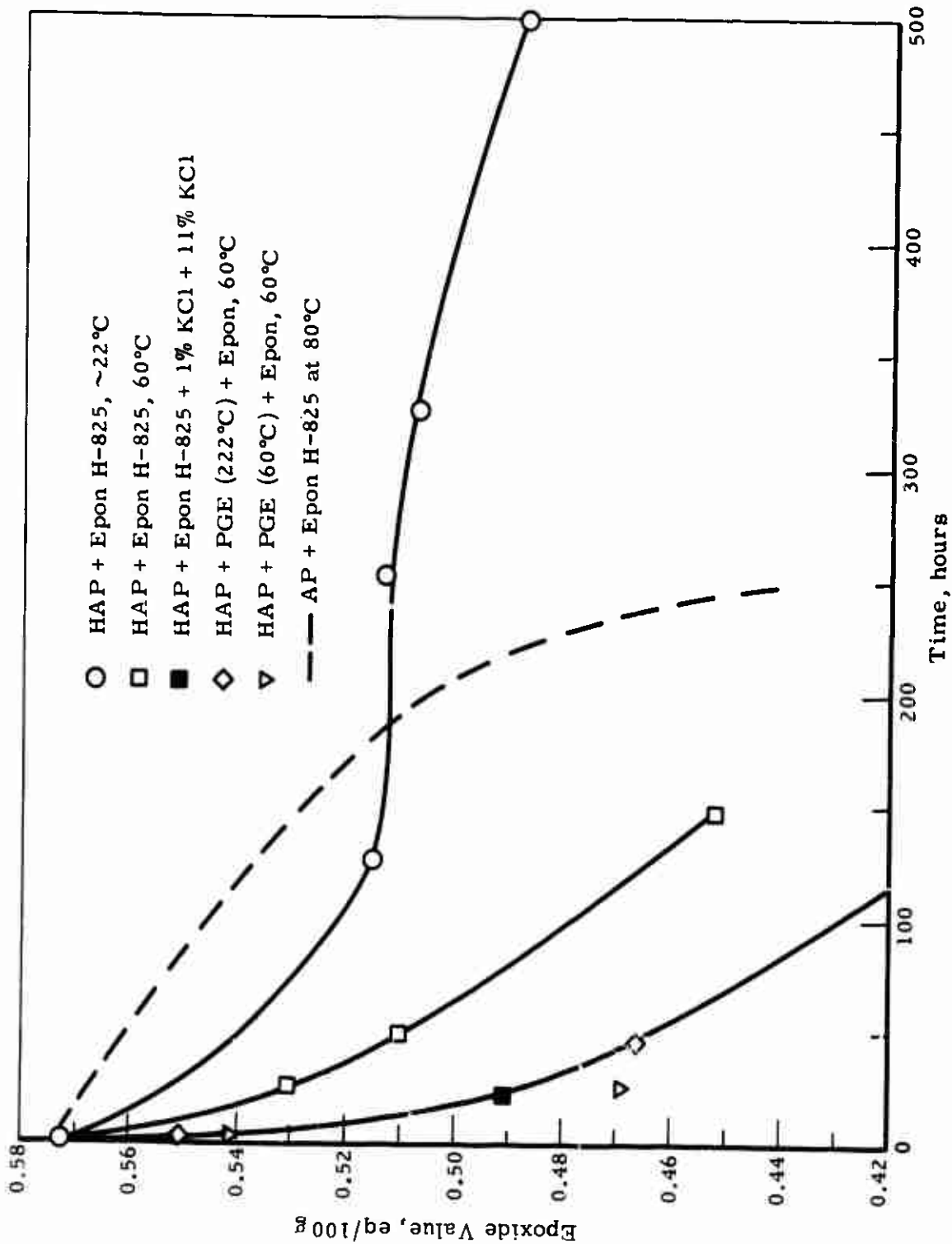
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Figure 51. REACTIVITY OF EPON H-825 WITH HAP

