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WATERBORNE POLYMERIC FILMS

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Research and Development Center
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February 1981

TECHNICAL REPORT AWFAL-TR-80-4197

Interim Report for the Period 15 September 1979 -
15 September 1980

Approved for public release; distribution unlimited

MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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SECURITY CLASSIFICATION OF THIS PAGE (*When Data Entered*)

(19) **REPORT DOCUMENTATION PAGE**		**READ INSTRUCTIONS BEFORE COMPLETING FORM**
1. REPORT NUMBER (14) AFWAL-TR-80-4197 ✓	2. GOVT ACCESSION NO. AD-A102490	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (*and Subtitle*) (6) Waterborne Polymeric Films	(9)	5. TYPE OF REPORT & PERIOD COVERED Interim Report, 15 Sep 1979 — 15 Sep 1980
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) (10) A.J. Tortorello, M.A. Kinsella, ~~and~~ R.T. Gearon	(15)	8. CONTRACT OR GRANT NUMBER(s) F33615-78-C-5096 ✓
9. PERFORMING ORGANIZATION NAME AND ADDRESS DeSoto, Incorporated 1700 South Mount Prospect Road Des Plaines, Illinois 60018		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS (16) Project 2422 Task 0201 (14)
11. CONTROLLING OFFICE NAME AND ADDRESS Materials Laboratory Air Force Wright Aeronautical Laboratories Air Force Systems Command Wright-Patterson AFB, Ohio 45433	(11)	12. REPORT DATE February 1981
		13. NUMBER OF PAGES 119 (12) 1 2 0
14. MONITORING AGENCY NAME & ADDRESS(*if different from Controlling Office*)		15. SECURITY CLASS. (*of this report*) Unclassified
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (*of this Report*)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (*of the abstract entered in Block 20, if different from Report*)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (*Continue on reverse side if necessary and identify by block number*)

Aqueous resins; Cationic dispersions; Anionic dispersions;
Aqueous primer; Aqueous topcoat; Solubility parameter.

20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

Air Force contract F33615-78-C-5096 proposes the development of an aqueous resin system to functon as the pigment binding vehicle of a waterborne coating for aircraft.

Four series of novel polymers were synthesized, dispersed into aqueous medium, formulated with crosslinking agents, and evaluated for fluid resistance and flexibility.

The series of anionic acrylic dispersions produced four members capable of resisting all fluids except water. Flexibility was poor.

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The series of anionic urethane dispersions produced one resin capable of resisting all fluids except water. Flexibility again was poor.

The series of cationic urethanes produced one candidate capable of resisting all fluids except water. Flexibility was erratic.

The series of cationic acrylics produced three resins resisting all but water. Flexibility was poor.

PREFACE

This interim report covers the period from 15 September 1979 to 15 September 1980 as required under contract number F33615-78-C-5096 for the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson AFB, Ohio. The contract entitled Waterborne Polymeric Films, was initiated under Project Number 2422, Task Number 242202. The purpose of the program is to develop waterborne polymers which, under ambient conditions, will form high performance films suitable for formulation into aircraft primers and topcoats.

The project engineer is Mr. Michael Halliwell (AFWAL/MLBE).

The authors express appreciation to Dr. G.K. Noren for advice in developing the approach and consultations in data analysis. We also thank Ms. Mary Meinert for her part in preparing the manuscript.

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SUMMARY

Air Force contract F33615-78-C-5096 proposes the development of an aqueous resin system to function as the pigment binding vehicle component of a water-based coating for aircraft. The intended approach was designed to occur in three phases. The initial two phases have been completed and are the subject of a summary report. The third phase has begun and is the subject of this interim report.

Activity scheduled for phase three includes synthesis of novel aqueous resin systems. Design of these novel polymers was guided by the solubility parameter concept. The premise for selecting this guide was the potential for introducing inherent fluid resistance with minimal crosslinking. Thus the conbination of fluid resistance and enhanced flexibility could be achieved.

The fluids which the coating must resist were characterized and individual solubility parameters were determined. A spectrum of fluid solubility parameters was constructed and a gap was identified.

Theory predicts that fluid resistance is enhanced when the solubility parameter of the resin and fluid diverge. To test the generality of this concept, four distinct series of polymers were synthesized. Each series was constructed of members designed to have solubility parameter values approaching the midpoint of the gap in the fluid spectrum.

A series of anionic acrylic copolymers varying in solubility parameter from 11 to 14 was synthesized, dispersed into aqueous medium, formulated with polyfunctional aziridine crosslinkers, and evaluated for fluid resistance and flexibility. Resistance to all fluids except water was as predicted. Even in the single case of a noncrosslinked lacquer good fluid resistance was achieved. Water resistance was improved with a bake but was generally poor. Flexibility was poor.

A series of anionic polyurethane dispersions varying from 10 to 13 was prepared and formulated with aziridine crosslinkers. Performance in all fluids except water was as expected. Applying a bake improved water resistance somewhat. Flexibility was poor.

A series of cationic polyurethanes varying from 10 to 13 was formulated with difunctional epoxy resin crosslinking agents. Performance was in agreement with theory again with the exception of water. Applying a bake improves moisture resistance. In a few cases, excellent flexibility was achieved.

A series of cationic acrylic dispersions from 10 to 12.5 was formulated with epoxy resin crosslinkers. Performance was as predicted by theory and in agreement with previous observations.

Correlation of resin type as a function of solubility parameter was attempted. Plots of fluid resistance versus resin solubility parameter for immersion in each fluid were constructed. A family of curves indicating similar performance for each resin class was found. This correlation suggests general applicability of the concept for organic fluids.

Lack of consistent correlation in water suggests that other factors may contribute more significantly than solubility in predicting resistance to this fluid.

1. Introduction

Interest in waterborne coatings for industrial use increased significantly following enactment of the now famous Rule 66 by Los Angeles County. Prior to that time, waterborne coatings were accepted for industrial scale use primarily in automotive finishes.[1] As originally intended, Rule 66 controlled the type and amount of volatile and photochemically reactive solvents that were permitted as part of a paint formulation. Subsequent modification resulted in the stipulation that any newly developed waterborne coatings contain no more than 20 percent volatile organic materials on a volume basis.[2]

More specific to the Aerospace Industry is the recently proposed Rule 1124 of the South Coast Air Quality Management District. According to this regulation the amount of volatile organic compounds present in any primer in use after August 1, 1982 must be limited to 650 grams per liter less water. After January 1, 1985, the amount is reduced to 350 grams per liter.[3]

Legislation such as this coupled with rising solvent costs has led to some surprising reassesments in the markets for compliance coatings. By the year 1990, waterborne coatings are estimated to hold 25 percent (a small majority) of the total industrial coatings market in America.[4] The European market area offers the same 25 percent projection.[5]

A. Historical Background

The U.S. Air Force recognized the onsent of technology change and in the early 1970's awarded contract F33615-73-C-5179 in an attempt to develop water based replacements for the mil spec primer (Mil-P-23377) and topcoat (Mil-C-83286). These pioneering studies were conducted by a group at Lehigh University and dealt primarily with direct emulsification of the resins in use.[6]

For replacement of the epoxy-polyamide primer, each component was emulsified spearately with a proprietary surfactant system and mixed just prior to application as with a conventional two-component system. The main problems encountered were with slow cure rates and preferential reaction at the particle interface.

For replacement of the aliphatic polyurethane topcoat, direct emulsification of the isocyanate component was not possible due to reaction with water. Thus adducts of the isocyanate with polyols were prepared prior to emulsification. These emulsified polyurethanes formed tough films but mechanical homogenization was required for the reduced particle sizes necessary to stabilize the emulsions.

Continuing the effort to attain compliance with emission guidlines, the Air Force has recently initiated a more concentrated multi-faceted approach. The first aspect of this program involved successful replacement of pressurized air spray equipment with airless electrostatic equipment at the Air Logistics Centers (ALCs).

The second approach considered the use of high solids (65 volume percent) technology as an interim method. The result of a contracted effort over two years, a high solids coating was developed having acceptable film performance but lacking in sufficient pot-life.[7]

The third approach, concerted with the high solids development, began as a visiting scientist program designed to assess the potential use of waterborne technology. Prof. L.W. Hill, then of North Dakota State Univ., consulted with numerous manufacturers of commercial water-based resins in an effort to summarize the status of current technology and to project its use in meeting the high performance criteria established for aircraft coatings.[8] This effort subsequently evolved into the award of AFML contract F33615-78-C-5096 entitled "Waterborne Polymeric Films."

The goal of this contract is the development of a waterborne polymer system to function as the pigment binding vehicle for prospective primers and/or topcoats. The proposed approach was designed to follow three phases of effort. The initial two phases involved evaluation of commercial state-of-the-art (SOTA) resin systems and are the subject of an interim report.[9]

When the initial two phases failed to produce a viable coating system, implementation of the third phase was begun.

The activity for this phase was devoted to novel polymer systems. Consequently, a synthetic effort to develop novel water-based polymers was required.

In practice this synthetic approach involved four distinct stages prior to evaluation. The first task is design of a theoretical polymer incorporating characteristics intended to meet the various performance requirements. The second task is the actual synthesis of this proposed polymer. The third task is dispersion into aqueous medium. And the final task is blending with various formulating aids.

B. Polymeric Design

In considering the design of a theoretical polymer, applied film performance requirements must be well characterized. A complete description of the mechanical and chemical performance expected of the applied film as well as the required dispersion properties has been discussed in a previous report, and the interested reader is referred to this document.[9]

Upon reviewing all the application requirements the two most challenging are flexibility and fluid resistance. Unfortunately, these requirements are inversely related. Enhanced chemical resistance is usually incorporated at the expense of mechanical flexibility. Given this relationship, any resin found to have optimum chemical resistance in the non-crosslinked state could achieve the applied resistance requirements with minimal crosslinking. This in turn would optimize flexibility. The problem of selecting a criterion upon which to design a resin can thus be focused upon optimizing fluid resistance of the linear polymer.

1. Fluid Resistance

Fluid resistance may be interpreted as a measure of the incompatibility between a resin and a fluid which can be viewed as a solvent. The familiar Flory-Huggins equation[10] has shown that even in crosslinked polymers the extent of solvent incorporation is a function of the compatibility of the linear polymer and the solvent.

The compatibility of a solvent and a polymer has alternately been expressed in terms of the solubility parameter concept.[11] The design of a polymer to resist certain fluids can thus be guided by a consideration of the solubility parameter of the linear polymer as well as that of the various fluids.

2. The Solubility Parameter Concept[11]

In a solution process the states of matter are the solute, the solvent and the solution. This can be depicted in equation form as:

$$\text{solute} + \text{solvent} \longrightarrow \text{solution} \quad \text{(Eq. 1)}$$

The laws of thermodynamics require that for any physical change in matter to occur, the change in free energy (ΔG)

of the total system must be negative. For the process described in equation 1:

$$G(\text{solution}) < G(\text{solute}) + G(\text{solvent}) \qquad \text{(Eq. 2)}$$

The value of ΔG for any physical proces is given by the well known free energy equation

$$\Delta G = \Delta H - T\Delta S \qquad \text{(Eq. 3)}$$

Since the entropy term (ΔS) is always positive, the enthalpy term (ΔH) must be zero or lower in value than the $T\Delta S$ product term.

Hildebrand[11b] has shown that the value of the enthalpy term for a solution process is given by:

$$\Delta H = V\Phi_1\Phi_2(\delta_1 - \delta_2)^2 \qquad \text{(Eq. 4)}$$

where: V = total volume of system in question
Φ = volume fraction of respective components
δ = solubility parameter of respective components

Equation 4 reveals that closely matching the values of the solubility parameter for each component will minimize the value of the enthalpy term (ΔH) thus enabling the free energy change (ΔG) for the process to be favorable. For the solution of a polymer in a solvent, the respective solubility parameter values should be closely equal. Conversely, insolubility is favored when there is a disparity between solubility parameters. Hence, good fluid resistance can be predicted if the fluid and polymer have broadly distinct solubility parameter values.

3. Generic Polymer Type

After deciding upon a preferred polymeric solubility parameter, a choice of generic polymer type must be made. Historically, this choice would be made intuitively based on empirical performance. For example, a synthetic program might be limited to epoxy polymers because these are classically found to have better resistance to a certain fluid than say acrylics.

Invoking the solubility parameter concept removes the limitation on polymer type. Any polymer having the required solubility parameter value should display acceptable performance.

4. Functional Groupings

A considerable part of polymer design is selection of functional groups. Atomic groupings contribute to the total solubility parameter of a polymer[12,13,14] and in this manner can be used to prepare a synthetic polymer of known solubility parameter value.

Certain functional groups are incorporated for their ability to enhance dispersion into aqeuous medium. Acidic functional groups (carboxylic, sulfonic) are used where anionic dispersions are required. Alkaline functional groups (amine, sulfur) are used for cationic dispersions. And water miscible ethylene or propylene oxide repeating units are incorporated for nonionic dispersions.

Other functional groups may be considered for their ability to enter into crosslinking chemistry.

C. Polymer Synthesis

After designing a polymer to have a defined solubility parameter value with preferred functional group composition, actual synthesis of the polymer must be accomplished.

Factors considered during this task primarily involve reaction parameters. Monomeric feed rate, reaction temperature, overall reaction time, catalyst concentration all contribute to successful syntheses.

Reaction solvent is also a significant part of this task. The solvent must be judiciously chosen to be compatible with the polymer and simultaneously must tolerate an aqueous environment.

D. Aqueous Dispersion

Having synthesized the desired polymer, incorporation into aqueous medium is next required. Since polymers are organic materials and consequently are generally hydrophobic, inclusion into water results in a dispersion characterized by colloidal behavior.

1. Colloidal Characteristics

Colloids are distinct from true solutions in comparison of certain physical characteristics. Colloids are opaque; solutions are clear. Colloids sediment; solutions do not. Most of the distinctions arise from the fact that colloids are composed of discrete particles whereas true solutions are molecular entities.

Being particulate in nature, colloids are susceptible to aggregation. For reasons of long term stability, this flocculation must be prevented. Separation of particles to prevent aggregation is generally accomplished by two methods. Electrostatic charges on the particle surface result in mutual repulsion and accounts for one stabilization method. Steric layering of the surface prevents two particles from approaching closely enough for aggregation to occur and accounts for the second method of stabilization. Frequently, a combination of both methods is employed.

2. Emulsion Polymerization

Emulsion polymerization is unique in many respects. One of the unique aspects of this technology is the ability to combine synthesis and aqueous dispersion in one process. This combination is generally attributed to the action of surface active agents which mark another unique feature of emulsion polymerization technology.

Numerous texts have been devoted to the subject of emulsion polymerization[15] and a review is not warranted here.

3. Dispersion of Solution Polymers

When not practicing the technique of emulsion polymerization, solution polymerization and aqueous dispersion are separate processes. A necessary prerequisite to aqueous dispersion is incorporation of water-miscible characteristics. This can be accomplished simultaneous with or subsequent to polymerization.

One of the more common methods involves production of electrostatic charges after the polymerization.

a. Incorporation of Anionic Charges

Polymers synthesized with carboxylic acid functional groups can be converted to polyelectrolytes by reaction of the acid groups with base. This neutralization results in carboxylate anions pendant to the polymer backbone. Dispersion of this species into aqueous medium produces a colloid stabilized by anionic electrostatic charges and is termed an "anionic" dispersion.

b. Incorporation of Cationic Charges

Polymers synthesized with amine functional groups can also be converted to polyelectrolytes by reaction with acid. Upon dispersion, the resultant colloid is stabilized by cationic charges attributed to the reacted amine and is termed a "cationic" dispersion.

c. Dispersion Techniques

Following incorporation of water-miscible features into the polymer, dispersion into water is next required. This is generally accomplished by adding water to the polymer solution under high speed agitation. Originally a water-in-oil type dispersion is produced. However, continued addition of water to the desired concentration ultimately results in phase inversion with its accompanying dramatic viscosity reduction and an oil-in-water dispersion is prepared.

In certain cases, the polymeric solution viscosity may be too high to allow effective dispersion into water even under high shear. In these cases, the original solution is reduced in viscosity by addition of solvent (preferrably low boiling). Dispersion is then accomplished in the usual manner resulting in a concentration which is lower than that normally preferred. The concentration can be increased to the preferred level by removal of the low boiling added solvent usually under vacuum.

4. Film-formation from Dispersion

Since the dispersion prepared is colloidal in behavior, application to the substrate and subsequent film formation is much more complicated than in the case of molecular solutions. The complication arises as a result of the colloidal nature which requires coalescence of the discrete particles into a continuous molecular film.

Many factors affect the film formation process including the polymeric glass transition temperature, ambient temperature and humidity.

Many articles have been devoted to the subject of film formation from polymer dispersions[16] and a review will not be attempted. The point of introducing this topic is that film formation from dispersion cannot be taken for granted.

E. Formulation

After dispersing the synthetic polymer into aqueous medium, the final process prior to evaluation is formulation. Blending with various materials produces a mixture which is the functional coating. Some of these materials are: 1) coalescing agents which are used to assist in film formation from aqueous dispersion; 2) pigments which impart the desirable optical effects to the applied film; 3) a multitude of additives which correct a variety of defects from substrate wetting to defoaming; and 4) crosslinking agents which are used to enhance chemical properties of the applied film.

II. Results and Discussion

Phase three of contract F33615-78-C-5096 is devoted to the synthesis of novel waterborne polymers according to the original proposal. The lengthy introduction given in Section I stresses the fact that numerous underlying considerations were required prior to undertaking the actual task. Summarizing once again four steps are prerequisite to the evaluation of a novel waterborne polymer. These are; design, synthesis, dispersion and formulation.

The remainder of this report will discuss the evaluation of synthetically novel waterborne polymers and will correlate to the order of the four processing steps.

In section I-B-2 design of a polymer to resist certain fluids by using the solubility parameter concept was discussed. Inherent in this design is a knowledge of the solubility parameter value of the fluid. In this application there are five fluids which may potentially contact the coating. These are: water, Skydrol 500B hydraulic fluid, TT-S-735 type III hydrocarbon, Mil H5606 hydraulic fluid, and a lubricating oil composed of diisooctyl adipate and tricresyl phosphate. Thus, the solubility parameter value of each fluid must be characterized.

A. Solubility Parameter of Test Fluids

Equation 4 has been used to display the use of the solubility parameter concept in predicting solubility. At this point, the definition of solubility parameter is in order and is as follows:

$$\delta = \left(\frac{\Delta E}{V_m}\right)^{\frac{1}{2}} \qquad \text{(Eq. 5)}$$

where: δ = solubility parameter
ΔE = energy of vaporization
V_m = molar volume

The expression ($\Delta E/Vm$) is the energy of vaporization per cubic centimeter which has been defined as the "cohesive energy density." The solubility parameter is the square root of the cohesive energy density. In solving equation 5, the energy of vaporization (ΔE) is a difficult quantity to obtain. However, theory shows that

$$\Delta E = \Delta H - RT \qquad \text{(Eq. 6)}$$

where: ΔH = heat of vaporization at temperature T
R = universal gas constant

Equations 5 and 6 indicate that the most accurate means of determining the solubility parameter of a material is from the heat of vaporization at the desired temperature. In many cases, this information is unknown (as for the case of structurally ill-defined fluids) or experimentally indeterminate (as for very high molecular weight materials). Alternate methods must then be resorted to which of necessity constitute approximation of the solubility parameter. In this work, two alternate methods for determining the solubility parameter of the test fluids have been used.

Hildebrand has given[11b] a convenient method of estimating the heat of vaporization (ΔH) from the boiling point. The expression is as follows:

$$\Delta H = 0.020\, T_b^2 + 23.7\, T_b - 2950 \quad \text{(Eq. 7)}$$

where T_b = boiling point in absolute temp.

Several of the fluids of interest to this program are very high boiling mixtures of materials and an accurate determination of the boiling point becomes difficult. In these cases, an examination of the structural identity of the fluid was made and the best approximation of the boiling point of the pure material was used.

The second method of estimating the solubility parameter of each fluid was from surface tension measurements. Hildebrand has given[11b] the expression of solubility parameter as a function of surface tension as follows:

$$\delta = 4.1 \left(\frac{\gamma}{V^{1/3}}\right)^{0.43} \qquad \text{(Eq. 8)}$$

where: γ = surface tension in ergs/cm^2

This method has been criticized for its correlation with measured values.[17] But it offers a convenient experimental technique for cases in which the heat of vaporization may be difficult to obtain.

Techniques for solubility parameter determination other than those listed above have been reported.[18]

Table 1 presents some of the physical characteristics of the five test fluids. Only those constants which are significant to the determination of solubility parameter will be given.

Table 1

Physical Characteristics of Test Fluids

Fluid	MW(theor.)	Density, g/cc (lit.)	Vm, cc/mol(theor.)	T_b, °C (lit.)	γ, erg/cm^2
Water	18(18.02)	1.000	18(18.02)	(100)	87.1
Hydrocarbon	114	0.732	155.74(147.25)	101	37.2
Lube Oil	627(370.58)	0.908(0.922)	690.53(401.93)	(405)	52.4
Hydraulic Fluid	256	0.840	304.76	246	47.6
Skydrol 500B	**243(368.37)**	**1.051(1.064)**	**231.21(346.21)**	**(415)**	53.3

The identity of each fluid has been described in the summary report covering the first 12 month activity.[9] However, a description is required at this time in order to discuss the tabulated values.

The hydrocarbon is a fluid of Federal Specification

TT-S-735 which is defined as a mixture of 70 percent isooctane and 30 percent toluene.

Lubricating oil is a mixture of 98 percent diisooctyl adipate and 2 percent tricresyl phosphate.

Hydraulic fluid is MIL-H-5606 fluid which is a petroleum oil.

Skydrol 500B is a fire resistant hydraulic fluid available from Monsanto and which is primarily tricresyl phosphate.

In most cases, the above table presents two values of the various characteristics. The nonparenthetical listing corresponds to an experimentally determined value. Molecular weights were determined by vapor phase osmometry. Densities were determined in a weight per gallon cup and converted to metric values. Boiling points were determined on a micro scale. Surface tension (γ) was measured using a Du Nouy ring.

The value in parentheses corresponds to a theoretical value or a value reported in the literature for a pure substance. For example, the parenthetical values listed for Skydrol 500B are those found or calculated for tricresyl phosphate. Those listings for lube oil are based on pure di 2-ethylhexyl adipate.

Based on the values listed in Table 1, the solubility parameter for each fluid was calculated according to the two methods described by equations 7 and 8. These solubility parameter values are compared in Table 2.