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## C. Coating of HAP With Phenylglycidyl Ether

(C)   In view of the rapid interaction of the HAP-EPON H-825 system we proposed that if a small amount of monoepoxide such as phenylglycidyl ether (PGE) reacted with the HAP surface, the coating produced would inert the HAP against interaction with the EPON H-825. We tested this idea in the following manner. Fifty milliliters of a one percent PGE solution in CCl_4 were added to solid HAP. The concentration of PGE in these dispersions was 50%w based on HAP. One sample of HAP was mixed at room temperature for 2 days and the other sample was mixed at 60°C for the same time. Samples of the supernatant liquid were then withdrawn and titrated to determine the extent of reaction of PGE with HAP. The original PGE solution contained 0.0042 eq of epoxide/100 g. The supernatant liquid from the samples of HAP treated at room temperature and at 60°C contained 0.0042 and 0.0041 eq of epoxide/100 g, respectively. Comparing the titration values we concluded that the PGE apparently did not interact with the HAP samples at either ~22°C or 60°C. The excess PGE solution was then decanted from these two HAP samples. These samples were then placed in a vacuum oven at 30°C to remove the remaining CCl_4. Dried EPON H-825 then was added to the PGE-treated HAP samples. The samples were thoroughly mixed and placed in a 60°C oven. The HAP treated with PGE at both ~22°C and 60°C appears to interact more rapidly with the EPON than untreated HAP (see Figure 51). However, in both samples the EPON in contact with the HAP crystals cured to a solid. We speculate that some water may have been picked up by the HAP during handling in the PGE treatment and that this might account for the more rapid reaction rate.

D. Inerting HAP With Tolylene Diisocyanate (TDI) (2,4-Isomer)

(C)   We postulated that if any water remained in the EPON the TDI would react with it thus preventing the water from solvating HAP. Two samples of HAP were prepared as follows. To one sample we added TDI dissolved in carbon tetrachloride and then removed the CCl_4 by vacuum. In this case the concentration of TDI was 4%w based on HAP. Then EPON H-825 was mixed with the TDI-treated HAP and the sample was placed in an 80°C oven. To the other sample of HAP we added the TDI directly in an amount equal to 43%w TDI based on HAP. Assuming the following reaction routes for the interaction of TDI and HAP[15] as either:
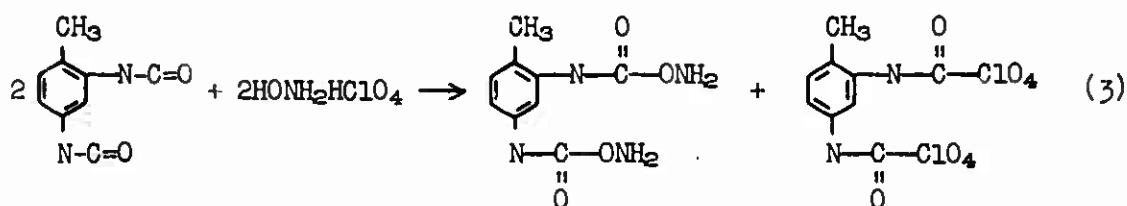

$$(1)$$

or

$$(2)$$
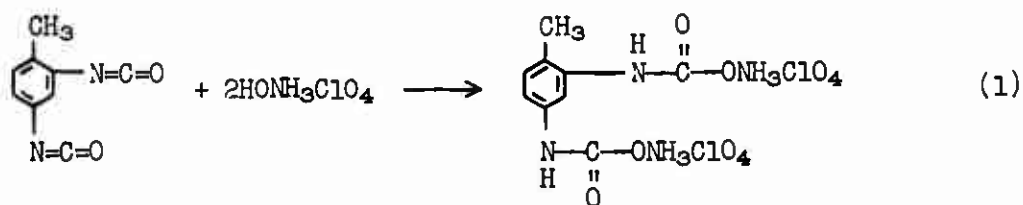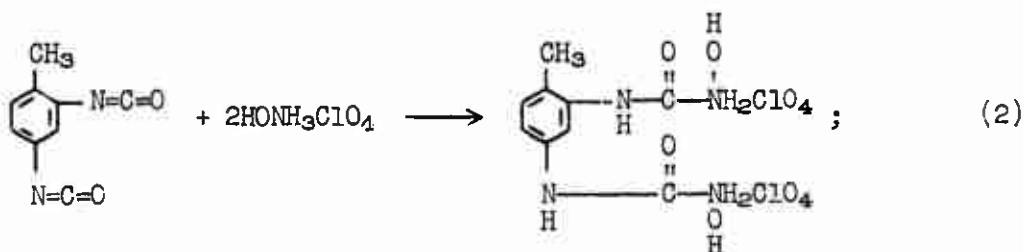
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then at this TDI concentration, 0.003 moles of TDI to 0.009 moles of HAP, all but ~0.003 moles of HAP would react with the diisocyanate. On the other hand if the HAP decomposes as follows $HONH_2HClO_4 \longrightarrow HONH_2 + HClO_4$ then the reaction may be as follows

$$2 \quad \begin{array}{c} CH_3 \\ \bigcirc \\ N-C=O \end{array} N-C=O \quad + \quad 2HONH_2HClO_4 \quad \rightarrow \quad \begin{array}{c} CH_3 \quad O \\ \bigcirc \\ N-C-ONH_2 \\ N-C-ONH_2 \\ O \end{array} \quad + \quad \begin{array}{c} CH_3 \quad O \\ \bigcirc \\ N-C-ClO_4 \\ N-C-ClO_4 \\ O \end{array} \quad (3)$$

In this case less HAP would be consumed and 0.006 moles of HAP should remain. The HAP plus the diisocyanate did form a gummy solid suggesting that an interaction occurred. Then we added the EPON H-825 and mixed but we found that the gummy clumps of HAP could not be dispersed into the EPON. These samples were then placed in the 80°C oven. Interaction of HAP with the EPON was measured by the decrease in the epoxide value as a function of time. The sample containing 4% TDI cured to an insoluble mass within thirty minutes having an estimated epoxide value of less than 0.2 eq/100 g. A reduction in the curing rate of EPON was found in the presence of 43%w TDI treated HAP, as shown in Figure 52. Within two hours this sample had also cured to an insoluble hard mass. We believe this retardation in curing rate is due to the previous interaction of HAP with TDI as postulated above. A treatment of HAP with an intermediate amount of TDI between 4% and 43% might be worth investigating.

E. HAP Interaction With EPON H-825 in Carbon Tetrachloride

(C)   Apparently HAP is stable in CCl_4 as shipped, the CCl_4 preventing water from solvating the HAP. We added CCl_4 directly to HAP (60%w carbon tetrachloride on basis of HAP) to see if the CCl_4 influenced the interaction of HAP with EPON H-825. The EPON was mixed with the HAP and the sample was then placed in an 80°C oven. This sample cured to a hard insoluble mass within 30 minutes, as shown in Figure 52. We estimated the epoxide value of the insoluble mass to be less than 0.2 eq/100 g.

F. Treatment of HAP With Potassium Sulfonate

(C)   We found previously that potassium sulfonate reduced the interaction of AP with EPON H-825. We added the potassium sulfonate dissolved in CCl_4 to the HAP and then removed the CCl_4 by vacuum. The concentration of potassium sulfonate was 2.5%w based on HAP. Dried EPON H-825 was added to the treated HAP, mixed and placed in the 80°C oven. This sample also cured to an insoluble mass within 30 minutes as shown in Figure 52.