Table 2

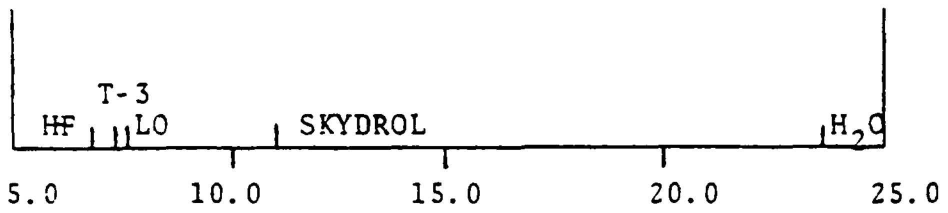
Comparative Solubility Parameters of Test Fluids

Fluid	$\delta(T_b)$	$\delta(\gamma)$	δ(lit.)
Water	21.2	18.5	23.5
Hydrocarbon	7.4	9.4	7.9
Lube Oil	7.4	8.8	7.7
Hydraulic Fluid	6.8	9.5	
Skydrol 500B	8.0	10.4	11.3

Included in the table is a value reported in the literature for pure substances which are approximations of the test fluids. For example, the literature value for Skydrol 500B is that value listed by Hansen[19b] for tricresyl phosphate. The values for water and Lube Oil (as dioctyl adipate) are also reported by Hansen[19]. The value for Type III hydrocarbon is that value listed by Hoy[20] for a 75:25 volume mixture of n-octane and toluene. No literature value for hydraulic fluid could be found.

As the table indicates the values obtained by the surface tension method are generally higher than those obtained from the boiling point data. The boiling point values are generally in closer agreement with values predicted from the literature.

Since any prospective coating must resist the entire body of fluids, an examination of the range of solubility parameters covered by the body of fluids may be helpful. A solubility parameter spectrum can be constructed from the data in Table 2 and is presented in figure 1.



Fluid Solubility Parameter (δ)

Figure 1. Solubility parameter spectrum of corrosive aircraft fluids.

As the figure indicates, three distinct solubility parameter groupings are apparent. Type III hydrocarbon (T-3), lubricating oil (LO), and H5606 hydraulic fluid (H-F) comprise one group at the low end of the spectrum; water is alone and comprises a group at the high end of the spectrum; and Skydrol 500B is also unique in the intermediate solubility parameter range. This positioning for Skydrol evidently accounts for the general lack of resistance of many commercial resins to this fluid.

In constructing a spectrum of this type, the feature of most striking interest to this application is the extreme gap between Skydrol and water. A resin designed to resist the body of fluids as a whole should have a solubility parameter value falling within this gap.

B. Solubility Parameter Value of Commercial Resins

In order to verify the postulate that a resin required to resist the body of fluids should have an intermediate solubility parameter value, examination of resins of known performance was conducted. Phases one and two provided identification of preferred resins for this purpose. And a characterization of the resin's solubility parameter to locate the positioning in relation to the spectrum of figure 1 was attempted.

As discussed previously, the most accurate means of determining the solubility parameter is from heat of vaporization data. This is impractical for high molecular weight polymers due to insufficient vapor pressure. As a result, indirect methods of solubility parameter determination are required.

Since the criterion for solution has been defined as a near equality of the solubility parameter values for the solute and solvent (Eq. 4), the solubility parameter of polymers is generally determined experimentally by solution properties in solvents of known solubility parameter. The solvent which imparts the optimum solution property defines the solubility parameter of the polymer.

One such solution property is physical observation. Since this is rather arbitrary and a number of solvents can give the same appearance of solubility, this technique normally produces a range of solubility parameters that characterize the polymer.

A more quantitative technique utilizes intrinsic viscosity as the solution property of interest.[21] As the solubility parameter of the polymer approaches that of the solvent a greater extension of the polymer coil is expected. This enhanced extension is manifest as increased viscosity. Thus a plot of intrinsic viscosity versus solvent solubility parameter should give a curve which reaches a maximum defining the solubility parameter of the polymer.

Using this technique, the solubility parameter of a few resins evaluated for performance in phases one and two have been determined. These resins are Amsco Res 200 (Union Chemicals), Carboset XL-11 (B.F. Goodrich) and Mor Flo 40 (Morton). All are acrylic resins. Amsco Res and Carboset meet the fluid resistance requirement when cross-linked; Mor Flo does not.

Unfortunately, the two urethane resins evaluated were found to be insoluble in a variety of solvents after isolation from the aqueous medium. Thus Neo Rez R960 (Polyvinyl) and Hypol WB 4000 (W.R. Grace) could not be subjected to solubility testing.

Likewise, XD7080 (Dow) acrylic was found to be insoluble. This is unusual behavior for an acrylic resin and some degradation is suspected. Upon isolation, the resin is white and soluble in typcial solvents. However, overnight drying, even in a vacuum at ambient temperature, causes discoloration and insolubility. Since XD7080 is an amine functional cationic resin, some type of oxidative cross-linking appears to be responsible for this variable solubility behavior.

1. Solubility Parameter of Amsco Res 200

After isolation from the aqueous dispersion, the intrinsic viscosity of Amsco Res 200 was determined in a series of five solvents. The solubility parameter value taken for these solvents were those published by Hoy.[20] The solvents were: MIBK (δ 8.6), ethyl acetate (δ 8.9), MEK (δ 9.4), cyclohexanone (δ 10.4), and acetonitrile (δ 12.1).

Figure 2 shows the curve which describes the data points of this plot. The maximum occurs around δ 9.4 which defines this value as the solubility parameter of Amsco Res 200.

2. Solubility Parameter of Carboset XL-11

The intrinsic viscosity of Carboset XL-11 was determined in MIBK (δ 8.6) ethyl acetate (δ 8.9), MIBK (δ 9.4) acetone (δ 9.6), and cyclohexanone (δ 10.4). Figure 2 indicates a maximum around δ 9.4 which is identical to that for Amsco Res 200. This result is consistent with the similar chemical performances found for these two resins.

3. Solubility Parameter of Mor Flo 40

The intrinsic viscosity of Mor Flo 40 was determined in MIBK (δ 8.6), 2-heptanone (δ 8.9), acetone (δ 9.6), cyclohexanone (δ 10.4) and butyrolactone (δ 12.9). Figure 2 indicates the maximum for this curve around δ 10.4.

4. Solubility Parameter of DER 331

Although XD7080 did not lend itself to a determination

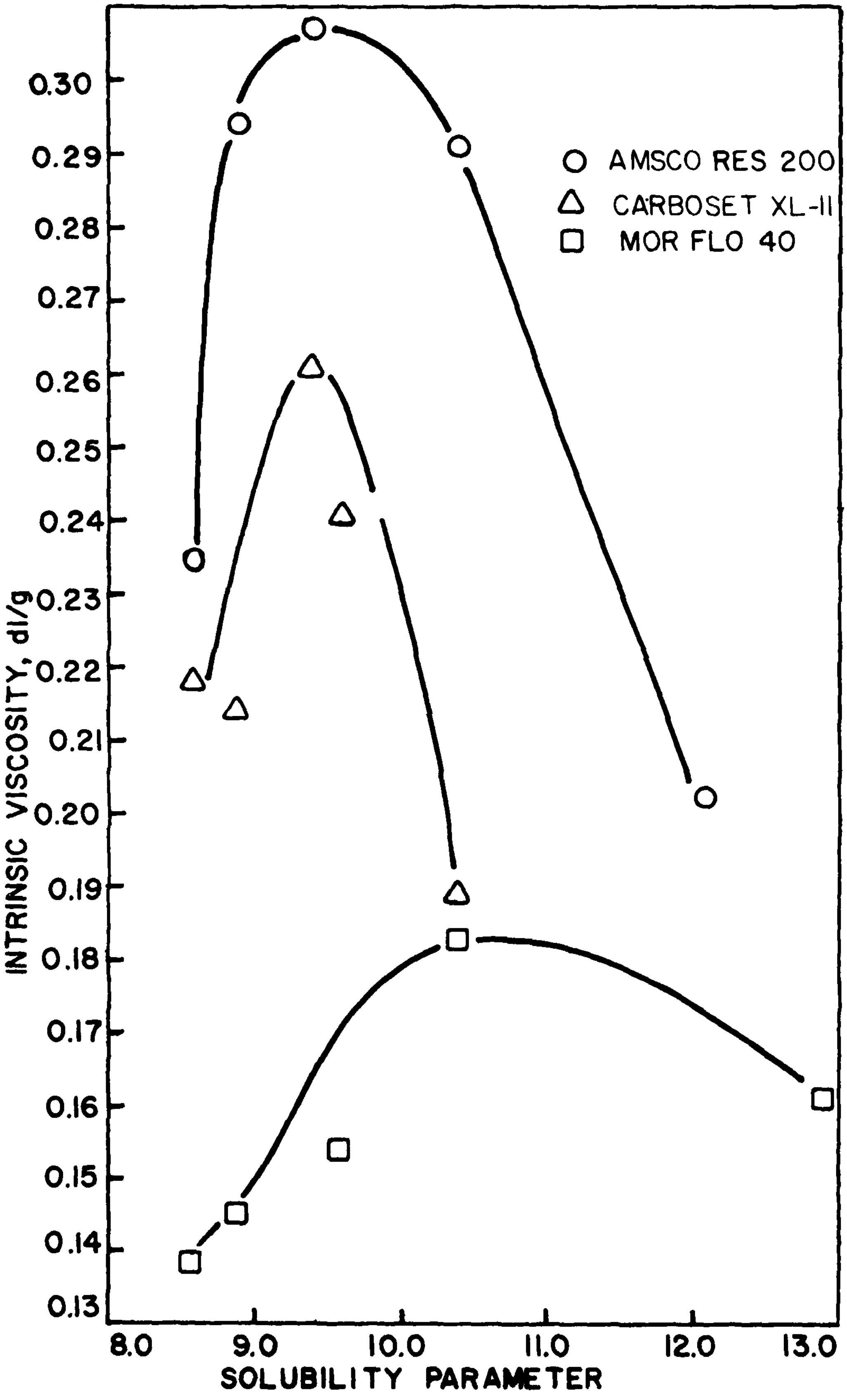


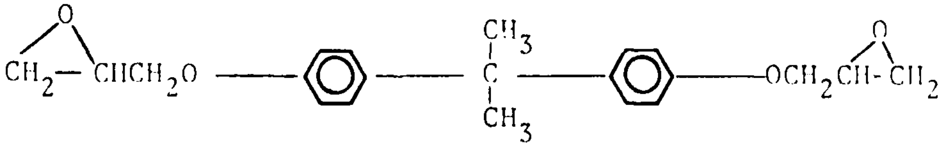
Figure 2. Solubility parameter determination of various commercial resin samples.

of solubility parameter for reasons cited, a co-component of that system was an epoxy resin, DER 331, recommended by Dow Chemical Co. This epoxy is a low molecular weight material and the intrinsic viscosity determination was not practical due to insufficient viscosity variation upon dilution. Yet, knowledge of the solubility parameter of this resin is important because the resin constitutes a significant amount of the total mass of the formulation.

In an original publication by Small[12] and in a follow up by Rheineck and Lin[13] knowledge of the structure of a polymer was shown to be sufficient to estimate the total solubility parameter of the resin. The contribution of each atomic grouping to the total solubility parameter was characterized and defined as the "Group Molar Attraction Constant." Summation of these constants over the total molecular structure gives a solubility parameter value in close agreement with the experimental value.

Recently, Fedors[14] has provided an extension to the number of groups available and eliminated the need for calculating the molecular density. Since the molecular structure of DER 331 is well defined, the solubility parameter was calculated according to Fedors' method as follows:

DER 331 strucuture:



Number	Group	Δe	Δe_i	Δv	Δv_i
2	C_6H_4	7630	15260	52.4	104.8
4	CH_2	1180	4720	16.1	64.4
2	CH	820	1640	-1.0	-2.0
4	O	800	3200	3.8	15.2
2	CH_3	1125	2250	33.5	67.0
1	C	350	350	-19.2	-19.2
2	ring,3 atoms	750	1500	18.0	36.0
			28,920		266.2

$$\delta = \left(\frac{\Sigma\Delta e_i}{\Sigma\Delta v_i}\right)^{1/2} = \left(\frac{28920}{266.2}\right)^{1/2} = 10.4 \text{ (9.9 lit.)}$$[22]

Examination of the solubility parameter values for the above four resins reveals that each falls closely within the same area of values for the fluids. In order for these resins to resist these fluids, extensive crosslinking is required. The level of crosslinking required would be expected to produce embrittlement. And these results are consistent with the performance displayed by these resins in phases one and two.[9]

C. Novel Polymer Synthesis

Location of the solubility parameter value of these resins in relation to the spectrum of fluids pertinent to this application gives an indication that a multi-purpose, commercially available resin may not suit the requirements. A specialty resin may be necessary.

This realization amounts to a justification to begin a study of synthetically novel polymers.

Section I-B-3 addressed the fact that generic polymer type is unimportant if resin solubility parameter is truly related to fluid resistance. To verify this premise, two types of polymers were considered viz. acrylics and urethanes. The only basis for deciding upon these two was their relative simplicity in laboratory synthesis.

Carrying the premise further, not only should the polymer type be unimportant, but the type of crosslinking should be equally unimportant for desirable fluid resistance. Two types of crosslinking reactions have been invoked for ambient cure and these have been discussed in detail.[9] The carboxylic acid-aziridine cure mechanism applies to anionic aqueous dispersions; the epoxy-amine mechanism is encountered with cationic dispersions. Hence, cationic and anionic dispersions of each polymer type were prepared.

Although the type of crosslink bond may be unimportant in achieving desirable fluid resistance, one aspect of crosslinking cannot be neglected when comparing performances. The effect of crosslink density must be considered. For this reason, one functionality level was selected and maintained constant within a series as well as among polymer and dispersion types.

Summarizing the planned approach to test the validity of the solubility parameter in guiding polymer synthesis, both cationic and anionic aqueous dispersions were considered.

Each dispersion type was to include a series of acrylic and a series of urethane polymers. And each series was to be constructed using members differing only in solubility parameter value while including the stipulation of constant functionality level.

1. Anionic Aqueous Dispersion

Anionic electrostatic charges are incorporated into the backbone of a solution polymer through the carboxylic acid functionality. Reaction of this functionality with volatile organic amines give rise to the carboxylate anion for stabilization of the dispersion. Upon film formation, the amine evaporates along with the other volatile components leaving the carboxylic acid functionality available for subsequent cure chemistries.

a. Anionic Acrylic Aqueous Dispersions

A series of acrylic solution polymers was designed varying solely in solubility parameter value. Part of the design included carboxylic acid monomers such as acrylic acid and itaconic acid. The polymers were treated with triethylamine and dispersed into water. The dispersions were then formulated with polyfunctional aziridine resins and spray applied to aluminum substrate. After seven days drying under constant temperature (23°C) and humidity (50%), the coated panels were evaluated for fluid resistance and flexibility. Details of the evaluation method have been discussed in a previous report.[9]

1. Acrylic Polymer Design by Solubility Parameter

A series of acrylic solution polymers was designed varying in solubility parameter values from 11 to 14. These values were chosen because they approach the midpoint of the gap in the solubility parameter spectrum between Skydrol and water. Construction of a hypothetical polymeric backbone having a given solubility parameter value was made using molar group assocition constants as suggested by Fedors[14].

According to this method, the contribution of each atomic grouping to the molar energy of vaporization and volume are summed over all the groupings comprising the molecular structure. The square root of the ratio of energy of vaporization and volume is then defined as the solubility parameter of the structure.

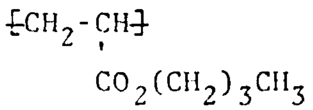
In the case of polymers, the molecular structure is considered to be the simplest repeating unit and ignores the end group contributions. For acrylic copolymers, the simplest repeating unit is ethylene with varying mole fractions of pendant functionalities. Thus in examining the solubility parameter of an acrylic copolymer, one must calculate the energy of vaporization and molar volume for each monomer present in the repeating unit. These values are multiplied by the mole fraction of that monomer. And these products are summed over the repeating unit structure to give the solubility parameter of the polymer.

The following examples will serve to illustrate the calculation.

Solubility Parameter Calculations for Some Acrylic Monomers

The contribution of each atomic group to the molar energy of vaporization and volume is summed over the molecular structure and the square root of the ratio is taken as the solubility parameter value.

For n-butyl acrylate the calculation is as follows:

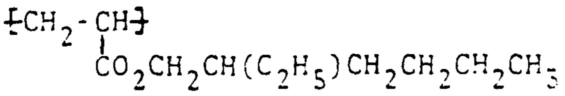


$$\left[CH_2-\underset{\displaystyle |\;\; CO_2(CH_2)_3CH_3}{CH} \right]$$

Group	Number	Δe	Δei	Δv	Δv_i
CH_3	1	1125	1125	33.5	33.5
CH_2	4	1180	4720	16.1	64.4
CH	1	820	820	-1.0	-1.0
CO_2	1	4300	4300	18.0	18.0
			10965		114.9

$$\delta = \left(\frac{\Sigma \Delta e_i}{\Sigma \Delta v_i}\right)^{1/2} = \left(\frac{10965}{114.9}\right)^{1/2} = 9.77$$

For 2-ethylhexyl acrylate the calculation is as follows:



$$\left[CH_2-\underset{\displaystyle |\;\; CO_2CH_2CH(C_2H_5)CH_2CH_2CH_2CH_3}{CH} \right]$$

Group	Number	Δe	Δei	Δv	Δv_i
CH_3	2	1125	2250	33.5	67.0
CH_2	6	1180	7080	16.1	96.6
CH	2	820	1640	-1.0	-2.0
CO_2	1	4300	4300	18.0	18.0
			15270		179.6

$$\delta = \left(\frac{\Sigma\Delta ei}{\Sigma\Delta v_i}\right)^{1/2} = \left(\frac{15270}{179.6}\right)^{1/2} = 9.22$$

Table 3 presents the values of the summation of the Δei and Δv_i terms for some common acrylic monomers. These values will be required for the calculation of the solubility parameter values of the copolymers to be synthesized.

Table 3

Energies of Vaporization and Molar Volumes of Some Acrylic Monomers

Monomer	$\Sigma\Delta ei$ (cal/mol)	$\Sigma\Delta vi$ (cm^3/mol)
n-Butyl acrylate (BA)	10965	114.9
2-Ethylhexyl acrylate (2EHA)	15270	179.6
Ethyl acrylate (EA)	8605	82.7
Methyl acrylate (MA)	7425	66.6
Vinyl acetate (VAc)	7425	66.6
Methyl methacrylate (MMA)	8080	81.9
Styrene (Sty)	9630	86.5
Acrylonitrile (AN)	8100	39.1
Acrylic acid (AA)	8600	43.6
Itaconic acid (Ita)	15910	70.0
Acrylamide (AM)	12000	32.6
Methacrylamide (MAM)	12655	47.9
2-Hydroxyethyl acrylate (HEA)	15780	75.3
2-Hydroxyethyl methacrylate (HEMA)	16435	90.6

In considering the design of acrylic copolymers having defined solubility parameter values, the entire molecular structure must be viewed. The molecular structure of the repeating unit is considered to be ethylene with varying mole fractions of functionalities pendant to the ethylene backbone. The solubility parameter of the copolymer then becomes a function of summations of the energies of vaporization and molar volumes for each monomer comprising the polymer multiplied by the mole fraction of that monomer. The following example will illustrate the calculations:

Polymer No. 2722-12

Monomer	Mol.Frac.(X)	$\Sigma\Delta ei$	$\Sigma\Delta ei*X$	$\Sigma\Delta v_i$	$\Sigma\Delta v_i*X$
EA	0.6173	8605	5311.9	82.7	51.1
Sty	0.3043	9630	2930.4	86.5	26.3
AN	0.0562	8100	455.2	39.1	2.2
Ita	0.0222	15910	353.2	70.0	1.6
			9050.7		81.2

$$\delta = \left(\frac{\Sigma\Delta ei*X}{\Sigma\Delta v_i*X}\right)^{\frac{1}{2}} = \left(\frac{9050.7}{81.2}\right)^{\frac{1}{2}} = 10.56$$

2. Synthetic Acrylic Solution Polymers

A series of polymers of increasing solubility parameter value was prepared. Since the carboxylic acid functionality undergoes reaction with the crosslinking agent (polyfunctional aziridine) in film formation, all the resins in the series were designed to have constant acid value. Maintaining consistent equivalent weight in this manner eliminates variation in crosslink density. Hence, the effect of the solubility parameter of the crosslink bond is minimized. Assuming the same extent reaction under the controlled drying conditions, chemical (fluid) resistance then becomes a function solely of the polymer's solubility parameter value.

Table 4 lists some of the physical properties of the acrylic polymer solutions that have been synthesized. The abbreviations on the line entitled "composition" refer to the acrylic monomers used to prepare the polymer. These abbreviations are relatively self-explanatory, but for clarification the reader is referred to Table 3.

Table 4

Physical Properties of Synthetic Polymers

	2722-12	2722-33	2722-50	2722-60	2722-71	2722-78
Composition	EA/Sty/AN/Ita	BA/MA/AN/AA	2EHA/Sty/AN/AA	EA/HEA/AN/AA	AM/HEA/AN/AA	BA/VAc/AN/AA
Solubility param. (δ)	10.6	11.4	12.0	12.8	13.8	11.4
Acid value, mg KOH/g-resin	26.6	24.39	21.92	21.85	24.65	31.90
Tg, °C (est)	15	28	34	57	59	41
Solids, percent	40.43	41.04	45.35	43.38	44.86	34.09
Conversion, percent	99.4	100	100	100	100	83.9
Solvent	IPA/EtOAc	MEK/EM	MEK/DMF	MIBK/NMP/MeCN	IPA/MeCN/NMP	MEK/EM
Brookfield viscosity, cps[a]	115 (3/20)	395 (3/20)	3490 (3/20)	147200 (7/20)	955 (3/20)	190 (3/20)

[a] Parenthetical entries indicate spindle/rpm for the Brookfield Synchrolectric Model RVT viscometer.

Some observations concerning the design of resins according to solubility parameter may be worthwhile here. Polymers with values up to 11 are not difficult to design. Various combinations of the more common monomers can be complied and usually result in resins ranging from 9 to 11.5. However, resins with values greater than 12 usually require the use of large mole fractions of the less common or less desirable monomers. For example, polymer 2722-50 is composed of almost 83 mole percent acrylonitrile (AN).

In addition to the design problems just referred to, the actual synthesis presents some unique problems also. Because of high solubility parameter, the selection of useful solvents in which to run the polymerization reaction becomes limited. The usual solvents such as butyl cellosolve and cellosolve acetate frequently result in polymer precipitation. Less desirable solvents such as dimethyl formamide and 2-methylpyrrolidinone must be used.

Polymer 2722-78 is an interesting addition to the study. This polymer possesses a composition identical to that of 2722-33 with one exception: vinyl acetate (VAc) is substituted directly for methyl acrylate (MA). Since the two monomers are isomeric in atomic structure, group contributions to the total solubility parameter are the same and result in the same value for each polymer.

If this study proves that polymeric solubility parameter has a direct effect on chemical performance, the two polymers should display nearly equal fluid resistance. The significance lies in the fact that equivalent chemical resistance can be achieved with the cost advantages associated with vinyl acetate as compared to methyl acrylate.

3. Aqueous Dispersion

Once a candidate polymer having the appropriate solubility parameter value has been successfully synthesized in organic solvent, dispersion into aqueous medium is the next processing step. As indicated previously, for non-neutral species, incorporation of electrostatic charges into the polymeric backbone is accomplished during this step. It is also during this step that the physical properties of the fluid mixture are transposed from a true solution to a colloidal dispersion.

Table 5 lists the properties of the aqueous dispersions prepared from the polymer listed in Table 4. All are anionic dispersions formed by neutralization of carboxylic acid functionality with triethylamine.

Table 5

Physical Properties of Synthetic Acrylic Aqueous Dispersions

	2722-16	2722-35	2722-52	2722-67	2722-73	2722-73a	2722-30
Polymer No.	2722-12	2722-33	2722-50	2722-60	2722-71	2722-71	2722-78
Solids, percent	40	30	30	38	35	40	35
Acid value, mg KOH/g-resin	26.6	24.39	21.92	21.85	24.65	24.65	31.9
pH	8.5	8.4	8.9	8.4	7.6	6.9	7.8
Density, lbs/gal	8.7	-	8.6	8.91	8.66	-	8.66
Brookfield vis, cps*	26(3/20)	-	160 (3/20)	30(3/20)	605(3/20)	1025(3/20)	70(3/20)

*Parenthetical values refer to spindle/rpm.

Two members of the series listed in the table are worthy of note. Dispersion number 2722-73a is a higher solids version of 2722-73. In accordance, increased viscosity is displayed.

Dispersion number 2722-80 is composed of a polymer (2722-78) having identical solubility parameter to dispersion 2722-35. As stated previsouly, this comparison is made to determine if solubility parameter can be used to realize an economic savings without compromising performance.

4. Formulations of Anionic Acrylic Dispersions

After the synthetic polymer has been successfully dispersed into aqueous medium, formulation into the final fluid mixture that is the actual coating is required. For a fair evaluation of the merits of the polymer alone, mixtures devoid of pigments were prepared. The dispersed polymer was blended with polyfunctional aziridine crosslinking agents as the primary additive.

Since the ultimate coating is to be applied by pressurized air spray, limitations on viscosity exist; thus the candidate formulations were prepared to meet this restriction.

Table 6 summarizes the fluid properties of the formulations prepared.

The formulations were calculated to have stoichiometrically equivalent amounts of crosslinking agent and carboxylic acid groups. This was to insure consumption of the acid which, if not completely reacted, would provide a site of water sensitivity.

Table 6

Anionic Acrylic Clear-film Formulations

	2722-19	2722-37	2722-54	2722-70	2722-75	2722-75a	2722-82
Dispersion No.	2722-16	2722-35	2722-52	2722-67	2722-73	2722-73a	2722-80
Polymer No.	2722-12	2722-33	2722-50	2722-60	2722-71	2722-71	2722-78
Solubility parameter, δ	10.6	11.4	12.0	12.8	13.8	13.8	11.4
Crosslinking agent	XAMA-7	XAMA-7	XAMA-7	XAMA-7	XAMA-7	NONE	XAMA-7
Solids, percent	38.5	25.0	31.2	39.5	22.5	18.2	29.9
pH	8.9	8.9	9.0	8.6	8.7	8.3	8.6
Viscosity, sec (#2 Zahn)	21	25	17	18	43	34	25
VOC, percent*	-	17.6	22.0	15.8	39.6	25.2	21.7

*Volatile organic compounds determined as a weight percent of the total formulation mass.

Formulation 2722-75a represents a curiosity. Previous results[9] have suggested that extensive crosslinking would be necessary to meet the performance requirements. But these results were based on commercially available resins whose solubility parameters have been determined to fall within an area predicting attack by Skydrol. Formulation 2722-75a thus represents a study of the need for crosslinking in the case of a specialty resin designed for chemical resistance based solely on solubility parameter considerations.

As indicated previously, formulation 2722-82 represents a comparison with formulation 2722-37. Both are based on resins having identical solubility parameter values, but the former is synthesized from less expensive starting materials.

5. Clear-film Evaluations

After formulation with crosslinking agents and possibly other additives, the coating is ready for application and evaluation. Coated panels are allowed to dry seven days at constant temperature (23°C) and humidity (50%). Fluid resistance and flexibility are the most significant tests evaluated.[9]

Immersion of the coated panels in Skydrol 500B, TT-S-735 type III hydrocarbon, and H5606 hydraulic fluid is for seven days at ambient temperature. Immersion in water is for four days at 38°C (100°F). Immersion in lubricating oil is 24 hours at 121°C (250°F). Fluid resistance is recorded as a decrease from original pencil hardness determined immediately after immersion. Loss of not more than one pencil unit is considered acceptable.

Three types of flexibility tests are performed. Reverse impact using a G.E. model impact tester is recorded on panels at room temperature and on panels heat aged four hours at 149°C (300°F). A minimum of 60 percent elongation is required. Low temperature mandrel flexibility (pass/fail) is performed on coated panels maintained four hours at -54°C (-65°F). A successful coating must accept a bend around the 1 inch diameter mandrel.

Fluid Resistance

Table 7 summarizes the fluid resistance performance of the coatings listed in Table 6.

Table 7

Fluid Resistance of Anionic Acrylic Coatings

Formulation	Film Thickness,mil	Original Hardness	Lubricating Oil(δ,8)	Water (δ,23)	H5606 (δ,7)	Skydrol 500B(δ,11)	TT-S-735 (δ, 7.5)
2722-19	2.5-3.1	<4B	<4B	<4B	3B	<4B	<4B
2722-37	1.4-2.4	B,HB	HB	<4B	HB	3B,4B	B
2722-54	0.5-2.0	HB	HB,F	3B,<4B	HB	HB	HB
2722-70	1.1-2.2	HB	F	<4B	HB,F	F	F
2722-75	0.8-1.0	HB	H,F	<4B	HB,F	HB	HB
2722-75a	1.0-1.3	HB	F	DF*	HB	HB	HB
2722-82	1.3-2.1	HB	HB	<4B	HB	HB	HB

***Film was dissolved by fluid.**

Since the tests are performed in duplicate, a number of entries show the result of both tests were different.

Some noteworthy trends are indicated in the table. Formulation 2722-19 was prepared from a polymer (2722-12) having a Tg (15°C) well below room temperature. As a result, the film is very soft (<4B) even prior to fluid immersion.

There appears to be a break-off point in solubility parameter where resistance to Skydrol can be expected. The break-off occurs somewhere around 12 as evidenced in the performance of 2722-37 ($\delta=11.4$) and 2722-54 ($\delta=12.0$). All the resins above solubility parameter 12 display no softening when immersed in Skydrol (or any of the organic fluids). This behavior is in agreement with the solubility parameter concept if the value for Skydrol is taken to be as observed around 11 and the others between 7 and 9. Perhaps the most striking support of this theory is indicated in the performance of 2722-75a. Recall that this formulation was prepared without a crosslinking agent. The performance of this resin as a lacquer (not crosslinked) displays resistance to all the organic fluids.

Also worthy of note is the comparative performances of 2722-37 and 2722-82. Recall that both resins have identical solubility parameter values but that 82 is prepared from less expensive starting materials. The equivalent performance of each formulation is also in agreement with the solubility parameter concept. In fact, 2722-82 appears to be more resistant to Skydrol than 2722-37. However, this performance is believed to be an artifact of increased crosslink density. Formulation 2722-82 was prepared from a resin having a larger acid value than 2722-37.

The table indicates that all formulations are softened by water. In some cases such as 2722-75a (the lacquer), 2722-75, and 2722-60 (which contain water sensitive monomers) this can be expected. But water softening of 2722-54 is unaccountable.

This anomalous moisture sensitivity leads to the suspicion of incomplete solvent evaporation (recall the use of high boiling cosolvents viz DMF and NMP) or incomplete crosslinking resulting in unreacted carboxyl groups. As a result an additional evaluation was planned. After allowing the coated panels to dry for seven days under ambient conditions, the panels were then given a one hour bake at 250^{O}F to determine if performance is improved. Table 8 displays the performance of the same formulations after this bake.

Table 8

Fluid Resistance of Acrylic Coatings After Bake

Formulation	Film Thickness,mil	Original Hardness	Lubricating Oil (δ,8)	Water (δ,23)	H5606 (δ,7)	Skydrol 500B (δ,11)	TT-S-735 (δ, 7.5)
2722-37	1.4-2.4	HB	F,H	<4B	F	<4B	HB,F
2722-54	0.5-2.0	HB	HB,F	2B,B	HB	HB	HB
2722-70	1.1-2.2	F,H	H	<4B	H	2H	H
2722-75	0.8-1.0	F	F	<4B	HB,F	F	HB,F
2722-75a	1.0-1.3	HB,F	F,H	DF*	HB	HB,F	HB,F
2722-80	1.3-2.1	HB,F	HB	<4B	HB	F,H	F

---

*Dissolved film.

The table indicates improved performance for the baked panels in almost all cases. Water still attacks the films of formulations 37, 70, 75, 75a, and 80. All but formulation 37 can be accounted for as having unreacted sites of water sensitivity. The improvement in water resistance with bake displayed by formulation 2722-54 is encouraging. This improvement may be an indication that water sensitivity was, as expected, caused by incomplete solvent evaporation or extent crosslinking. These are properties which can be compensated for with proper formulation.

Lastly, an attempt was made to arrive at more quantitative values than pencil hardness units for the determination of fluid resistance. The method selected was to measure the amount of solvent uptake in a free-film sample which had been immersed in each fluid. Solubility parameter theory would predict that as the values between the fluid and resin converge, the solvent uptake should increase; and the converse applies as well. Table 9 displays the free-film solvent swelling of each formulation.

Table 9

Anionic Acrylic Free-film Solvent Swelling

Formulation	Lubricating Oil (δ,8)	Water (δ,23)	H5606 (δ,7)	Skydrol 500B (δ,11)	TT-S-735 (δ, 7.5)
2722-37	14.6	99.4	1.7	94.9	0.6
2722-54	32.9	90	21.6	32.1	2.2
2722-70	38.7	26.1	18.3	13.3	15.4
2722-75	24.2	12.2(DF)	1.7	2.4	6.7
2722-82	26.2	190	1.5	8.0	1.6

The values in the table represent the percentage of increase in mass after immersing the free-film in the indicated fluid. The immersion conditions are identical to those of the coated aluminum panels. However, prior to immersion, the films were dried seven days at ambient then baked one hour at 250^{o}F. This treatment applies to all cases except 2722-54 which was not baked.

The data in the table indicate a fair amount of scatter. Skydrol is the only fluid in which performance is as predicted by the solubility parameter theory. This inconsistent behavior can be attributed, at least in part, to losses in mass with film dissolution. The erratic swelling in water is a good example of complications caused by film solubility. Similar solubility, although not readily apparent upon inspection of the films, may also account for the scatter displayed in the other fluids.

One must conclude that free-film solvent swelling does not provide accurate correlation with fluid resistance as determined by pencil hardness. This is true at least in the limited experimentation of these tests. More sophisticated techniques to control solvent swelling may prove otherwise.

Flexibility Performance

As discussed previously, flexibility is recorded in terms of reverse impact and low temperature mandrel bend. Table 10 details the performance of the coatings listed in Table 9.

Table 10

Flexibility of Anionic Acrylic Coatings

Formulation	Film Thickness,mil	Ambient Impact	High Temp. Impact	Low Temp. Mandrel
2722-19	2.5-5.0	<0.5	<0.5	fail 1 inch
2722-37	1.3-2.8	<0.5	<0.5	fail 1 inch
2722-54	1.0-1.4	<0.5	<0.5	fail 1 inch
2722-70	0.8-2.1	0.5	5.0	fail 1 inch
2722-75	0.7-1.2	<0.5	<0.5	fail 1 inch
2722-82	1.3-2.0	<0.5	<0.5	fail 1 inch

Entries in reference to reverse impact are recorded in units of percent elongation using a G.E. impact tester. Low temperature flexibility is a pass/fail test and refers to the diameter of the mandrel in use.

The table indicates a general lack of flexibility in all cases which is consistent with the observation that good flexibility is difficult to attain with acrylic copolymers.

b. Anionic Polyurethane Aqueous Dispersions

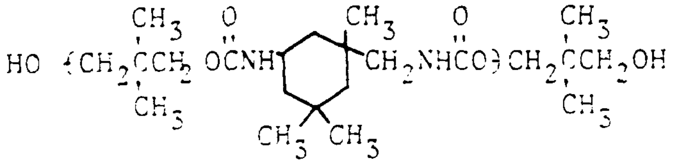
A series of urethane solution polymers varying in solubility parameter from 9 to 13 was designed. As was the case with the class of acrylics, carboxyl containing monomers were included in the design in order to make the aqueous dispersions anionic in charge. Since the desired polymers are to be carboxy-functional urethanes, the carboxyl monomer must also be hydroxy-functional. Use of such multi-functional monomers in urethane synthesis has been reported in the German patent literature.[23]

1. Urethane Design by Solubility Parameter

In the synthesis of urethane polymers, trifunctional polyols and/or isocyanates are frequently employed to produce the effect of branching. Gellation in these types of systems is to be expected but can also be prevented by adjusting stoichiometry.[24] However, in designing polymers according to solubility parameter, branching complicates the structure and introduces error into the calculations.

Consequently, all the polymers were designed to be linear and synthesized from relatively simple diols and diisocyanates.

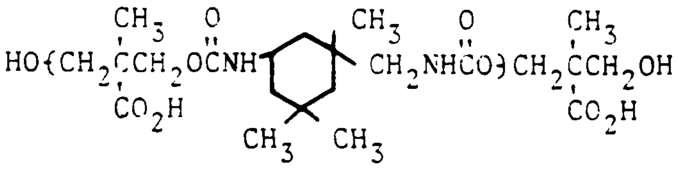
The design begins with a consideration of the smallest repeat unit structure and the contribution of each atomic grouping in this structure to the total energy of vaporization and molar volume as suggested by Fedors.[14] The group contributions are then summed over the entire molecular structure and ratio of the energy of vaporization to molar volume is calculated. The square root of this ratio is the estimated solubility parameter value. The calculations will be illustrated using the polymer of neopentyl glycol (NPG) and isophoronediisocyanate (IPDI) as an example:



Group	Number	Δe(cal/mol)	Δe_i	Δv(cm^3/mol)	Δv_i
CH_3	5	1125	5625	33.5	167.5
CH_2	6	1180	7080	16.1	96.6
CH	1	820	820	-1.0	-1.0
C	3	350	1050	-19.2	-57.6
NHCOO	2	6300	12600	18.5	37.0
6 atom ring	1	250	250	16.0	16.0
chain atoms	16				32.0
			27425		290.5

$$\delta = \left(\frac{\Sigma\Delta e_i}{\Sigma\Delta v_i}\right)^{1/2} = \left(\frac{27425}{290.5}\right)^{1/2} = 9.7$$

The above polymer, however, is not the polymer of interest because it has no carboxyl functionality. The desired polymer will be prepared using dimethylolpropionic acid (DMPA) as part of the diol mixture. The true polymer will then be a copolymer of isophoronediisocyanate with neopentyl glycol and dimethylolpropionic acid. And the solubility parameter calculations must include this additional polymeric unit.



Group	Number	Δe(cal/mol)	Δe_i	Δv(cm^3/mol)	Δv_i
CH_3	4	1125	4500	33.5	134.0
CH_2	6	1180	7080	16.1	96.6
CH	1	820	820	-1.0	-1.0
C	3	350	1050	-19.2	-57.6
NHCOO	2	6300	12600	18.5	37.0
CO_2H	1	6600	6600	28.5	28.5
6 atom ring	1	250	250	16.0	16.0
chain atoms	16				32.0
			32900		285.5

$$\delta = \left(\frac{\Sigma \Delta e_i}{\Sigma \Delta v_i}\right)^{\frac{1}{2}} = \left(\frac{32900}{285.5}\right)^{\frac{1}{2}} = 10.7$$

Table 11 presents the values of the summation of the Δe_i and Δv_i terms for some hypothetical homopolymers prepared from some common diols and diisocyanates. These values will be useful in the calculation of the solubility parameter values of the copolymers to be synthesized.

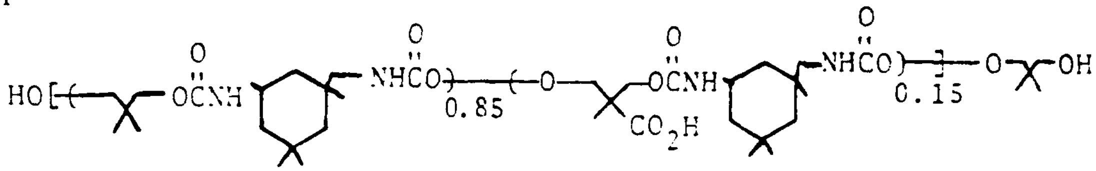
Table 11

Energies of Vaporization and Molar Volumes of Some Polyurethanes

Isocyanate	Polyol	$\Sigma\Delta e_i$ (cal/mol)	$\Sigma\Delta v_i$ (cm^3/mol)
Isophorone (IPDI)	Neopentyl(NPG)	27425	290.5
IPDI	Dimethylolpropionic(DMPA)	32900	285.5
DDI-1410	NPG	60040	696.6
DDI-1410	DMPA	65515	691.6
IPDI	2,2,4-Trimethyl-1,3-pentanediol (TMPD)	30135	339.4
Bis(4-cyclohexyl) methane (Des W)	TMPD	34670	338.8
Des W	DMPA	37435	284.9
Des W	2-Ethyl-1,3-hexanediol(EHD)	35610	339.3
IPDI	1,6-Hexanediol (DHH)	29545	313.1
IPDI	Cyclohexanedimethanol(CHDM)	31435	331.1
IPDI	Polymeg Q650	27985	246.7
IPDI	Niax PCP-0200	35825	313.0
Des W	PCP-0200	40360	344.4
IPDI	2,2'-Sulfonyl diethanol(SDE)	33425	262.4
Toluenediisocyanate (TDI)	DHH	28435	236.5
TDI	DMPA	31790	208.9
Diphenylmethane (MDI)	CHDM	38010	268.5
MDI	DMPA	39475	232.9
MDI	PCP-0200	42400	292.4
TDI	PCP-020	34715	238.4

The calculation for the solubility parameter of the copolymer must consider the mole fractions of each polymeric unit. The energy of vaporization term for the copolymer is taken as the sum of the product of energy of vaporization and mole fraction for each polymeric unit. Likewise, the molar volume for the copolymer is calculated as the sum of the product of molar volume and mole fraction for each polymeric unit. The solubility parameter, as always, is the square root of the energy of vaporization and molar volume ratio.

These calculations are illustrated for a hypothetical copolymer of isophoronediiisocyanate with a diol mixture of 85 mol percent neopentyl glycol and 15 mol percent dimethylolpropionic acid.



Copolymer Unit	Mol. Frac. (X)	$\Sigma\Delta e_i$	$\Sigma\Delta e_i{*}x$	$\Sigma\Delta v_i$	$\Sigma\Delta v_i{*}x$
IPDI · NPG	0.85	27425	23311.25	290.5	246.9
IPDI · DMPA	0.15	32900	4935.00	285.5	42.8
			28246.25		289.7

$$\delta = \left(\frac{\Sigma\Delta e_i{*}x}{\Sigma\Delta v_i{*}x}\right)^{\frac{1}{2}} = \left(\frac{28246.25}{289.7}\right)^{\frac{1}{2}} \approx 9.9$$

The desired copolymer will have an estimated solubility parameter value of 9.9.

2. Synthetic Urethane Solution Polymers

A series of urethane solution polymers varying in solubility parameter value from 10-13 was designed. Since performance is to be viewed as a function of solubility parameter, the fluid resistance of the class of urethanes can ultimately be compared to the class of acrylics. To keep the comparison valid, all resins must have similar crosslink densities. Therefore, all resins in this class were designed to have acid values similar to the resins in the acrylic class i.e. acid value (hence crosslink density) is held constant among classes as well as within a particular class.

Table 12 presents the properties of the synthetic polyurethane solutions prepared.

Table 12

Solution Properties of Synthetic Polyurethanes

	2524- 98	2524- 126	2722- 174	2524- 134	2722- 163	2722- 168	2722- 184	2722- 159
Composition[a]	IPDI/NPG	IPDI/DHH	MDI/EHD	IPDI/Q650	DesW/DANT[b]	TDI/DHB[c]	TDI/DANT[b]/DHB[c]	TDI/DANT[b]
Solubility parameter, δ	9.0	9.9	10.8	10.9	11.2	11.5	12.2	12.8
Solids, percent	70.5	61.1	62.9	60.0	64.8	67.1	65.5	63.8
Solvent[d]	MIBK	DME/EEOAc	DME	DME/EEOAc	DME	DME	DME	DME
NCO, percent	0.39	0.10	0.0	0.10	0.38	0.15	0.0	[illegible]
Acid value, mg KOH/g-resin	23.05	25.96	25.95	26.43	24.56	23.95	24.52	23.66
Brookfield vis, cps	60,800	20,000	11,420	800	11,260	19,850	15,160	
(spindle/rpm)	(4/2.5)	(3/20)	(3/5)	(3/20)	(3/5)	(3/2.5)	(3/20)	

---

a. All resins contain DMPA for carboxyl functionality; b. Bis(2-hydroxyethyl) dimethylhydantion; c. 1,4-Dihydroxybutane; d. All solutions include 2-methylpyrrolidinone (NMP) along with the solvents listed.

The identity of the materials abbreviated under "composition" can be found in Table 11 except where described in footnotes. In addition to those materials listed in the table, all polymers were designed to include dimethylolpropionic acid (DMPA) for carboxylic acid functionality as part of the diol mixture.

Table 12 indicates the acid values and NCO contents to be reasonably well within agreement. Viscosities are considerably distinct and most likely reflect variation in solvents used. Difficulties in selection of solvents have been discussed in the section dealing with acrylics and apply equally well to urethanes.

The table lists two entries for solubility parameter 9.9. Duplication was necessary because 2524-98 was found to give a non-uniform film. The discontinuous film was attributed to the solvent used (MIBK) which evaporates too quickly. Selection of 1,2-dimethoxyethane (DME) in 2524-126 remedied this problem.