(C)   Thus far our attempts to retard the interaction of EPON H-825 with HAP treated with small concentrations of various compounds has been unsuccessful. We are not surprised by the rapid interaction of HAP with EPON H-825 in the presence of additives in view of the recent reports on the decomposition of HAP at and above 25°C with the possible formation of perchloric acid and hydroxylamine. Both of these compounds are curing agents for EPON H-825.
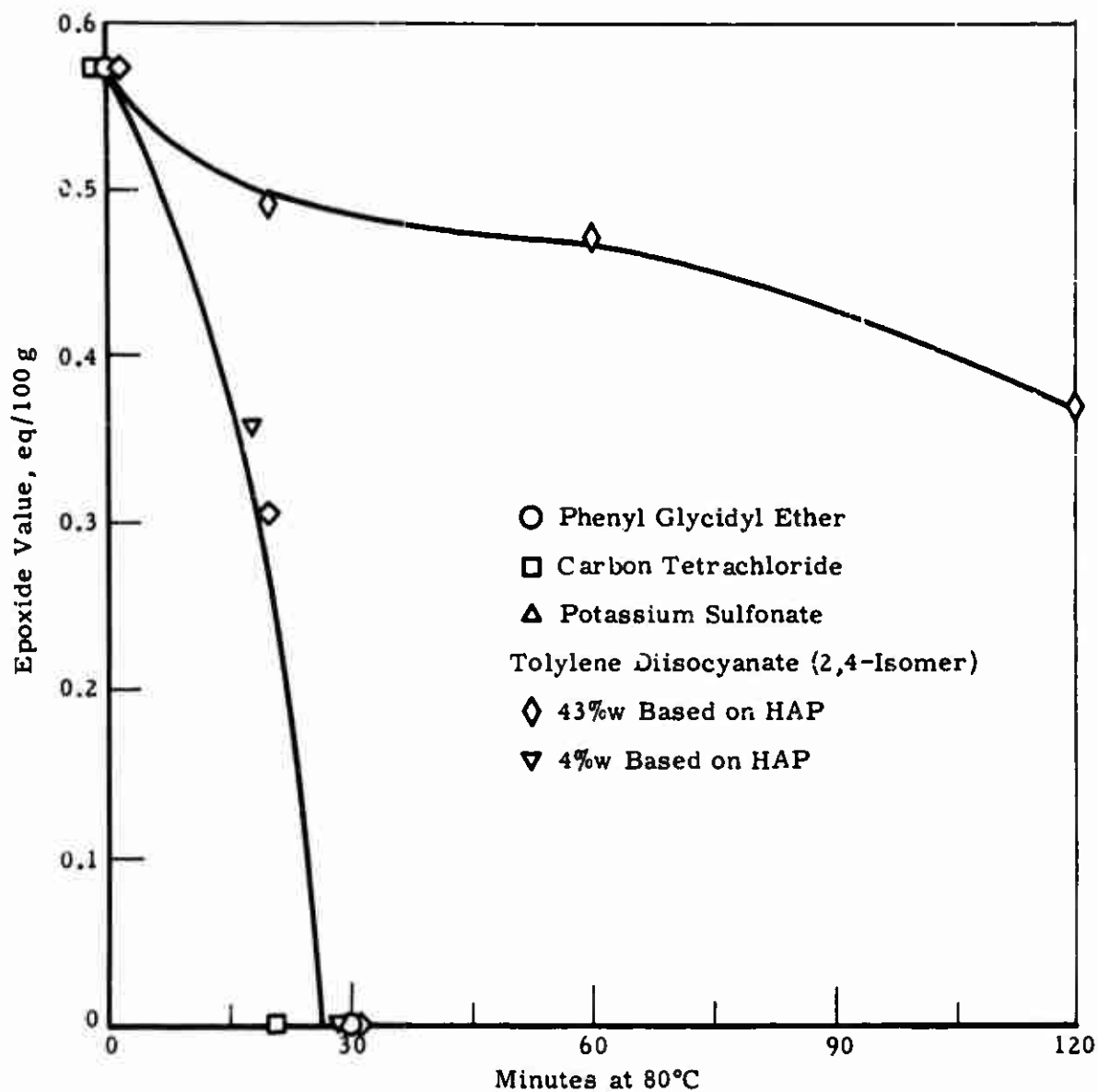
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Figure 52. INERTING OF HYDROXYL AMMONIUM PERCHLORATE