3. Anionic Aqueous Polyurethane Dispersions

Colloidal dispersions of the synthetic polyurethane solutions were prepared by reaction of the carboxylic acid functionality with triethylamine. The reacted polymer is then compatible with water because of the electrostatic charges associated with the backbone.

Table 13 summarizes the properties of the aqueous dispersions prepared from the polymers listed in Table 12.

Table 13

Aqueous Dispersion Properties of Synthetic Polyurethanes

	2524-100	2524-128	2722-175	2524-136	2722-164	2722-169	2722-185	2722-160
Polymer No.	2524-98	2524-126	2722-174	2524-134	2722-163	2722-168	2722-184	2722-159
Solids, percent	35	35	38	30	29	45	37	30
Acid value, mg KOH/g-resin	23.05	25.96	25.95	26.43	24.56	23.95	24.52	23.66
pH	7.80	7.45	7.60	7.38	8.50	7.45	7.75	7.75
Density, lbs/gal	8.30	8.87	8.81	8.55	8.76	9.89	9.53	9.05
Brookfield visc,cps*	300	20	75	37.5	1785	54	80	140

*All values recorded with spindle #3 at 20 rpm on Model RVT.

Dispersion 2524-100 and 2524-128 were prepared from polymers having identical solubility parameter values. The reason for this duplication was as stated previously. Dispersion

2524-100 formed an inconsistent film because of excessively rapid solvent (MIBK) evaporation. However, the film from dispersion 2524-128 was acceptable.

The variation in solids concentration is an indication of differences in dispersion technique. The first two entries were prepared by direct dispersion i.e. the polymers were diluted with water directly to the concentration desired. The final six entries were prepared by the indirect technique in which low boiling solvent is added to dilute the original solution; this is then followed by aqueous dispersion to a low concentration then removal of the solvent by flash evaporation to a higher concentration. These techniques were described previously in section I-D-3.

4. Formulation of Anionic Polyurethane Dispersions

Formulations of the aqueous polyurethanes with equivalent amounts of aziridinyl crosslinking agents were prepared. Stiochiometric amounts were used to react all the carboxylic acid functionality in an attempt to remove any site of water sensitivity.

As with the class of anionic acrylics, all formulations were prepared without pigmentation to obtain a fair evaluation of the merits of the polymer alone.

Table 14 summarizes the fluid properties of the formulations developed for clear-film testing.

Table 14

Anionic Polyurethane Clear-film Formulations

	2524-102	2524-130	2722-177	2524-138	2722-166	2722-171	2722-167	2722-162
Dispersion No.	2524-100	2524-128	2722-175	2524-136	2722-164	2722-169	2722-185	2722-160
Polymer No.	2524-98	2524-126	2722-174	2524-134	2722-163	2722-168	2722-184	2722-159
Solubility parameter, δ	9.9	9.9	10.8	10.9	11.2	11.5	12.2	12.8
Solids, percent	33.5	24.3	37.6	20.9	25.6	40.9	35.3	28.2
pH	8.30	8.06	8.60	8.04	9.10	8.50	8.82	9.00
Viscosity, sec. (#2 Zahn)	27	26	22	28	25	20	26	30
VOC, percent*	18.7	22.4	10.3	16.5	14.5	16.9	13.3	15.5

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*Volatile organic compounds determined as a weight percent of the total formulation mass.

All formations were prepared to incorporate XAMA-7 polyfunctional aziridine as the crosslinking agent. So for brevity this material was not listed as part of the table.

Since the intended application method was air pressurized spray, efficient atomization places a limitation on viscosity. At a pressure of 55 psi, a viscosity range of 17-23 seconds measured with a #2 Zahn cup is recommended. All formulations were initially prepared in accordance with this restriction but higher viscosities were found to be tolerable.

5. Clear-film Evaluations

After formulation, the coatings are spray applied to aluminum substrate for evaluation. The coatings are allowed to dry seven days in a controlled environment and then tested for fluid resistance and flexibility. The nature of these tests has been discussed in previous sections of this report.

Fluid Resistance Performance

Table 15 summarizes the fluid resistance performance of the formulations in Table 14. The values are in units of pencil hardness. And since the tests were performed in duplicate, both values are recorded where different.

Table 15

Fluid Resistance of Anionic Polyurethane Coatings

Formulation(δ)	Film Thickness,mil	Original Hardness	Lubricating Oil (δ,8)	Water (δ,23)	H5606 (δ,7)	Skydrol 500B (δ,11)	TT-S-735 (δ,7.5)
2524-102 (8.9)	2.1-3.4	B,2B	<4B	<4B	HB	DF*	HB,B
2524-130 (9.9)	1.0-1.9	B,2B	HB	<4B	HB	<4B	2B
2722-177 (10.8)	0.8-1.3	HB	<4B	<4B	HB,B	DF*	HB,B
2524-138 (10.9)	TACKY AFTER 2 WEEKS; NOT EVALUATED						
2722-166 (11.2)	0.5-0.7	B	F	<4B	HB	<4B	F,HB
2722-171 (11.5)	0.7-1.0	HB	F	<4B	HB	DF*	HB,B
2722-167 (12.2)	0.7-1.1	B	F	<4B	2B	DF	HB
2722-162 (12.8)	0.5-0.8	HB	F,H	<4B	HB	4B,<4B	HB

---

*Dissolved film.

The most notable of the table entries is formulation 2524-138. The film of this polymer was soft and sticky to the touch even after two weeks drying. This behavior can be attributed to the polymer upon which this formulation is based. Specifically, the polymer was prepared from an oligomeric diol, Polymeg Q650, marketed for its ability to enhance flexibility. Apparently, the effect of this oligomer is to lower the Tg. The resulting polymer has a Tg well below room temperature manifest as a very soft film.

The remaining formulations exhibit the expected trends. As the polymeric solubility parameter diverges from that of the fluid, resistance is obtained. However, this trend does not apply to water and Skydrol 500B. All formulations are attacked by these two fluids.

With respect to similar performance for the class of anionic acrylics, this apparent inconsistency with predicted results was believed to be an artifact of residual high boiling cosolvent (NMP) rather than an indication of the polymer's performance. As with the class of acrylics then, the panels were given at bake cycle of 250°F (121°C) for one hour after drying seven days at ambient temperature.

Table 16 lists the fluid resistance performance of the coatings dried seven days at 23°C, then baked at 121°C for 60 minutes.

Table 16

Fluid Resistance of Anionic Polyurethanes After Bake

Formulations (δ)	Film Thickness, mil	Original Hardness	Lubricating Oil (δ,8)	Water (δ,23)	H5606 (δ,7)	Skydrol 500B(δ,11)	TT-%-735 (δ,7.5)
2524-102 (9.9)	2.1-3.4	HB	<4B	<4B	HB	DF*	HB
2524-130 (9.9)	1.0-1.9	HB	HB	<4B	F	<4B	F
2722-177 (10.8)	0.8-1.3	HB	<4B	HB,2B	HB	<4B	HB
2524-158 (10.9)	TACKY FILM; NOT EVALUATED						
2722-166 (11.2)	0.5-0.7	HB,F	HB,F	<4B	HB	<4B	HB,F
2722-171 (11.5)	0.7-1.0	HB,F	F	<4B	HB	<4B	HB,F
2722-187 (12.2)	0.7-1.1	F,H	H	<4B	HB,F	<4B	F
2722-162 (12.8)	0.5-0.8	HB,F	H	<4B	HB,F	HB,F	HB,F

---

*Dissolved film.

The table indicates a general overall improvement upon baking; this is particularily noticeable in ratings of the original film hardness. Whether this improvement is attributed to loss of residual solvent from the film or to greater crosslinking is not clear. Probably both effects contribute.

The results of this study however seem to support the solubility parameter premise for organic fluids. Resistance to each fluid is achieved as the polymeric solubility parameter deviates from that of the fluid. Even resistance to Skydrol is attained with a resin of solubility parameter 12.8. This is consistent with the observation for acrylics.

Resistance to water, however, appears to be a different case. In only one formulation (δ, 10.8) was water resistance achieved. In viewing very similar performance for anionic acrylics, use of the solubility parameter theory to predict water resistance may not apply. Factors other than pure solubility (e.g. hydrolysis reactions or hydrogen bonding effects) may be more significant in accounting sensitivity to this particular fluid.

Flexibility Performance

As previously described three types of flexibility tests are performed on the coated panels. Two tests are related to reverse impact and one test is designed to rate the low temperature flexibility.

Table 17 details the flexibility performance of the anionic polyurethane formulations.

Table 17

Flexibility of Anionic Polyurethane Formulations

Formulation	Film Thickness,mil	Ambient Impact	High Temp. Impact	Low Temp. Mandrel
2524-102	3.5-5.0	<0.5	<0.5	fail 1 inch
2524-130	1.5-2.7	<0.5	<0.5	fail 1 inch
2722-177	0.6-1.4	<0.5	<0.5	fail 1 inch
2524-138	NOT EVALUATED			
2722-166	0.4-0.8	<0.5	<0.5	fail 1 inch
2722-171	0.6-1.0	<0.5,0.5	<0.5	fail 1 inch
2722-187	0.8-1.2	<0.5	<0.5	fail 1 inch
2722-162	0.6-1.0	<0.5	<0.5	fail 1 inch

The table indicates that flexibility is very poor in all formulations evaluated.

2. Cationic Aqueous Dispersion

Cationic electrostatic charges are incorporated into a polymeric backbone through the amino functionality. Reaction of this functionality with volatile organic acids produces the ammonium cation which is responsible for dispersion stabilization. Upon film formation, the acid evaporates along with other volatile components of the formulation and leaves the amine group available for cure reactions.

The epoxy functionality is commonly used in conjunction with amines for ambient curing reactions. However, when the amine is part of a polymeric backbone, steric hindrance prevents rapid, complete reaction. For this reason, pendant amine functionality is desirable. Furthermore, since the amine group is to react with an epoxy group, primary or secondary amines are preferrable to tertiary amines.

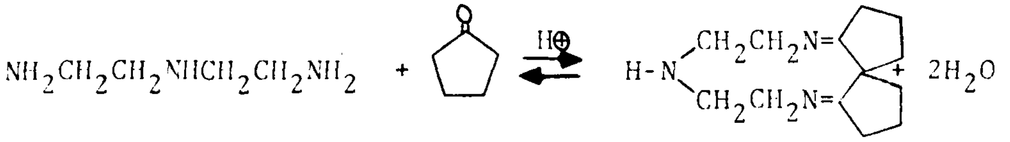
These latter merely catalyze epoxy-epoxy reactions whereas the former actually react to form covalent bonds with the epoxide.

a. Cationic Polyurethane Aqueous Dispersions

The incorporation of amino fucntionality pendant to a polyurethane backbone is not as simple as the analogous carboxylic acid functionality. The amino group is more reactive with an isocyanate than is the hydroxyl group. Consequently, the polyurethane must be synthesized prior to reaction with an amino group.

Literature techniques[25] have reported addition of a triamine in the presence of excess ketone solvent to an isocyanate terminated prepolymer. Gellation is presumably prevented by intermediate formation of the ketimine.

A similar technique will be employed for the synthetic urethanes. The ketimine (3) of diethylenetriamine (1) and cyclopentanone (2) will be synthesized and isolated according to equation 9.



(Eq. 9)

1 2 3

The imine (3) will then be added to an isocyanate terminated prepolymer. The resultant adduct will be designed to have an amine equivalent weight similar to the acid equivalent weight of the anionic acrylics and urethanes. In this fashion, variation in crosslink density will be minimized. And, assuming complete reaction, performance can be interpreted as a function solely of solubility parameter.

Upon reaction with volatile acid and dispersion into water, the imine is hydrolyzed leaving primary amine groups for crosslinking with epoxy groups.

1. Urethane Design by Solubility Parameter

The design of polyurethanes having selected solubility parameter values has been discussed in section II-C-1-b-1 for anionic dispersions. The calculations presented therein apply equally well for cationic urethanes. However, since cationics are prepared by reaction subsequent to prepolymer synthesis, copolymers are not encountered as in the case of anionics. The calculation of the polymer's solubility parameter value then becomes simplified in that mole fractions of coreactants are not required.

2. Synthetic Polyurethane Solutions

A series of urethane solution polymers ranging from 10 to 13 in solubility parameter value was designed. In order to evaluate the effect of the resin solubility parameter alone, all resins were designed to have similar equivalent weights. Furthermore, the desired equivalent weight was calculated to be similar to that of the anionic acrylic and anionic urethane polymers.

Table 18 describes the solution properties of the synthetic urethane prepolymers prior to imine addition.

Table 18

Solution Properties of Urethane Prepolymers

	2722-109	2722-105	2722-140	2722-116	2722-132	2722-149	2722-17[illegible]	[illegible]
Composition	DesW/HD	IPDI/CHDM	MDI/Q650	DesW/PCP-0200	TDI/BisA	DesW/DANT	TDI/DANT/CHDM	[illegible]
Solubility parameter, δ	9.[illegible]	9.7	10.1	10.4	11.5	11.3	[illegible]	[illegible]
Solids, percent	62.5	64.4	40.0	61.3	50.0	50.0	40.0	[illegible]
Solvent	DME/BL	DME/LEOAc/BL	DME/NMP/CH	DME/BL	DME/BL/CH	DME/BL	DME/BL	DM[illegible]
NCO, percent	0.83	0.88	0.94	0.53	0.83	0.85	0.68	[illegible]

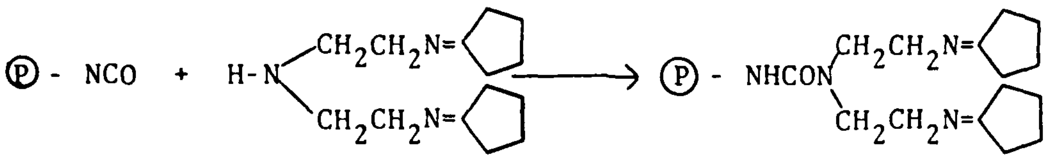
For clarification of the symbols describing resin composition, the reader is referred to Table 11. The only materials not listed in the table are bisphenol A (Bis A) and bis (2-hydroxyethyl) dimethylhydratoin (DANT). Polymeg Q650 and NIAX PCP-0200 are difunctional hydroxy-terminated prepolymers. Polymeg Q650 is a tetramethylene glycol polyether and PCP-0200 is a caprolactone polyester.

As was the case with acrylics, selection of efficient solvents to run the polymerization is difficult particularily with the higher solubility parameter resins. Most of the solvent blends were modified to use butyrolactone (BL) as the high solubility parameter component replacing 2-methylpyrrolidinone (NMP). Because of amine-like character and the potential for flocculation, use of NMP as a cosolvent is not a preferred choice. In some cases, cyclohexanone (CH) was required.

The relatively large values of percent NCO reflect the fact that the polymers are isocyanate terminated but are substantial in molecular weight.

No values for solution viscosity were recorded because the solutions were extremely viscous-another indication of high molecular weight.

After synthesis in solution, the prepolymer is reacted with imine 3 (Eq. 9) to produce prepolymer adduct terminated with imine functionality. Equation 10 displays the reaction.



(Eq.10)

3

Table 19 summarizes the solution properties of the prepolymer adducts.

Table 19

Solution Properties of Prepolymer-Imine Adducts

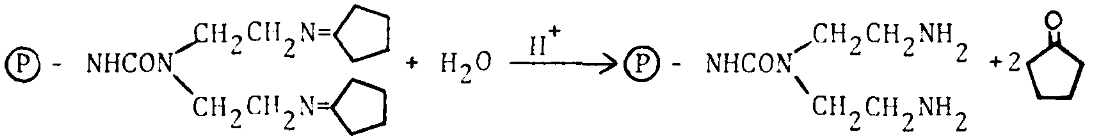
	2722-110	2722-105	2722-141	2722-117	2722-134	2722-150	2722-180	2722-155
Polymer No.	2722-109	2722-103	2722-140	2722-116	2722-132	2722-149	2722-179	2722-154
Solids, percent	50.0	50.0	40.4	50.0	51.4	53.0	43.7	42.9
Equivalent wt.	2366.3	2118.0	2011.3	4038.5	2688.0	2248.0	3227.5	2024.7

With the exception of adducts 2722-117 and 2722-180, the amine equivalents are fairly well within agreement. These values are also similar to carboxyl equivalent weights of the anionic acrylics and urethanes.

The reduced solids concentrations compared to the original solutions indicate the extreme viscosities. Prior to addition of the imine 3, the polymer solutions had to be diluted for efficient agitation. In spite of this, the resultant mixtures were equally high in viscosity. Presumably, the effect of hydrogen bonding associated with introduction of amine groups contributes to the increased viscosity.

3. Aqueous Dispersion

The prepolymer-imine adduct is made dispersible into water by reaction with acetic acid. Since imine formation (equation 9) is an equilibrium reaction, dispersion into water hydrolyzes the imine. The resultant product is a polymer with pendant primary amine groups as shown in equation 11.



(Eq.11)

The liberated amines are neutralized by the acetic acid forming ammonium cations which stabilize the dispersion. Upon film formation, acetic acid evaporates along with other volatile components leaving free amine for cure reactions.

Table 20 lists the properties of the cationic polyurethane colloidal dispersions.

Table 20

Dispersion Properties of Cationic Polyurethanes

	2722-111	2722-106	2722-142	2722-118	2722-135	2722-151	2722-181	2722-156
Adduct No.	2722-110	2722-105	2722-141	2722-117	2722-134	2722-150	2722-180	2722-155
Solids, percent	25	25	25	27.9	30	36.4	35	31.3
Equivalent weight	2366.3	2118.0	2011.3	4038.5	2688.4	2248.0	3227.5	2024.7
pH	5.15	5.20	5.15	5.45	4.10	4.85	5.45	4.85
Density, lbs/gal	8.73	8.62	8.60	8.62	8.95	8.99	9.07	9.13
Brookfield vis, cps*	30	445	399	50	20	210	95	48

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*All values recorded with spindle #3 at 20 rpm on model RVT.

An indication that the dispersions are cationic is the low pH values which result from the presence of acetic acid.

The variation in solids concentration is an indication of the dispersion technique. In all cases, the indirect method of dispersion was used. The differences in direct and indirect dispersion techniques were discussed in section II-C-1-b-3.

4. Formulation of Cationic Polyurethane Dispersions

Formulations of the cationic polyurethane dispersions blended with epoxy crosslinking agents were prepared. Quantities were calculated to be in stoichiometric equivalence so as to react all the water sensitive sites.

As previously, pigmentation was not considered so as to evaluate the merits of the polymer alone. Table 21 lists the dispersion properties of the formulations developed for clear-film evaluation.

Table 21

Cationic Polyurethane Clear-film Formulations

	2722-113	2722-108	2722-144	2722-120	2722-137	2722-153	2722-183	2722-158
Dispersion No.	2722-111	2722-106	2722-142	2722-118	2722-135	2722-151	2722-181	2722-156
Adduct No.	2722-110	2722-105	2722-141	2722-117	2722-134	2722-150	2722-180	2722-155
Solubility parameter, δ	9.6	9.7	10.1	10.4	11.3	11.3	12.0	12.9
Solids, percent	24.1	23.2	22.2	25.9	26.0	33.6	33.5	28.7
pH	5.30	5.35	5.30	5.60	4.50	4.95	5.50	5.00
Viscosity, sec. (#2 Zahn)	27	25	40	17	16	24	21	25
VOC, percent*	9.5	13.4	20.8	9.2	16.2	11.1	16.5	20.0

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*Volatile organic compounds determined as weight percent.

Dow epoxy resin (DER) 331 was used in all cases as the crosslinking agent. This material is designed to give hard chemically resistant films.

5. Clear-film Evaluations

The formulations of Table 21 were spray applied to aluminum substrate and dried seven days under controlled environment. The resultant films were then evaluated for fluid resistance and flexibility.

Fluid Resistance Performance

After drying, the coated panels are subjected to immersion in various fluids. The conditions for these tests have been disussed in previous sections of this report. Table 22 describes the fluid resistance displayed by the coatings when cured under ambient conditions.

Table 22

Fluid Resistance of Cationic Polyurethane Formulations

Formulation (δ)	Film Thickness,mil	Original Hardness	Lubricating Oil (δ,8)	Water (δ,23)	H5606 (δ,7)	Skydrol 500B (δ,11)	TT-S-735 (δ, 7.5)
2722-113 (9.6)	0.4-1.5	H,2H	<4B	<4B	2H,3H	DF*	HB
2722-108 (9.7)	1.3-2.0	HB	HB	<4B	HB	DF*	HB
2722-144 (10.1)	0.4-0.8	HB	<4B	<4B	HB	<4B	<4B
2722-120 (10.4)	0.7-1.2	HB,H	2B,3B	3B,<4B	H	<4B	<4B
2722-137 (11.3)	0.3-0.5	HB,H	HB,F	DF*	F	DF*	F
2722-153 (11.3)	0.7-1.2	HB	HB,F	<4B	HB	DF*	HB
2722-183 (12.0)	1.0-1.4	HB	H,2H	<4B	HB	DF*	HB
2722-158 (12.9)	0.6-1.2	HB	2H	<4B	HB	F,H	HB

---

* Dissolved film.

As before, fluid resistance is recorded in terms of loss of original pencil hardness. Since tests are performed in duplicate, both values are indicated where different.

In relation to the solubility parameter concept, the trend in fluid resistance is as expected in most cases. The coatings immersed in lubricating oil display softening below a value of 10.4 and resistance above this value. All coatings resist H5606 hydraulic fluid. Immersion in Skydrol 500B causes softening below solubility parameter 12 while values above resist this fluid. Such performance is substantiated by the class of anionic acrylics and urethanes.

Only with TT-S-735 type III hydrocarbon does anomalous behavior appear. Two resins with solubility parameter 10.1 and 10.4 are attacked. The reason for this behavior is unaccounted.

Once again, water severely attacks all films. The effect of incomplete solvent evaporation or insufficient crosslinking under ambient conditions must be considered as contributing to this lack of resistance. Both effects would provide a mechanism of attack by water.

In order to verify these concerns, additional panels were subjected to a bake cycle to assist solvent evaporation and crosslinking. After drying for seven days under ambient conditions, the dry panels were baked at 121°C (250°F) for 60 minutes. The baked panels were then given the same immersion.

Table 23 lists the fluid resistance performance of the coatings given the above treatment.

Table 23

Fluid Resistance of Cationic Polyurethanes After Bake

Formulation (δ)	Film Thickness, mil	Original Hardness	Lubricating Oil (δ,8)	Water (δ,23)	H5606 (δ,7)	Skydrol 500B(δ,11)	TT-S-735 (δ,7.5)
2722-113 (9.6)	0.4-1.5	H,2H	<4B	2B,HB	3H,4H	<4B	H,2H
2722-108 (9.7)	1.3-2.0	F,H	HB	B,HB	F	<4B	F
2722-144 (10.1)	0.4-0.8	HB	<4B	<4B,3B	HB	<4B	<4B
2722-120 (10.4)	0.7-1.2	HB,2H	HB	B,4B	H	<4B	HB
2722-137 (11.3)	0.3-0.5	F,2H	F,H	F,H	H	DF*	F
2722-153 (11.3)	0.7-1.2	F,H	HB,F	3B	F	DF*	HB,F
2722-183 (12.0)	1.0-1.4	H	H	<4B	H	<4B	H
2722-158 (12.9)	0.6-1.2	F,2H	2H,3H	<4B	2H	2H	H,2H

*Dissolved film.

The table indicates a general overall improvement upon baking. This is expected. But applying a bake also appears to rule out extraneous effects particularly in the case of water immersion. As predicted by the solubility parameter theory, softening in water is detected as the polymer solubility parameter increases and approaches that of water but resistance is seen at lower values. The apparent erratic water softening seen around a value of 10 can be accounted for by the fact that a hydroxy-terminated polyester was used to synthesize the urethane. Polyesters hydrolyze readily.[26] And this type of behavior seems to support the premise introduced earlier that factors other than solubility may contribute more significantly to moisture sensitivity.

Performance in the other fluids is as expected and predicted by solubility parameter considerations. All the resins resist H5606 hydraulic fluid. Lubricating oil attacks the resins with lower values but has no effect on those with higher values. The performance in Skydrol is consistent with that of ambient cured films. Resistance is found above a value of 12. And TT-S-735 hydrocarbon displays predictable performance in most cases. In only one case (δ, 10.1) was attack noted. The previous study found attack at a value of 10.4 also.

Flexibility Performance

In addition to fluid resistance, the aluminum panels coated with these cationic polyurethane dispersions were tested for reverse impact and mandrel bend flexibility. Reverse impact is performed on substrate maintained at room temperature and on substrate heat aged for four hours at 149°C (300°F). Values are recorded in units of percent elongation. Mandrel bend flexibility pertains to panels maintained at -54°C (-65°F) for four hours and is a pass/fail test.

Table 24 displays the flexibility of the coatings cured under ambient conditions.

Table 24

Flexibility of Cationic Polyurethane Coatings

Formulation	Film Thickness,mil	Ambient Impact	High Temp. Impact	Low Temp. Mandrel
2722-113	0.6-1.2	60	60	fail 1 inch
2722-108	0.9-1.2	1	1	fail 1 inch
2722-144	0.3-0.9	60	60	pass 3/8 inch
2722-120	0.5-0.9	60	60	pass 3/8 inch
2722-137	0.5-0.8	<0.5	<0.5	fail 1 inch
2722-153	0.5-0.9	0.5	1	fail 1 inch
2722-183	1.7-1.7	<0.5	<0.5	fail 1 inch
2722-158	0.7-1.3	<0.5	<0.5	fail 1 inch

Some interesting structural features account for the variations in flexibility as seen in the table. Formulation 2722-113 was prepared from Desmodur W, bis(4-cyclohexyl) methane diisocyanate. Stereochemistry predicts that the cyclohexane structure is capable of chair-twist-boat conformational transpositions. Upon impact, these transpositions impart flexibility. However, the molecule can be frozen into one preferred conformation at low temperature. This phenomenon is reflected in a loss of flexibility under the mandrel bend conditions.

Somewhat improved flexibility for other polymers containing the cyclohexane structure (formulations -108, and -153) is further support that this molecule is useful in achieving flexibility. However, the lack of excellent overall flexibility indicates that other molecular features are important also.

The polymers prepared from oligomeric components (formulations -120 and -144) display the usefulness of these materials in attaining desired flexibility.

b. Cationic Acrylic Aqueous Dispersions

The incorporation of amine fucntionality pendant to an acrylic backbone is more readily accomplished than with urethanes. This procedure only requires the use of amino-functional acrylic monomers. A number of these monomers, such as dimethylaminoethyl methacrylate, are commercially available. And, as a result, cationic acrylic colloidal dispersions are relatively common, particularly in the changing electrocoat technology.

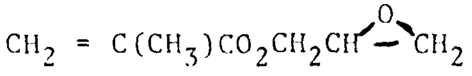
However, the restriction to ambient cure in aircraft applications requires the use of primary or secondary amine functionality for direct reaction with epoxy resin crosslinkers. Because of a preferred rearrangement to an amide in esterification with hydroxy-functional primary and secondary amines, acrylic monomers with primary amine functionality are not common.

Similarly, the literature dealing with primary amine containing acrylics is scant. In a patent issued to the Dow Chemical Company,[27a] the preparation of amine-functional acrylics by a secondary reaction with ethyleneimine was taught. Because of suspect health hazards, ethyleneimine is not a reagent of choice.

More recently, McGinniss[28] utilized the reaction of an epoxy prepolymer with a ketimine blocked diethylenetriamine adduct similar to structure 3. Unfortunately, the structure of this adduct was never fully characterized.

A similar technology was employed for the preparation of acrylic polymers of preferred solubility parameter having pendant primary amine functionality. The key feature is the reaction of an epoxy functional acrylic copolymer with a ketimine blocked adduct.

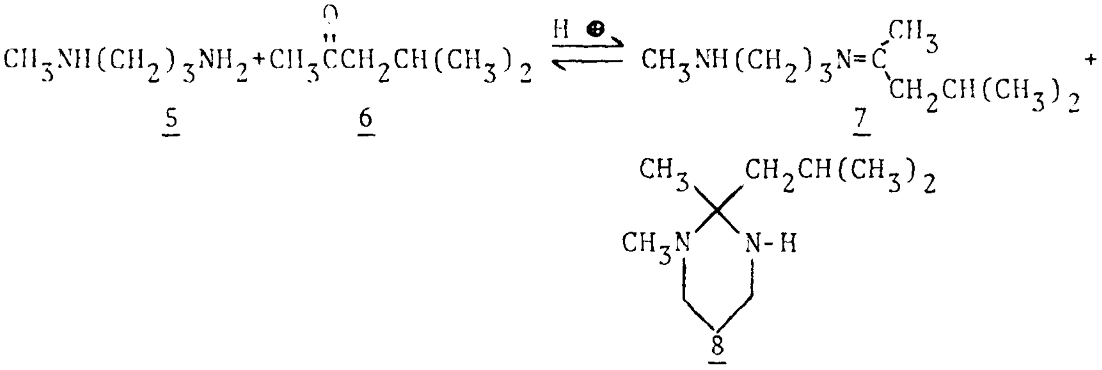
The acrylic polymers were prepared using glycidyl methacrylate (GMA, 4) to introduce epoxy functionality.



$$CH_2 = C(CH_3)CO_2CH_2\overset{O}{CH-CH_2}$$

4

The ketimine blocked adduct was the reaction product of N-methyl-1,3-propanediamine(5) and methyl isobutylketone (6) according to equation 12.



(Eq.12)

Equation 12 indicates the possibility of two structural isomers (7 and 8) in the product mixture. After addition to the epoxy polymer followed by hydrolysis upon aqueous dispersion, cyclic diamine 8 would give a polymer with secondary amine fucntionality. Isomer 7 would give a polymer with primary amine functionality. Since epoxy cure reactions are faster with unhindered primary amines, isomer 7 is preferred. Fortunatley, isomer 7 is the only material isolated as characterized by carbon and proton NMR and infrared spectroscopy.

1. Acrylic Design by Solubility Parameter

The design of acrylic polymers to have selected solubility parameter values has been discussed in section II-C-

1-a-1. The calculations described therein apply equally well to the case of cationic acrylics. However, since the primary amine functionality is introduced as a secondary reaction, the solubility parameter value of the theoretical product of GMA (4) and N-methyl-1,3-propanediamine (5) was used.

2. Synthetic Acrylic Solution Polymers

A series of acrylic solution polymers varying only in solubility parameter was designed. As was the case in the previously discussed series, all resins were designed to have consistent equivalent weights and these equivalent weights were to be consistent with those of the previously discussed series.

Table 25 lists the solution properties of these epoxy-functional acrylic copolymers.

Table 25

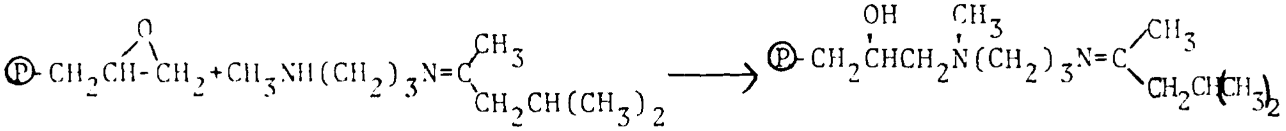
Solution Properties of Epoxy-functional Acrylic Copolymers

	2830-01	2722-193	2524-186	2830-08
Composition[a]	BA/MMA	MA/AN	BA/AN	EA/AN
Solubility parameter, δ	9.7	11.2	12.0	12.4
Solids, percent	41.1	45.2	31.6	36.4
Conversion, percent	100	100	88.5	100
Solvent	DME/MeCN/BL	DME/BL	DME/MeCN/BL	DME/MeCN/BL
Epoxide eq. wt.	1977.5	2095.2	1786.2	1798.0
Tg, °C (est.)	30	30	34	59
Brookfield vis, cps[b]	115	1290	600	2320

a. All polymers contain glycidyl methacrylate (GMA) for epoxide functionality; b. Recorded with spindle #3 at 20 rpm on model RVT.

As referred to previously in the discussion of anionic acrylics, designing acrylic polymers with solubility parameter values greater than 12 is difficult. The problem is compounded in the case of epoxy-functional acrylics. In order to obtain high solubility parameter values, use of functional monomers (such as acrylamide) is required. However, in the presence of epoxy-functionality, these monomers cause gellation. As a consequence, the design is pretty much limited to acrylonitrile (AN) to raise the solubility parameter value. This difficulty is reflected in the small number of resins which comprise this series.

After synthesis in solution, the polymer is reacted with imine 7 to produce an adduct with pendant imine functionality as indicated in equation 13.



7 9

(Eq. 13)

Table 26 lists the properties of the acrylic polymer-imine adducts.

Table 26

Solution Properties of Acrylic-Imine Adducts

	2830-03	2722-195	2830-15	2830-10
Polymer No.	2830-01	2722-193	2524-186	2830-08
Solids, percent	41.1	45.2	34.2	36.4
Amine eq. wt.	1076.5	1047.6	871.6	899.0

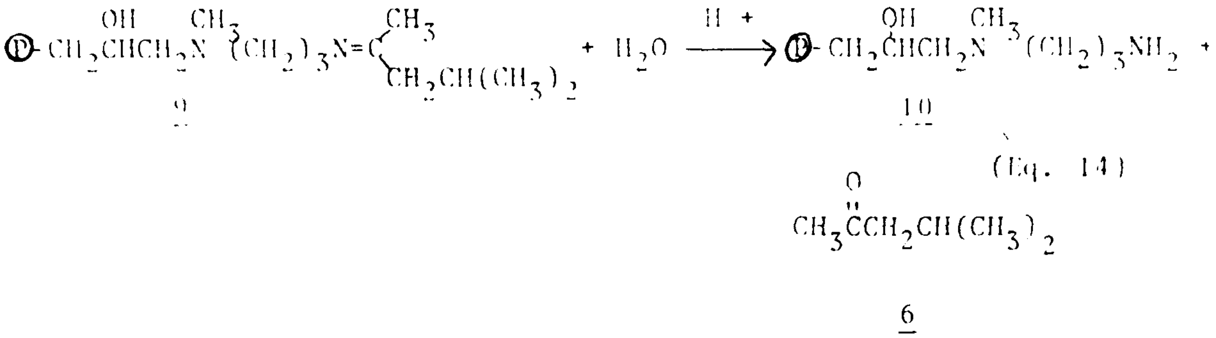
The values for the amine equivalent weight do not appear to be in line with the epoxide equivalent weight. However, upon inspection of structure 9, two amine groups are found to be present. The fact accounts for the decreased equivalent weights.

Since one of the two amino groups is seen to be tertiary amine, this group will not enter into a direct reaction with an epoxide group. The other amino group is a protected primary amine which will react directly with an epoxide. In terms of equivalent weight for crosslink density, the primary amine equivalent weight is important. And this value is twice that reported in the table. Thus, while not readily apparent, the resins of Table 26 are found to have similar equivalent weights to the resins evaluated in the previous series. And the concept of maintaining consistent crosslink density among the series still applies.

3. Aqueous Dispersions

Dispersion into aqueous medium is accomplished by first treating the polymer-imine adduct with acetic acid then adding water to the mixture under high shear. Initially, a water-in-oil emulsion is formed but further dilution with water results in inversion to an oil-in-water dispersion.

Since the formation of the imine (equation 12) is an equilibrium reaction, dispersion into water under acidic conditions results in a polymer with pendant primary amine groups. Equation 14 depicts the reaction.



$$\text{Ⓟ}-CH_2\overset{OH}{C}HCH_2\overset{CH_3}{N}(CH_2)_3N{=}C\begin{matrix}CH_3\\CH_2CH(CH_3)_2\end{matrix} + H_2O \xrightarrow{H^+} \text{Ⓟ}-CH_2\overset{OH}{C}HCH_2\overset{CH_3}{N}(CH_2)_3NH_2 + CH_3\overset{O}{C}CH_2CH(CH_3)_2$$

9 10 6

(Eq. 14)

In acidic medium, the amines are protonated and account for cationic electrostatic charges which stabilize the dispersion. The volatile acid evaporates upon film formation leaving free amines for cure reactions.

Table 27 lists the dispersion properties of the cationic acrylic polymers.

Table 27

Cationic Acrylic Dispersion Properties

	2830-05	2722-196	2830-17	2830-11
Adduct No.	2830-03	2722-195	2830-15	2830-10
Solids, percent	10	22.2	9.3	14
Amine eq.wt.	1076.5	1047.6	871.6	899.0
pH	5.5	6.5	5.6	5.4
Density, lbs/gal	7.90	8.64	8.12	8.56
Brookfield vis, cps*	215	345	580	10

*Recorded with spindle #3 at 20 rpm.

Again, the amine equivalent weight recorded is based on total amine available. The primary amine equivalent is twice the value reported in the table and more closely indicates the reactivity in crosslinking.

In all cases, the dispersions were formed by the in-direct method beginning with dilution, then disper[illegible] finally concentration by flash evaporation.

4. Formulation of Cationic Acrylic Dispersions

Formulations of the cationic acrylic dispersions with epoxy crosslinking agents were prepared. Using the value of primary amine equivalent weight, amounts were calculated to be in stoichiometric equivalence. Table 28 summarizes the formulations developed.

Table 28

Cationic Acrylic Clear-film Formulations

	2830-06	2722-198	2830-19	2830-13
Dispersion No.	2830-05	2722-196	2830-17	2830-11
Solubility parameter, δ	9.7	11.2	12.0	12.4
Solids, percent	10.2	18.4	9.6	14.7
pH	5.6	6.3	5.4	5.4
Viscosity, sec. (#2 Zahn)	35	32	30	16
VOC, percent*	23.5	7.5	46.2	20.9

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*Volatile organic compounds - by weight

All formulations were prepared with DER 331 as the crosslinking epoxy resin.

5. Clear-film Evaluations

The coatings listed in Table 28 were spray applied to aluminum substrate and dried under ambient, controlled conditions for seven days. Coated panels were then tested for fluid resistance and flexibility.

Fluid Resistance

Resistance to the various test fluids is measured as a decrease from the original pencil hardness after immersion for a defined time period. The details of the evaluation method have been discussed.

Table 29 lists the fluid resistance performance of the formulations described in Table 28.

Table 29

Fluid Resistance of Cationic Acrylic Coatings

Formulation (δ)	Film Thickness,mil	Original Hardness	Lubricating Oil (δ,8)	Water (δ,23)	H5606 (δ,7)	Skydrol 500B(δ,11)	TT-S-735 (δ,7.5)
2830-06 (9.7)	0.5-1.0	HB	<4B	<4B	HB	<4B	<4B
2722-198 (11.2)	0.5-0.9	HB	H,2H	<4B	HB	HB	HB
2830-19 (12.0)	0.7-0.9	HB	F	<4B	HB,F	HB	HB
2830-13 (12.4)	0.5-0.8	F,H	H,2H	<4B	HB	HB	F

Fluid resistance performance for the class of cationic acrylics is as predicted by the solubility parameter concept. Resistance to all fluids except water is achieved with resins having solubility parameter values above approximately 10. Below this value, attack by all fluids except H5606 hydraulic fluid can be expected.

Once again to verify the ambiguous performance in water, separate panels were given a 121°C (250°F) bake for one hour after ambient cure for seven days. Table 30 displays the fluid resistance performance of the coatings cure in this manner.

Table 30

Fluid Resistance of Anionic Acrylics After Bake

Formulation (δ)	Film Thickness,mil	Original Hardness	Lubricating Oil (δ,8)	Water (δ,23)	H5606 (δ,7)	Skydrol 500B(δ,11)	TT-S-735 (δ,7.5)
2830-06 (9.7)	0.5-1.0	HB	<4B	HB	HB	<4B	<4B
2722-198 (11.2)	0.5-0.9	F,H	H	3B	H	F,H	F,H
2830-19 (12.0)	0.7-0.9	HB,F	F	<4B	F	HB	F,H
2830-13 (12.4)	0.5-0.8	H	2H	HB	F H	F,H	H,2H

Application of a bake cycle to cationic acrylic coatings results in performance which is consistent with previous observations on baked coatings. Resistance is generally improved. Once again, however, some ambiguities are apparent in water. Moisture resistance should decrease as the solubility parameter of water is approached. This is found to be the case for the first three resins; however, the fourth resin completely resists softening in water where attack should have occurred.

Flexibility Performance

Reverse impact and mandrel bend flexibility were performed on aluminum panels coated with these cationic acrylic copolymers. Details of the tests have been discussed previously in this report.

Table 31 lists the flexibility of these cationic acrylic coatings.

Table 31

Flexibility of Cationic Acrylic Coatings

Formulation	Film Thickness,mil	Ambient Impact	High Temp. Impact	Low Temp. Mandrel
2830-06	0.5-1.1	0.5	1.0	fail 1 inch
2722-198	0.5-0.9	1.0	5.0	fail 1 inch
2830-19	0.5-0.8	<0.5	2.5	fail 1 inch
2830-13	0.5-0.9	<0.5	60	fail 1 inch

Values for reverse impact are in units of percent elongation; low temperature flexibility is a pass/fail test.

Table 31 indicates that in general the flexibility of cationic acrylic coatings is found to be poor.

D. Correlation of Fluid Resistance with Polymeric Solubility Parameter

The introductory section on Polymeric Design (I-B) discussed the reasoning for selecting the solubility parameter concept to direct the synthesis of resins displaying specified fluid resistance. One advantage was removal of any limitation on generic polymer type. Polymers having the same solubility parameter value should have very similar fluid resistance performance regardless of generic type.

This premise can be tested by construction of a plot of resin solubility parameter versus resistance in a specified fluid. Theory predicts that resistance should be enhanced as the resin solubility parameter diverges from that of the fluid-and the converse. Furthermore, a plot of several resin types on the same graph should produce a family of curves of very similar performance.

Graphs like those just described were constructed from the fluid resistance performance data compiled in the foregoing tables. Unfortunately, fluid resistance performance is recorded in terms of pencil hardness units. A plot of pencil hardness versus solubility parameter does not give the full impact of resistance to the specified fluid. A plot of decrease from the original hardness rating after immersion in the fluid is more significant.

Since all tests were performed in duplicate some results indicate different pencil hardness ratings. A convention to indicate these differing results in values that can be easily plotted was defined. The convention selects an arbitrary number for each pencil hardness rating according to the following scale:

4H	3H	2H	H	F	HB	B	2B	3B	4B	<4B
9	8	7	6	5	4	3	2	1	0	MAX

Consider as an example, the performance of anionic acrylic coating 2722-37 in TT-S-735 hydrocarbon. The polymer solubility parameter was 11.4. Two retain panels not immersed were rated for pencil hardness as B and HB. These pencil ratings provide an average arbitrary scale rating of 3.5. Upon immersion in the hydrocarbon fluid two panels were each given a pencil rating of B. This transforms to a scale rating of 3. And the decrease in pencil hardness for the coating immersed in this fluid would be 0.5. The point on a graph of fluid resistance in TT-S-735 versus resin solubility parameter would have coordinates 0.5, 11.4.

In some cases, pencil hardness ratings after immersion were found to be greater than before immersion. This was frequently found to occur in lubricating oil which is conducted at 121°C (250°F) and may be attributed to an incidentally imposed bake. In cases such as these, the decrease was rated as 0 instead of indicating the actual increase.

Likewise any coating softened to a pencil rating less than 4B was given a MAX rating for decrease rather than the corresponding 4 or 5 scale units.

All coatings were evaluated after curing under two sets of conditions. Fluid resistance was recorded after curing under ambient conditions and after curing under ambient followed by a bake. Correlation of resin types under both sets of cure conditions was attempted.

1. Ambient Curing

Performance of the various resin types cured under ambient conditions can be compared by examining data for immersion in each fluid. This data is found in the various tables which discuss clear-film evaluations of fluid resistance recorded in units of pencil hardness.

The data has been compiled, transposed to scale units suitable for graphical representation, retabulated and plotted. Tables A-1 to A-5 of the appendix section list this compiled data.

a. H5606 Hydraulic Fluid (6, 7)

Figure 3 presents the performance of the various resin classes cured under ambient conditions and immersed in H5606 hydraulic fluid. The overlap of all the curves indicates that each resin class effectively resists this fluid. Each series begins with a resin of solubility parameter well removed from that of the fluid and increases from this initial point. Thus the performance is as expected.

b. TT-S-735 Type III Hydrocarbon (δ, 7.5)

Figure 4 displays the resistance of the various classes cured under ambient conditions to TT-S-735 hydrocarbon fluid. The figure indicates that complete resistance to this fluid can be achieved with resins of solubility parameter above 11.0. The softening displayed by resins below 10.0 is understandable considering the solubility parameter of this fluid (7.5). However, the severe attack displayed by the cationic urethanes around δ 10.5 is unaccountable. The fact that the cationic resins seem to be more susceptible to attack by this fluid than the anionic resins may be an effect of incomplete crosslinking of the aromatic epoxy (DER 331).

c. Diester Lubricating Oil (δ, 8)

Figure 5 depicts the resistance of the various resins cured under ambient conditions to the diester lubricating oil. The curves indicate very similar performance among the various classes with good resistance above a solubility parameter value of approximately 11. This fluid can be expected to attack resins with solubility parameters below about 10.5.