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G. Influence of HAP on PBAN 703-EPON H-825 Cure With and Without AP Present

(C)   The influence of a more energetic oxidizer, HAP, on the PBAN 703-EPON H-825 cure was also evaluated using the Ball Penetration method. Ball penetration tests on duplicate samples of stoichiometric mixtures of PBAN 703-EPON H-825 containing 20%w HAP indicated this oxidizer interferred with the PBAN-EPON cure. After 24 hours at 80°C these samples had penetration values of 54-56 compared to values of 10-14 for the neat binder system. After 200 hours at 80°C the samples containing HAP had penetration values of 20-25. This result is surprising in view of all the rapid cures observed before with HAP present.

(C)   In view of the fact that HAP easily decomposes to hydroxyl amine and perchloric acid at relatively low temperatures, we postulated that the addition of a small amount of HAP might reduce the AP interference with binder cure by depressing the dissociation of AP to NH_3 and perchloric acid. Ball penetration tests on duplicate samples of stoichiometric mixtures of PBAN 703-EPON H-825 containing 20%w AP and 2%w HAP indicated the presence of HAP decreased the AP interference with the PBAN-EPON cure. After 24 hours at 80°C these samples had penetration values of 14-28 compared to values of ~40 for PBAN-EPON systems containing AP alone. After approximately 200 hours at 80°C the samples containing the HAP and AP had penetration values of 12-15 which are characteristic of complete cure of the binder system.

(C)   In view of these exploratory results it is suggested that the interference of these oxidizes on the PBAN-EPON cure might be controlled by varying the AP/HAP ratio in the system.

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13 ABSTRACT(U) This report describes the results of a project designed to study the influence of solid oxidizers on the curing of binders for solid propellants and to explore the possibilities of minimizing interaction of oxidizers and binder components by surface coating of the oxidizer or by introduction of chemical agents so that the binder systems might more nearly achieve their maximum physical properties. Kinetic studies showed that in binders involving epoxy resins and carboxyl groups in polybutadiene-acrylic acid-acrylonitrile terpolymers, the rate of the polymerization reaction is reduced and the epoxy groups are consumed faster than carboxyl groups in the presence of ammonium perchlorate (AP). The evaluation of over 200 surface coatings adsorbed from solution on AP, deposited on a fluidized bed of the oxidizer or merely added to the propellant formulation is described. Coatings evaluated include polyethyleneimines, linear polyalkylenepolyamines, alkylamines, amides and polyamides, quaternary ammonium compounds, fatty acids and polymerized fatty acids, and a variety of polymers. Since consumption of epoxy groups in AP-epoxy resin mixtures was shown to be independent of amounts of AP present, it was concluded that this interaction is related to the solubility of AP in the binder system. Methods of chemically capturing AP or its ionization or decomposition products as they appear in solution were investigated. K, Rb and Cs salts which form perchlorates of very low solubility in organic system were effective in reducing the AP-epoxy interaction. A group of proprietary compounds including potassium salts of carboxylic, sulfonic and phosphonic acids decreased AP-epoxy interaction and reduced viscosity during propellant mixing by delaying the cure reaction. A most effective solution to the AP-epoxy interaction was to convert the polybutadiene-acrylic acid-acrylonitrile terpolymer to the K, Rb or Cs salts which resulted in reasonably rapid binder cures and much improved propellant physical properties.

(C) A brief investigation of methods of reducing the interaction of hydroxylammonium perchlorate (HAP) with epoxy resins was made. Pretreatment of HAP with tolylene diisocyanate or use of a mixture of AP and HAP showed some promise.

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14. KEY WORDS

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Chemically inert AP
Epoxy-carboxyl reactions
Binder reaction stoichiometry
Binder reaction rate
Polyethyleneimine coating
Polyamide coating
Polyalkylene polyamine coating
K salts
Rb salts
Cs salts
HAP coating