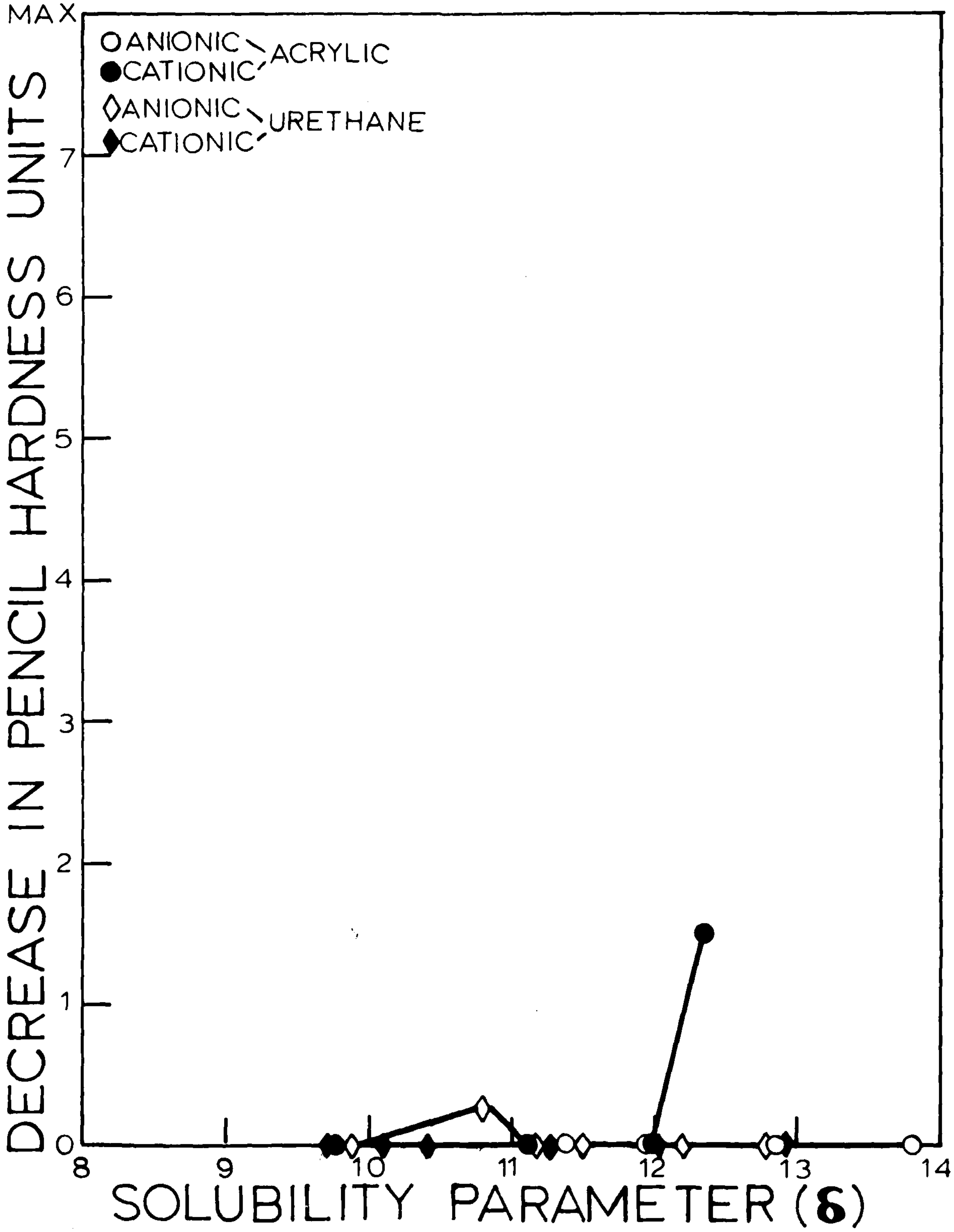

Figure 3. Effect of solubility parameter on resistance to H5606 hydraulic fluid (δ,7). Ambient cure.

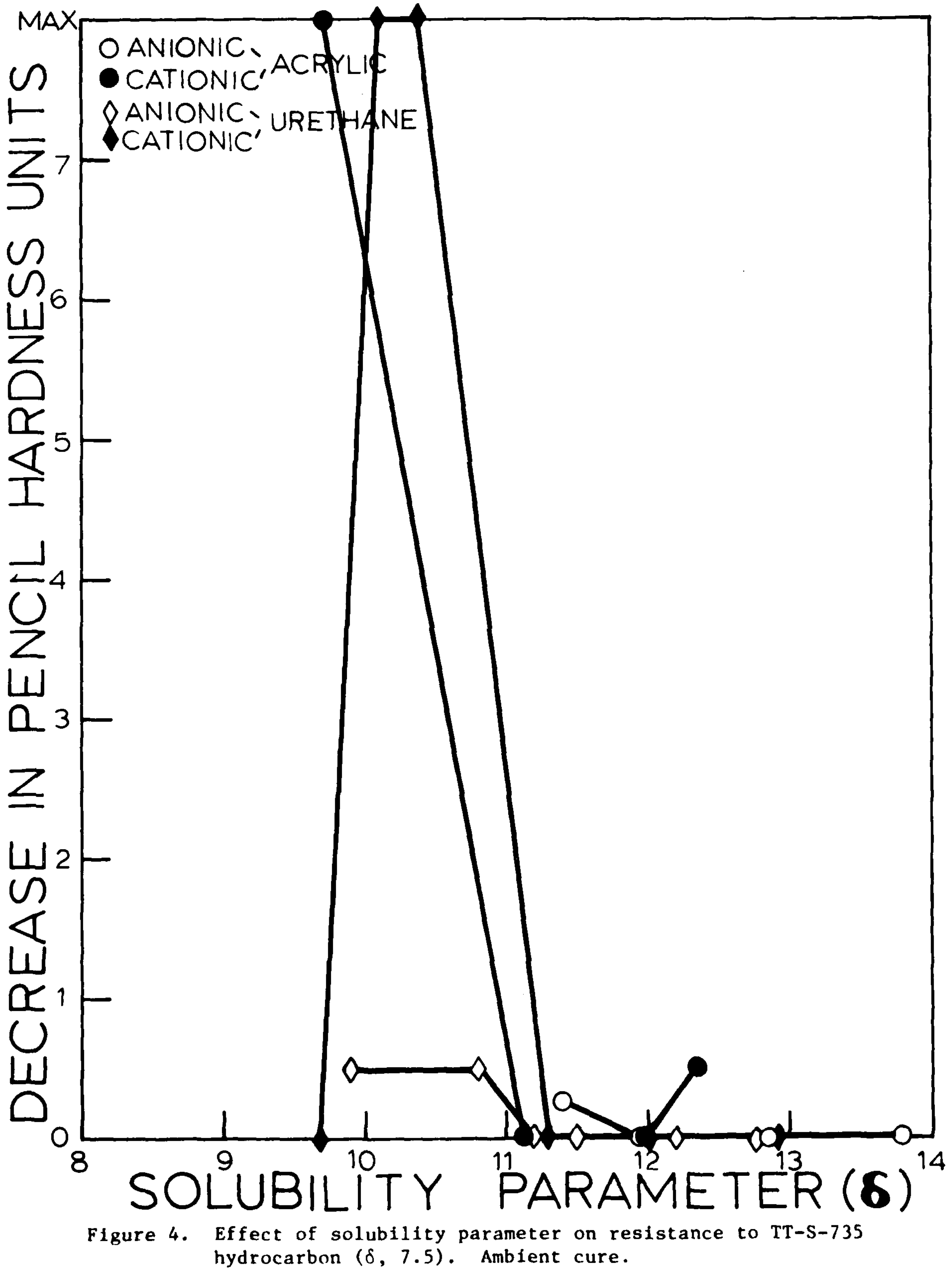

Figure 4. Effect of solubility parameter on resistance to TT-S-735 hydrocarbon (δ, 7.5). Ambient cure.

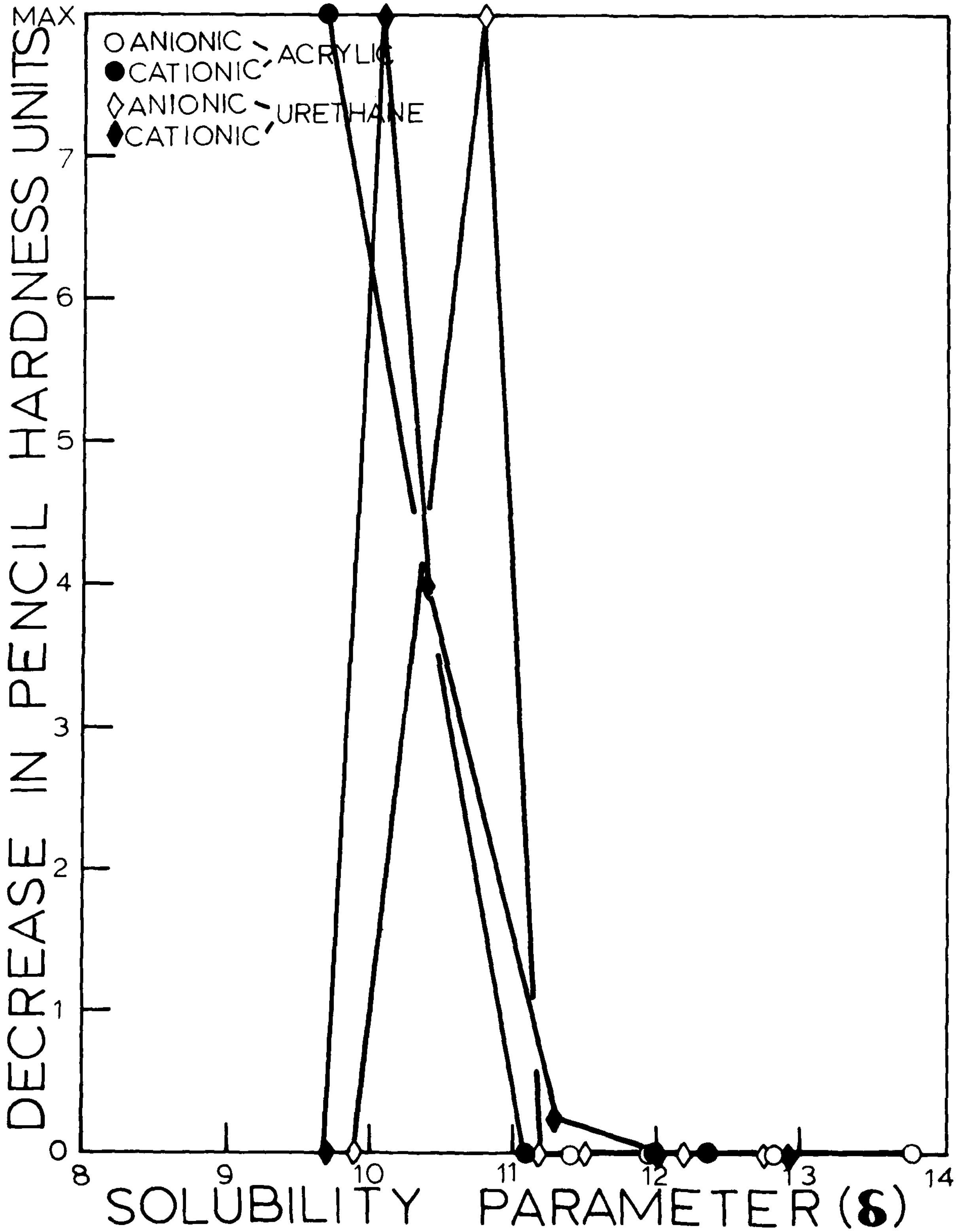

Figure 5. Effect of solubility parameter on resistance to diester lubricating oil (δ,8). Ambient cure.

d. Skydrol 500B Hydraulic Fluid (δ, 11)

Figure 6 is the ambient cured resin resistance to Skydrol 500B hydraulic fluid. The plot indicates a reasonably consistent family of curves for this fluid. Resistance to this fluid can be predicted for resins above solubility parameter about 12.5. For some unaccounted reason, this value is lowered to about 12.0 for the class of acrylic resins. This lowering may be related to the fact that these acrylic resins are largely based on acrylonitrile monomer which may enhance resistance due to some other factor. For example, one of the partial components of total solubility parameter[19] may be more significant for acrylonitrile and result in a change in the effecitve solubility parameter value.

e. Deionized Water (δ, 23)

Figure 7 displays the fact that all the resins cured solely under ambient conditions are destroyed by water. As was pointed out previously in this text, use of the solubility parameter concept to predict water resistance may not apply. Other factors (such as incomplete cosolvent evaporation or crosslinking) may play a greater role than solubility where moisture sensitivity is concerned.

2. Ambient Plus Bake Curing

In addition to curing under ambient conditions alone, the same resins were evaluated where cured by a 121°C (250°F) bake after initial ambient drying for seven days. Data relating the clear-film performance of resins cured in this

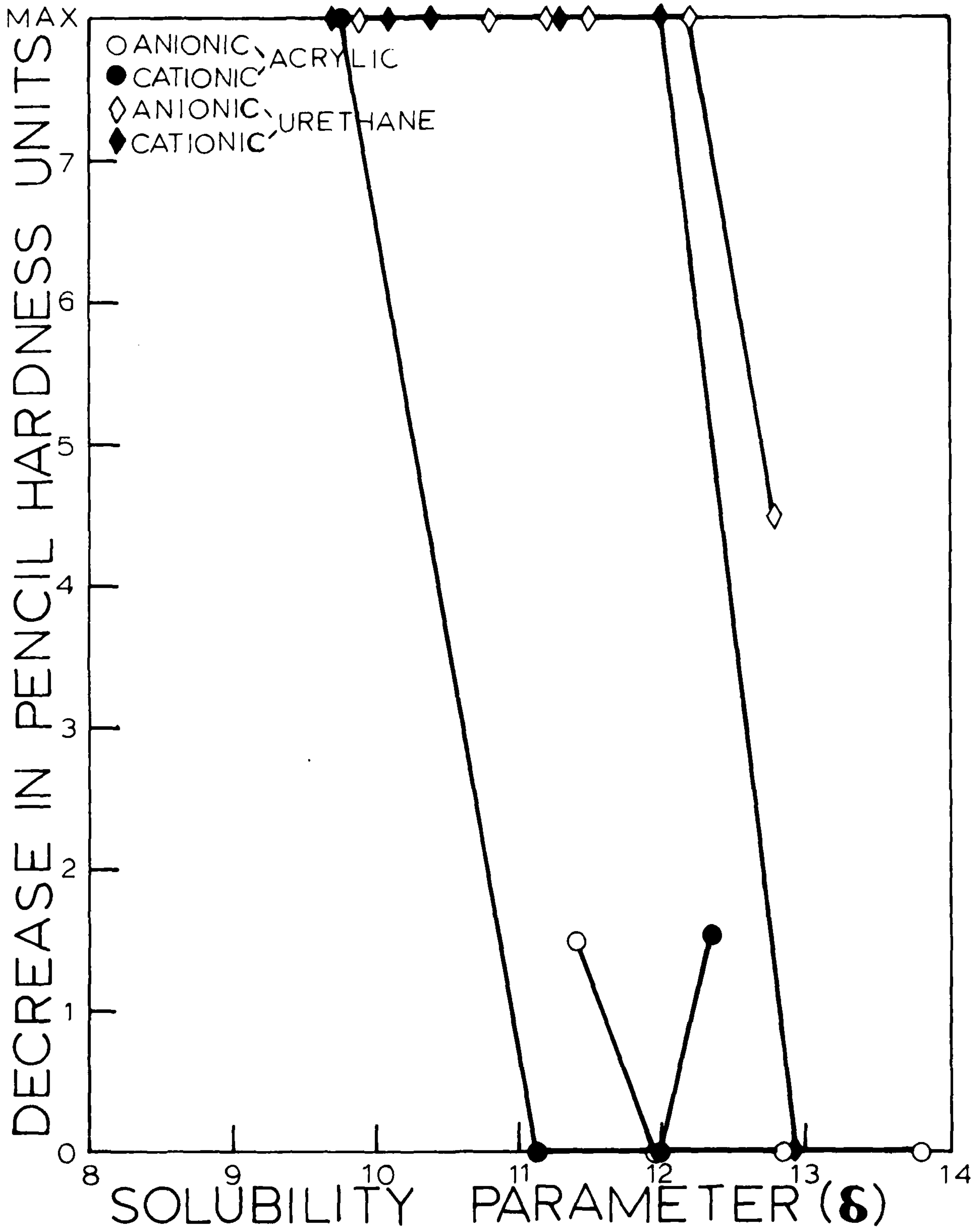

Figure 6. Effect of solubility parameter on resistance to Skydrol 500B (δ,11). Ambient cure.

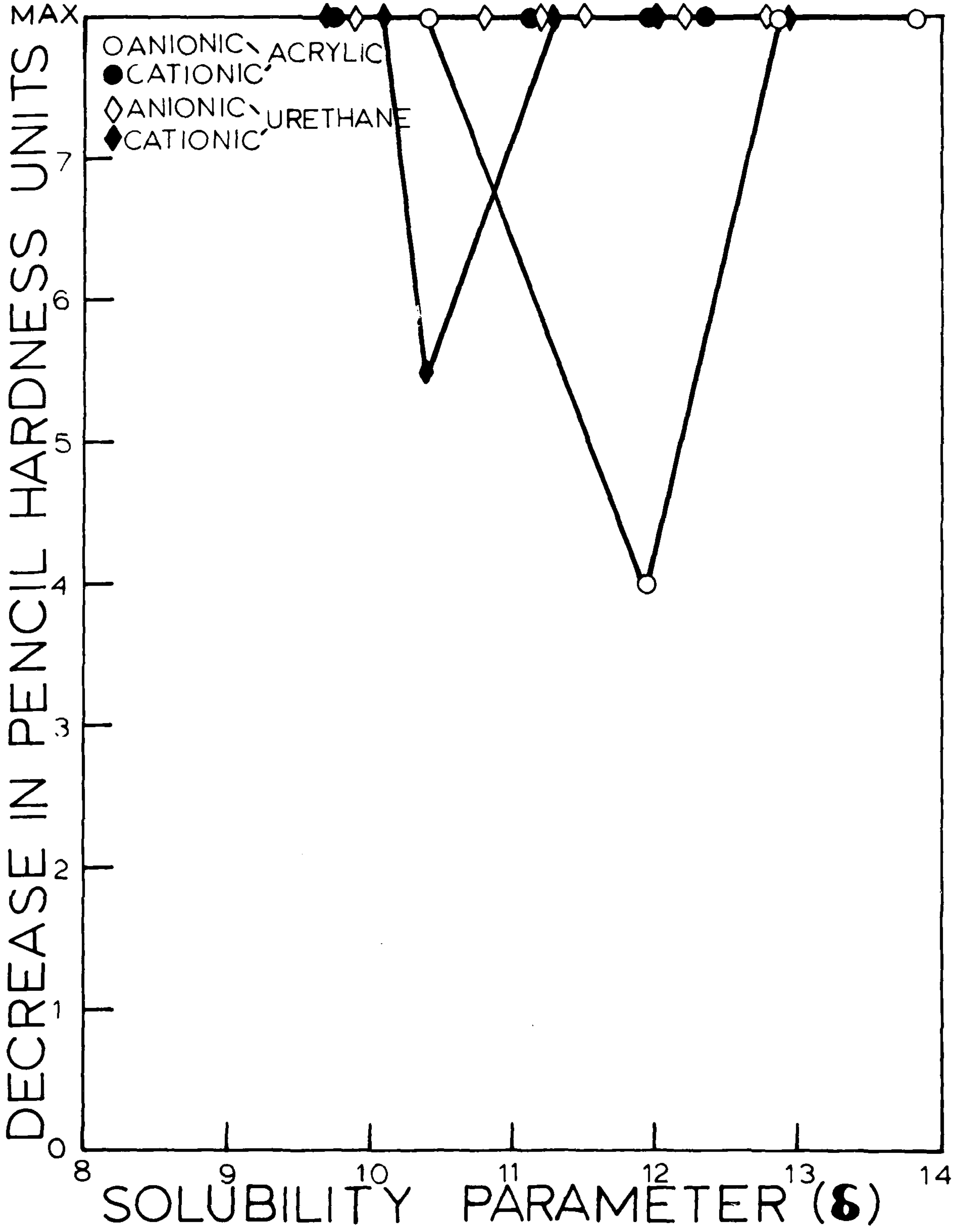

Figure 7. Effect of solubility parameter on resistance to deionized water (δ,23). Ambient cure.

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manner has been reported in the various tables of this text.

For comparison of resin classes, this data has been compiled, transposed for plotting, and retabulated. Tables A-6 to A-10 of the Appendix section list this compiled data.

a. H5606 Hydraulic Fluid (δ, 7)

Figure 8 displays the resistance to H5606 hydraulic fluid of all the resins cured as discussed above. Here, as was true for the ambient cured resins, resistance is very good. For the class of amionic urethanes, there appears to be a slight softening around δ, 11. However, this anomalous behavior is believed to be within the experimental limits of the test and thus does not constitute actual attack by the fluid.

b. TT-S-735 Type III Hydrocarbon

Figure 9 depicts the resistance of the cured resins to TT-S-735 hydrocarbon. Resistance to this fluid can be predicted for resins above a solubility parameter of about 11. Severe attack is experienced around δ 10.5. This is consistent with the same observation for resins cured under ambient conditions alone.

c. Diester Lubricating Oil (δ, 8)

Figure 10 indicates the resistance of the various resins cured with an assisting bake to diester lubricating oil. The curves are fairly consistent in predicting softening in this fluid for resins of solubility parameter below about 10.5.

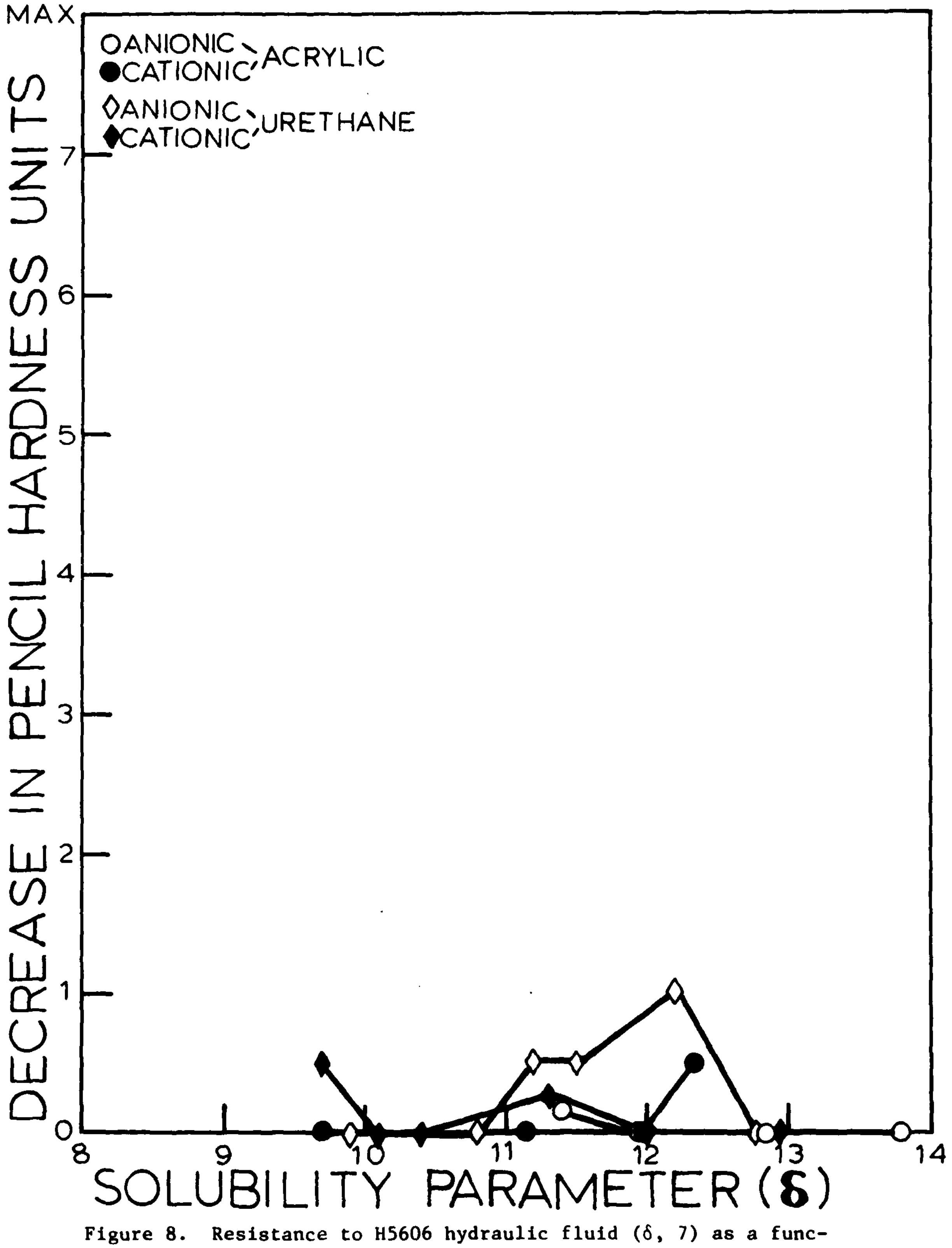

Figure 8. Resistance to H5606 hydraulic fluid (δ, 7) as a function of resin solubility parameter. Ambient cure plus bake.

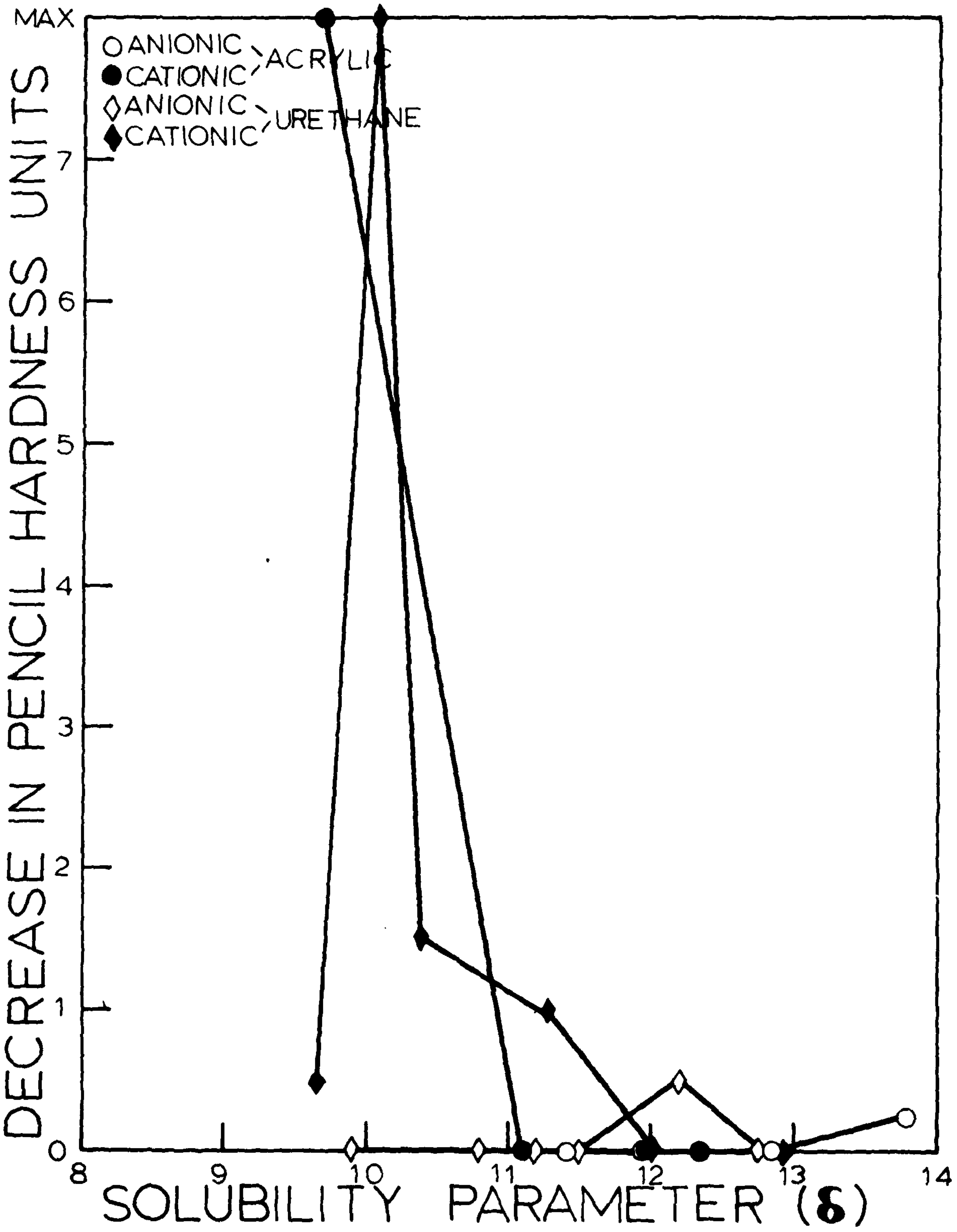

Figure 9. Resistance to TT-S-735 hydrocarbon (δ, 7.5) as a function of resin solubility parameter. Ambient cure plus bake.

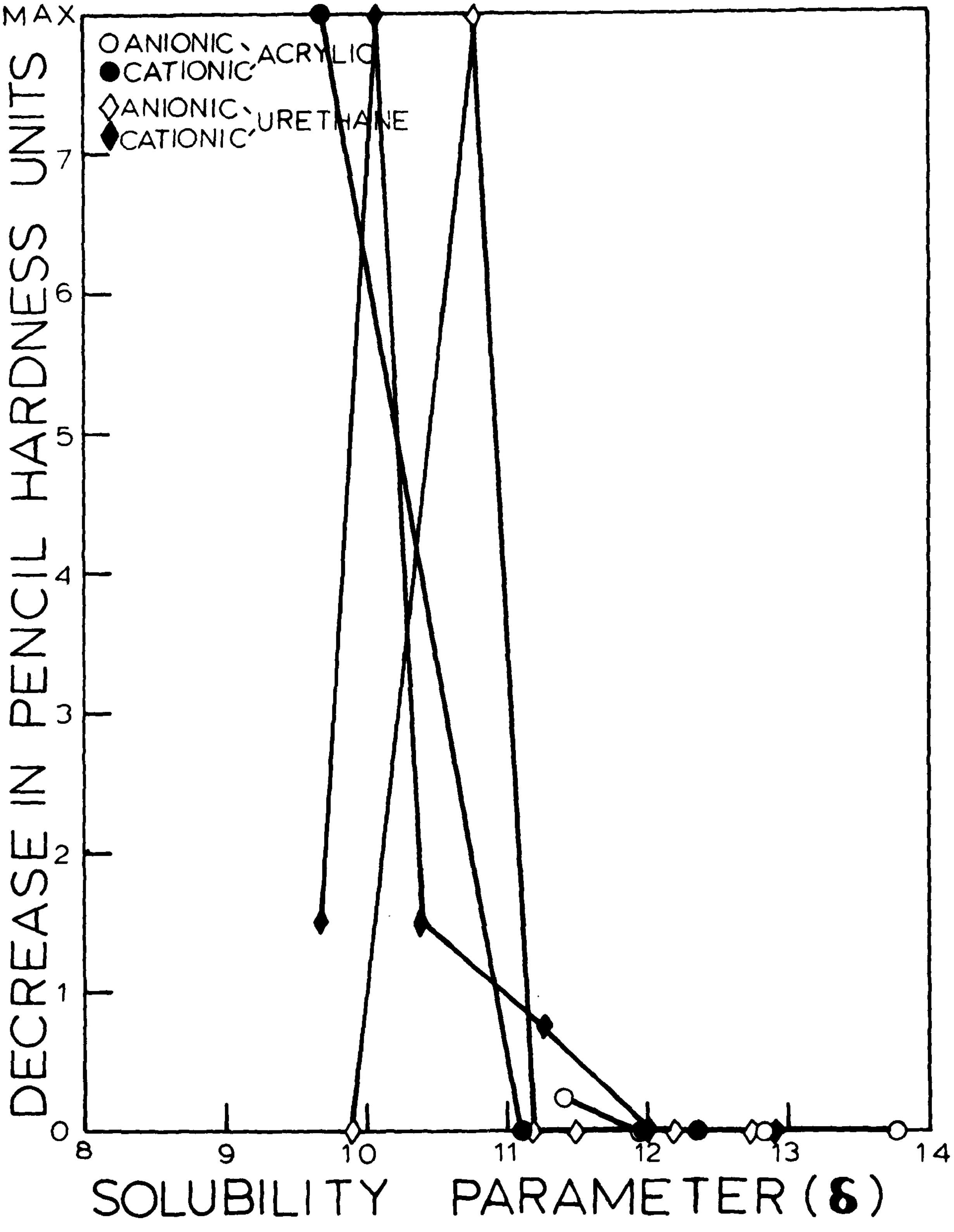

Figure 10. Resistance to diester lubricating oil (δ,8) as a function of resin solubility parameter. Ambient cure plus bake.

Above values of approximately 11, resistance can be predicted.

This performance is in agreement with that of the ambient cured resins.

d. Skydrol 500B Hydraulic Fluid (δ, 11)

Figure 11 plots the resistance of the various resin to Skydrol 500B. Consistent with the observations for ambient cured resins, these curves indicate attack for resins below a value of about 12.5. For acrylics based primarily on acrylonitrile, resistance can be predicted at values lower than 12.5 as far down as approximately 11.5.

e. Deionized Water (δ, 23)

Figure 12 displays the softening in water experienced by most of the resin classes. Attack is not as dramatic as encountered in the ambient cured resins and this fact seems to support the premise introduced previously that other factors may be more significant than solubility in assessing moisture sensitivity.

Perhaps the most striking evidence that water is unique among the fluids is the variation in behavior. For most fluids, the resins classes perform fairly consistently cured ambient or when baked. And a family of curves can be found. However, the curves for immersion in water, particularly when baked, display distinct inconsistency and no continuity in trend is apparent.

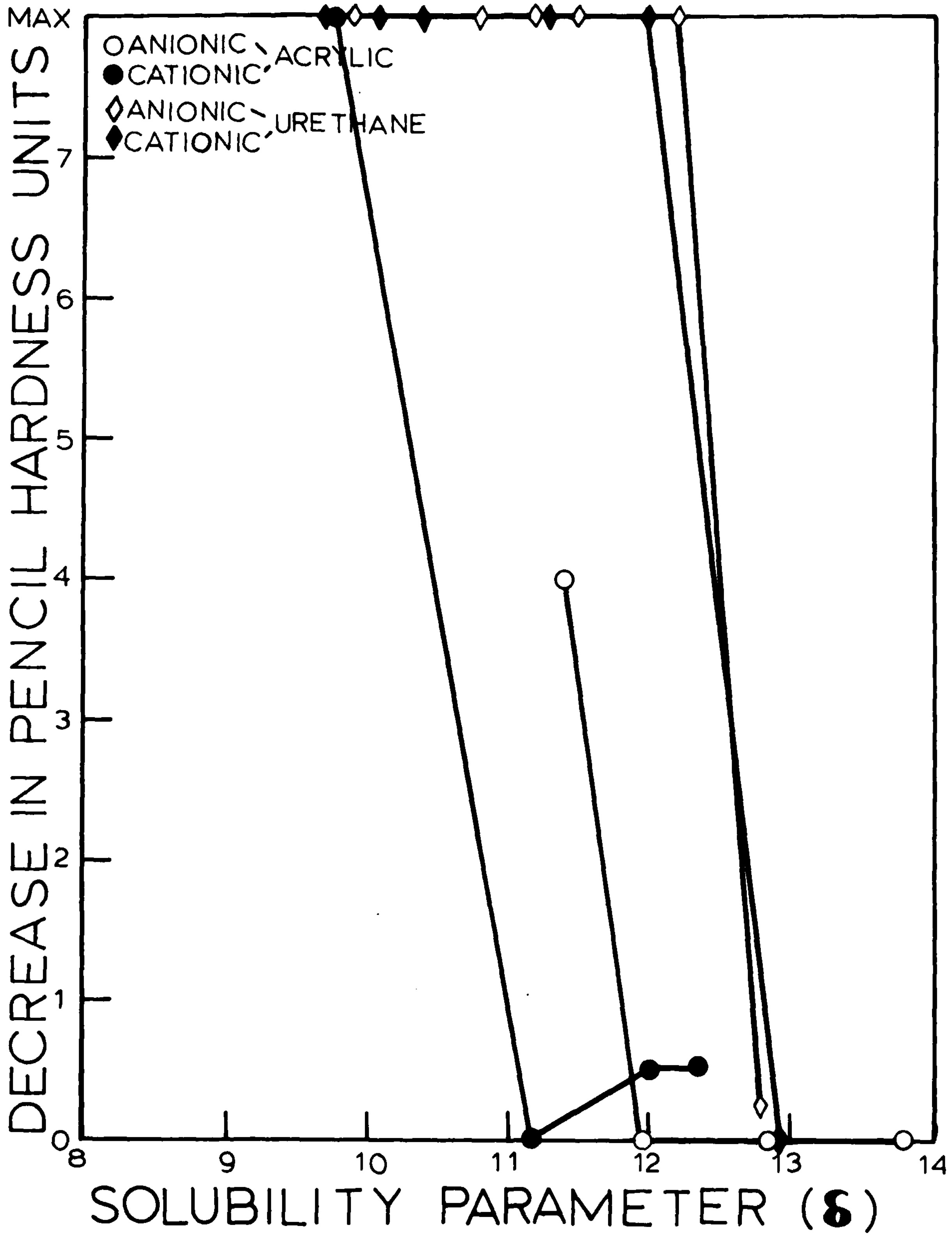

Figure 11. Resistance to Skydrol 500B (δ,11) as a function of resin solubility parameter. Ambient cure plus bake.

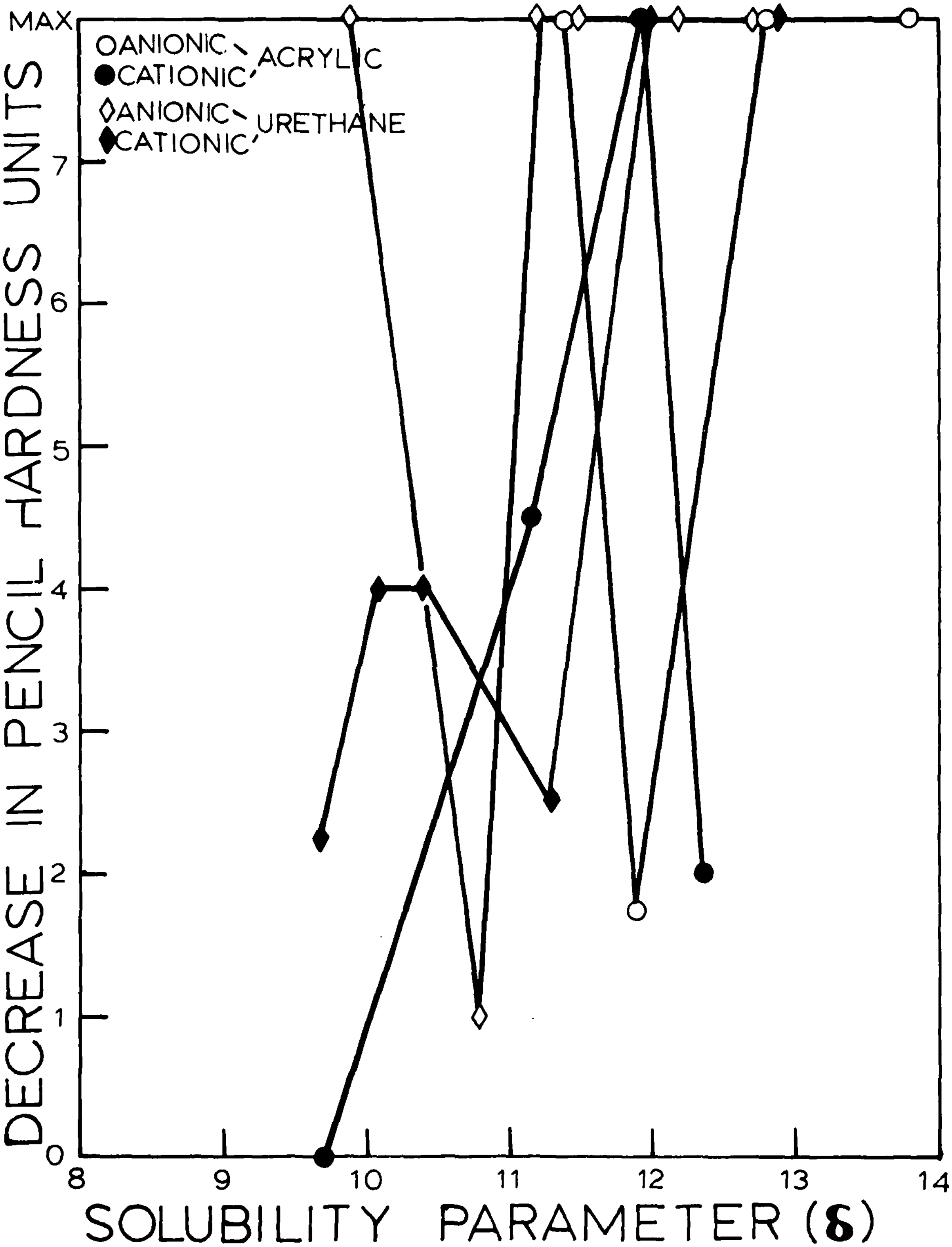

Figure 12. Resistance to deionized water (δ,23) as a function of resin solubility parameter. Ambient cure plus bake.

III. Experimental

This section will briefly summarize the techniques used to determine the solubility parameter of the test fluids and the commercial resins. Since most of the techniques are standard methods, references will replace elaborate descriptions of experimental detail.

Also included in this section will be a discussion of the synthetic techniques used in the preparation of polymer solutions, aqueous dispersion, and clear-film formulation.

A. Solubility Parameter of Test Fluids

The solubility parameter values for the test fluids were determined by surface tension and boiling point techniques.

1. Surface Tension

Molecular weight for each fluid was determined on a Hitachi Perkin-Elmer Model 115 Molecular Weight Apparatus according to theory proposed by Hill.[29]

Surface tension was measured on an Instron Mechanical Testing Apparatus using a DuNouy Ring Detachment method in ASTM D971-50.

2. Boiling Point

Boiling point determinations were made on micro scale quantities. The procedure was taken from a general organic chemistry laboratory text.[30]

B. Solubility Parameter of Commercial Resins

Solubility parameter values for commercial resins were determined from a plot of intrinsic viscosity in solvents of known solubility parameter.[21] A curve is constructed and the maximum defines the solubility parameter of the resins.

Solvents selected were purified according to recommended procedures.[31]

Isolation of the resin from aqueous medium was accomplished by neutralization of dispersion charges resulting in precipitation of the polymer. For anionic dispersions dilute acetic acid was used as the coagulating agent; for cationic dispersion dilute ammonium hydroxide was the coagulant.

The precipitated polymer was then washed with water on a Buchner funnel numerous times and dried in a vacuum oven at 39°C (100°F) or at 23°C (72°F).

The intrinsic viscosity of each resin in a series of solvents was determined according to ASTM D2857-70. A linear least squares program was used to define the intrinsic viscosity with correlation coefficients greater than 0.95 being acceptable.

C. Synthetic Polymers

This section will discuss the synthesis, dispersion and formulation of the novel polymers prepared for evaluation. Since a number of polymers describe a class, a general procedure will be given with tables of material composition being the medium of comparison.

1. Anionic Dispersions

The following section will detail the acrylic and urethane polymers designed for anionic aqueous dispersion.

a. Acrylic Copolymers

1. Synthesis

The following table presents the material composition (in grams) of the acrylic copolymers synthesized for evaluation as anionic dispersions.

The physical properties of these polymer solutions have been reported in section II.

	2722-12	2722-33	2722-50	2722-60	2722-71	2722-78
Monomer:						
Methyl acrylate		267.5				
Ethyl acrylate	398.1			75.5		
Butyl acrylate		83.2				83.2
2-Ethylhexyl acrylate			139.5			
2-Hydroxyethyl acrylate				96.0	203.5	
Acrylonitrile	19.2	268.8	416.0	448.0	320.0	268.8
Styrene	204.1		64.0			
Acrylamide					96.0	
Vinyl acetate						267.5
Itaconic acid	18.6					
Acrylic acid		20.5	20.5	20.5	20.5	20.5
Solvent:						
Isopropanol	672.0				288.0	
2-Ethoxyethyl acetate	288.0					
MEK		768.0	768.0			768.0
Methyl isobutyl ketone				384.0		
2-Methoxyethanol		192.0				192.0
N,N-Dimethylformamide			192.0			
2-Methylpyrrolidinone				288.0	192.0	
Acetonitrile				288.0	480.0	
Initiator:						
t-Butylperoxy-pivalate	19.2	19.2	19.2	19.2	19.2	19.2

A general procedure for the synthesis of the above acrylic solution polymers is as follows:

A four-neck round bottom reaction flask is equipped with mechanical stirrer, thermometer, reflux condenser and inlet lines for nitrogen gas, monomer feed, and initiator feed. The solvent mixture is then poured into the flask and set under an atmosphere of nitrogen. The flask is then immersed in a water bath thermostatically controlled to monitor the internal contents of the flask. The solvent mixture is then heated to the desired temperature (80°C) and maintained ± 1°C.

As the desired polymerization temperature is attained, 10 percent of the initiator is added to the solvent mixture. Addition of the monomer mixture is then begun. Addition is made to occur at a continuous rate over a three hour period. Simultaneous with monomer addition, the remainder of the initiator is added.

The flask contents are held at the desired temperature during addition and a slight positive pressure of nitrogen is maintained.

After addition, the percent conversion is checked at 1 hour intervals adding 1.0 gram of initiator until conversion is complete.

The polymer solution is then cooled to room temperature and transferred to a glass jar.

2. Aqueous Dispersion of Acrylic Copolymers

The following table compares the material composition (in grams) of the anionic dispersions prepared from the synthetic acrylic copolymers presented in the previous section.

	2722-16	2722-35	2722-52	2722-67	2722-73	2722-80
Polymer:						
2722-12 (67.3%)	241.2					
2722-33 (71.7%)		228.2				
2722-50 (45.4%)			281.6			
2722-60 (43.4%)				338.5		
2722-71 (59.3%)					224.4	
2722-78 (60.3%)						155.3
Cosolvent:						
Tetrahydrofuran			37.7	28.6		
2-Methoxyethanol					15.1	7.4
Triethylamine	5.1	4.8	4.0	4.9	4.7	4.3
Water	159.5	109.3	102.4	215.4	136.1	100.4

A general proceudre for aqueous dispersion by the direct method is as follows:

The sample is concentrated by flash evaporation under vacuum to increase the non-volatile content to the value indicated in the table. The sample is then transferred to a stainless steel beaker and mixed with triethylamine and cosolvent under low shear agitation.

When the solution viscosity is consistent, the rate of shear is increased and water is slowly added in small increments to prevent precipitation by shocking. Water is added continuously until the desired concentration is reached. The dispersion is then filtered through paint strainers.

All dispersions except 2722-52 and 2722-67 were prepared by this method. The two exceptions required the use of THF which was removed after dispersion. This procedure is the indirect technique and will be discussed in section III-C-1b-2.

3. Anionic Acrylic Coating Formulations

The following table compares the material composition (in grams) of the coating formulations developed for clear-film evaluation.

	2722-19	2722-37	2722-54	2722-70	2722-75	2722-82
Dispersion:						
2722-16	300.0					
2722-35		279.4				
2722-52			290.6			
2722-67				287.9		
2722-73					274.4	
2722-80						168.0
XAMA-7	8.4	5.4	5.0	6.6	6.2	5.0
Water	25.0	50.0			65.0	40.0
Isopropanol					90.3	
Fluorad FC-170 (1%)				1.1		

No special procedure is required for preparation of the above formulations. The materials are merely blended under low shear agitation to insure complete mixing.

b. Urethane Polymers

1. Synthesis

The following table compares the material composition (in grams) of the urethane polymers synthesized for evaluation as anionic dispersions.

	2524-98	2524-126	2722-174	2524-134	2722-163	2722-168	2722-184	2722-159
Diisocyanate:								
Isophorone	202.9	198.8		79.0				
Toluene						196.4	165.1	133.8
Diphenymethane			188.1					
Bis(4-cyclohexyl) methane					163.7			
Diol:								
Neopentyl	98.0							
1,6-Hexane		102.1						
Polymeg Q650				221.9				
Dantocol DHE					137.2		83.6	167.1
1,4-Butane						104.5	52.2	
2-Ethyl-1,3-hexane			112.8					
Dimethylol-propionic acid	19.1	19.1	19.1	19.1	19.1	19.1	19.1	19.1
Solvent:								
Methyl isobutyl ketone	149.3							
2-Ethoxyethyl acetate		42.7		42.7				
1,2-Dimethoxy-ethane		149.3	149.3	149.3	149.3	149.3	149.3	149.3
2-Methylpyrolidinone	64.0	21.3	64.0	21.3	64.0	64.0	64.0	64.0
Dibutyl tin dilaurate (1%)	1.2	1.1	1.0	1.1	0.8	1.5	1.2	1.0

A general procedure for the synthesis of the above polyurethane solutions is as follows:

A four neck round bottom flask is equipped with mechanical stirrer, thermometer, reflux condenser, dropping funnel and nitrogen inlet. Into the flask is poured the solvent mixture and the contents are set under a positive pressure of dry nitrogen. The solvent mixture is then heated to the reaction temperature ($80^{\circ}C$) and thermostated to $\pm$ $1^{\circ}C$.

To the solvent mixture is then added the blend of diols and the mixture stirred at reaction temperature until solution is complete at which point the catalyst is added. After catalyst addition, the isocyanate component is added dropwise over a specified time period (usually 3 hrs).

After isocyanate addition is complete, the NCO content is monitored every hour until the theoretical value is attained. The polyurethane solution is then cooled to 45°C and transferred.

2. Aqueous Dispersion of Polyurethane Solutions

The following table compares the material composition (in grams) of the anionic dispersions prepared from the polyurethane solutions of the previous table.

	2524-100	**2524-128**	**2722-175**	**2524-136**	**2722-164**	**2722-169**	**2722-185**	**2722-160**
Polymer:								
2524-98	200.0							
2524-126		250.0						
2722-174			168.1					
2524-134				200.0				
2722-163					196.5			
2722-168						184.4		
2722-184							191.3	
2722-159								143.6
Cosolvent:								
Methyl isobutyl ketone	19.8							
Tetrahydrofuran			96.1		103.6	103.1	104.8	91.7
2-Methylpyrrolidinone					35.0	21.7	18.2	34.7
Triethylamine	4.7	5.7	4.7	4.6	6.2	5.3	6.1	4.4
Water	178.1	172.9	153.8	195.4	212.3	180.2	226.2	198.1

Section III-C-1a-2 described a general procedure for the aqueous dispersion of acrylic copolymers using the direct method. This section will detail the procedure for the indirect method of dispersion.

The polymer solution is weighted into a stainless steel beaker and diluted with a volatile water-miscible cosolvent (usually THF). The mixture is then reacted with triethylamine using low shear agitation. After mixing a few minutes to allow complete reaction, the shear rate is increased to high speed. Water is then added slowly in small increments to prevent precipitation. As water is added the viscosity increases until inversion occurs as evidenced by a dramatic viscosity reduction. The remainder of the water is then added slowly.

The resultant dispersion is then transferred to a tared flask for evaporation. The dispersion is then concentrated by flash evaporation of the low boiling cosolvent and the concentration is adjusted to the desired level by adding water as needed. The concentrated dispersion is then filtered.

3. Anionic Polyurethane Coating Formulations

The following table compares the material composition (in grams) of the formulations developed for evaluation as anionic polyurethane coatings.

	2524-102	2524-130	2722-177	2524-138	2722-166	2722-171	2722-187	2722-162
Dispersion:								
2524-100	300.0							
2524-128		200.0						
2722-175			180.1					
2524-136				200.0				
2722-164					352.4			
2722-169						189.9		
2722-185							287.7	
2722-160								275.0
XAMA-7	6.4	4.9	4.7	4.2	6.6	5.4	6.9	5.1
Water	25.0	83.3		94.2	50.7	10.0	10.0	20.0
2-Methylpyrrolidinone		19.5	8.0	8.4	7.0	10.0	10.0	5.0
Fluoral FC-170 (1%)	1.1		1.9		8.1	7.2	6.1	5.7

2. Cationic Dispersions

The following section will detail the synthesis, dispersion, and formulation of acrylic and urethane polymers designed for evaluation as cationic aqueous dispersions. Also discussed will be the synthesis of the imine-blocked adducts used to incorporate amino-functionality.

a. Imine-blocked Adduct 2722-104 (3)

Into a single neck round bottom flask is poured 95.3g diethylenetriamine (1) and enough anhydrous benzene to make a final volume of 1.5 liters. To this solution is added 2-3g of Dowex 50W-X8 ion exchange resin as catalyst. This addition is followed by addition of 174.6g cyclopentanone (2).

The flask is then equipped with a Dean-Stark trap and reflux condenser with a drying tube. The solution is heated to reflux and maintained until the stoichiometric amount of water is collected.

The solution is then cooled, filtered, and flash evaporated to remove all the solvent. The product is transferred to an amber bottle, sealed under nitrogen and refrigerated. IR (cm^{-1}): 3300 (bd. singlet), H-H; 1670 (sharp singlet), C=N.

b. Urethane Solution Polymers

1. Synthesis

The following table describes the material composition (in grams) of the urethane polymers synthesized for evaluation as cationic dispersions.

Polymer	2722-109	2722-103	2722-140	2722-116	2722-132	2722-149	2722-179	2722-154
Adduct	2722-110	2722-105	2722-141	2722-117	2722-134	2722-150	2722-180	2722-155
Diisocyanate:								
Isophorone		197.2						
Bis(4-cyclohexyl) methane	208.8			112.8		179.6		
Toluene					142.0		160.4	146.2
Diphenylmethane			95.2					
Diol:								
1,4-Cyclohexanedimethanol		122.8					63.9	
2-Ethyl-1,3-hexane	111.2							
Niax PCP-0200				207.4				
Bisphenol A					178.0			
Polymeg Q650			224.8					
Dantocol DHE						140.4	95.7	173.8
Solvent:								
1,2-Dimethoxyethane	149.3	149.3	240.0	149.3	160.0	224.0	336.0	224.0
2-Ethoxyethyl acetate		42.7						
Butyrolactone	64.0	21.3		64.0	96.0	96.0	144.0	96.0
Cyclohexanone			72.0		64.0			
2-Methylpyrrolidinone			168.0					
Dibutyltindilaurate (1%)	0.9	1.1		0.5	1.0	0.8	1.1	1.0
2722-104 } mix	18.3	19.5	20.9	11.6	18.4	18.6	16.4	22.8
Solvent: } mix								
1,2-Dimethoxyethane	74.7			73.5				108.5
Butyrolactone	32.0			31.5				46.5
Diacetone alcohol		86.2						

Synthesis of the urethane polymers described in the above table is conducted analogously to the procedure detailed in section III-C-1b-1. When the synthesis is complete, the polymer's NCO content is determined and the corresponding equivalent weight is calculated.

Simultaneously, the amine equivalent weight of the imine-blocked adduct, 2722-104 (3), is determined. The polymer is then reacted with a solution of 3 equivalents of the adduct in the solvent mixture indicated in the table. This reaction is conducted at 60°C and allowed to proceed for 30 minutes with good agitation. The infrared absorption of the isocyanate group is monitored during this time. When substantially complete, the mixture is cooled and the viscous solution is poured into glass containers. The amine equivalent weight of the polymer is then determined.

2. Aqueous Dispersion

The following table compares the material composition (in grams) of the cationic aqueous dispersions of the polymers described in the previous table.

	2722-111	2722-106	2722-142	2722-118	2722-135	2722-151	2722-181	2722-156
Adduct:								
2722-110	162.4							
2722-105		175.5						
2722-141			360.3					
2722-117				150.4				
2722-134					224.6			
2722-150						222.9		
2722-180							211.7	
2722-155								272.3
Tetrahydrofuran	108.3	117.0	120.1	100.3	160.3	114.6	90.7	117.1
Acetic acid, glacial	2.1	2.5	4.3	1.1	2.6	3.2	1.6	3.5
Water	268.6	290.0	476.1	249.5	189.9	375.3	225.2	386.0

Since the solutions of the polymer-imine adducts were extremely viscous, solvent reduction was a necessary first step in the dispersion process. Consequently, all dispersions were prepared by the indirect technique detailed in section III-C-1b-2.

3. Formulation of Cationic Polyurethane Coatings

The following table compares the material composition (in grams) of the formulations developed for evaluation as cationic aqueous polyurethane coatings.

	2722-113	2722-108	2722-144	2722-120	2722-137	2722-153	2722-183	2722-158
Dispersion:								
2722-111	171.0							
2722-106		119.6						
2722-142			309.9					
2722-118				180.0				
2722-135					274.0			
2722-151						238.5		
2722-181							195.0	
2722-156								351.2
Cosolvent:								
2-Methylpyrrolidinone	8.6			9.0	54.8			
Diacetone alcohol	8.6	6.0						
Butyrolactone		12.0		9.0		10.0	5.0	40.0
DER 331	3.4	2.6	5.7	2.3	5.7	7.2	3.9	10.1
Water						15.0		
Fluorad FC-170 (1%)				2.5	3.4	12.8	12.2	18.6

c. Imine-blocked Adduct 2524-156 (7)

Into a 2-liter single neck round bottom flask is weighed 44.08g N-methyl-1,3-propanediamine (5) and 250 ml anhydrous benzene. To the mixture is added 55.09g urethane grade methyl isobutyl ketone (6) and 500 ml benzene. The solution is catalyzed with 3-4g Dowex 50W-X8 ion exchange resin.

The flask in then fitted with a Dean-Stark trap and a reflux condenser equipped with a drying tube. The solution is then heated to reflux until the stoichiometric amount of water is collected.

The solution is then cooled, filtered, and flash evaporated to a slightly amber colored liquid. The product is tranferred to an amber bottle and stored under nitrogen at room temperature.

IR(cm^{-1}): 3300(bd.singlet), N-H; 1655(sharp singlet), C=N.

Proton and carbon magnetic resonance spectra confirm the linear structure (7).

d. Cationic Acrylics

1. Synthesis

The following table compares the material composition (in grams) of the acrylic polymers synthesized for evaluation as cationic dispersions.

The table also includes the adduct formed by the reaction of the polymer with imine-blocked adduct 2524-156 (7).

Polymer	2830-01	2722-193	2524-186	2830-08
Monomer:				
Methyl acrylate		405.6		
Ethyl acrylate				133.7
Butyl acrylate	200.6		178.5	
Methyl methacrylate	387.9			
Acrylonitrile		188.9	416.0	460.8
Glycidyl methacrylate	45.5	45.5	45.5	45.5
Solvent:				
1,2-Dimethoxyethane	288.0	768.0	672.0	480.0
Acetonitrile	480.0		192.0	240.0
Butyrolactone	192.0	192.0	288.0	240.0
Azobis(isobutyronitrile)	10.1	10.1	10.1	10.1
Adduct	2830-03	2722-195	2830-15	2830-10
Polymer } mix	486.7	341.4	342.9	420.3
2524-156 } mix	17.2	12.5	10.7	14.5
Solvent:				
1,2-Dimethoxyethane		22.2		
Acetonitrile	25.8		20.7	25.3
Butyrolactone		5.6		

The procedure used to prepare the above polymers is analogous to that used for the anionic acrylic copolymers detailed previously.

To prepare the adduct, the following procedure was used:

The polymer was weighed into a tared 4-neck resin flask. The flask was then fitted with mechanical stirrer, thermometer, nitrogen inlet, reflux condenser and dropping funnel. The flask was immersed in a water bath thermostated to control the internal temperature.

The contents of the flask were placed under a nitrogen atmosphere and heated to reaction temperature (usually $60^{\circ}C \pm 1^{\circ}C$). To the polymer solution was then added a solution of the imine-blocked adduct dropwise usually in 10-20 minutes. The mixture was stirred vigorously and the reaction temperature maintained.

Periodically, a sample was withdrawn to determine the extent reaction by monitoring the remaining epoxide content. The reaction was terminated by cooling when 90 percent or more of the epoxide was reacted.

The resultant amine-functional polymer was dispersed into aqueous medium as quickly as possible because of a tendency to gel slowly (3 to 14 days).

2. Aqueous Dispersion

The following table compares the material composition (in grams) of the cationic aqueous dispersions prepared from the above amine-functional acrylic copolymers.

	2830-05	2722-196	2830-17	2830-11
Adduct:				
2830-03	196.4			
2722-195		183.1		
2830-15			144.0	
2830-10				133.9
Cosolvent:				
Acetonitrile		148.1	107.2	69.1
Butyrolactone	72.7		38.2	53.6
Acetic acid, glacial	4.1	2.4	2.7	2.8
Water	534.2	494.4	231.7	228.2
Flourad FC-170 (1%)				7.0

The dispersions were prepared by the indirect technique described in section III-C-1b-2 utilizing acetonitrile as the low boiling cosolvent. Tetrahydrofuran was not used as it was found to precipitate the polymer in most cases.

3. Cationic Acrylic Coating Formulations

The following table compares the material composition (in grams) of the formulations developed for evaluation as cationic acrylic coatings.

	2830-06	2722-198	2830-19	2830-13
Dispersion:				
2830-05	417.5			
2722-196		256.2		
2830-17			316.6	
2830-11				307.0
Cosolvent:				
Acetonitrile			10.0	7.0
Butyrolactone	5.0	5.0		
Toluene		6.6		
DER 331	3.6	5.1	3.0	4.5
Water	20.0	60.0	10.0	
Fluorad FC-170 (1%)		5.3	0.2	

IV. Appendix

Table A-1

Ambient Cure Resin Resistance to HS606 Hydraulic Fluid (δ,7)

	δ	Original Rating	Immersed Rating	Decrease
Anionic acrylics:				
2722-37	11.4	3.5	4.0	0
2722-82	11.4	4.0	4.0	0
2722-54	12.0	4.0	4.0	0
2722-70	12.8	4.0	4.5	0
2722-75	13.8	4.0	4.5	0
Anionic urethanes:				
2524-130	9.9	2.5	4.0	0
2722-177	10.8	4.0	3.5	0.5
2722-166	11.2	2.0	4.0	0
2722-171	11.5	3.0	4.0	0
2722-187	12.2	2.0	2.0	0
2722-162	12.8	4.0	4.0	0
Cationic urethanes:				
2722-108	9.7	4.0	4.0	0
2722-144	10.1	4.0	4.0	0
2722-120	10.4	5.5	6.0	0
2722-137	11.3	5.0	5.0	0
2722-153	11.3	4.0	4.0	0
2722-183	12.0	4.0	4.0	0
2722-158	12.9	4.0	4.0	0
Cationic acrylics:				
2830-06	9.7	4.0	4.0	0
2722-198	11.2	4.0	4.0	0
2830-19	12.0	4.0	4.5	0
2830-13	12.4	5.5	4.0	1.5

Table A-2

Ambient Cure Resin Resistance to TT-S-735 Hydrocarbon (δ, 7.5)

	δ	Original Rating	Immersed Rating	Decrease
Anionic acrylics:				
2722-37	11.4	3.5	3.0	0.5
2722-82	11.4	4.0	4.5	0
2722-54	12.0	4.0	4.0	0
2722-70	12.8	4.0	5.0	0
2722-75	13.8	4.0	4.5	0
Anionic urethanes:				
2524-130	9.9	2.5	2.0	0.5
2722-177	10.8	4.0	3.5	0.5
2722-166	11.2	2.0	4.5	0
2722-171	11.5	3.0	3.5	0
2722-187	12.2	2.0	4.0	0
2722-162	12.8	4.0	4.0	0
Cationic urethanes:				
2722-108	9.7	4.0	4.0	0
2722-144	10.1	4.0	MAX	MAX
2722-120	10.4	5.5	MAX	MAX
2722-137	11.3	5.0	5.0	0
2722-153	11.3	4.0	4.0	0
2722-183	12.0	4.0	4.0	0
2722-158	12.9	4.0	4.0	0
Cationic acrylics:				
2830-06	9.7	4.0	MAX	MAX
2722-198	11.2	4.0	4.0	0
2830-19	12.0	4.0	4.5	0
2930-13	12.4	5.5	5.0	0.5

Table A-3

Ambient Cure Resin Resistance to Lubricating Oil (δ, 8)

	δ	Original Rating	Immersed Rating	Decrease
Anionic acrylics:				
2722-37	11.4	3.5	4.0	0
2722-82	11.4	4.0	4.5	0
2722-54	12.0	4.0	4.5	0
2722-70	12.8	4.0	5.0	0
2722-75	13.8	4.0	5.5	0
Anionic urethanes:				
2524-130	9.9	2.5	4.0	0
2722-177	10.8	4.0	MAX	MAX
2722-166	11.2	2.0	5.0	0
2722-171	11.5	3.0	5.0	0
2722-187	12.2	2.0	5.0	0
2722-162	12.8	4.0	5.5	0
Cationic urethanes:				
2722-108	9.7	4.0	4.0	0
2722-144	10.1	4.0	MAX	MAX
2722-120	10.4	5.5	1.5	4.0
2722-137	11.3	5.0	4.5	0.5
2722-153	11.3	4.0	4.5	0
2722-183	12.0	4.0	6.5	0
2722-158	12.9	4.0	7.0	0
Cationic acrylics:				
2830-06	9.7	4.0	MAX	MAX
2722-198	11.2	4.0	6.5	0
2830-19	12.0	4.0	5.0	0
2830-13	12.4	5.5	6.5	0

Table A-4

Ambient Cure Resin Resistance to Skydrol 500B (δ,11)

	δ	Original Rating	Immersed Rating	Decrease
Anionic acrylics:				
2722-37	11.4	3.5	0.5	3.0
2722-82	11.4	4.0	4.0	0
2722-54	12.0	4.0	4.0	0
2722-70	12.8	4.0	5.5	0
2722-75	13.8	4.0	4.5	0
Anionic urethanes:				
2524-130	9.9	2.5	MAX	MAX
2722-177	10.8	4.0	MAX	MAX
2722-166	11.2	2.0	MAX	MAX
2722-171	11.5	3.0	MAX	MAX
2722-187	12.2	2.0	MAX	MAX
2722-162	12.8	4.0	-0.5	4.5
Cationic urethanes:				
2722-108	9.7	4.0	MAX	MAX
2722-144	10.1	4.0	MAX	MAX
2722-120	10.4	5.5	MAX	MAX
2722-137	11.5	5.0	MAX	MAX
2722-153	11.3	4.0	MAX	MAX
2722-183	12.0	4.0	MAX	MAX
2722-158	12.9	4.0	5.5	0
Cationic acrylics:				
2830-06	9.7	4.0	MAX	MAX
2722-198	11.2	4.0	4.0	0
2830-19	12.0	4.0	4.0	0
2830-13	12.4	5.5	4.0	1.5

Table A-5

Ambient Cure Resin Resistance to Water (δ,23)

	δ	Original Rating	Immersed Rating	Decrease
Anionic acrylics:				
2722-37	11.4	3.5	MAX	MAX
2722-82	11.4	4.0	MAX	MAX
2722-54	12.0	4.0	0.0	4.0
2722-70	12.8	4.0	MAX	MAX
2722-75	13.8	4.0	MAX	MAX
Anionic urethanes:				
2524-130	9.9	2.5	MAX	MAX
2722-177	10.8	4.0	MAX	MAX
2722-166	11.2	2.0	MAX	MAX
2722-171	11.5	3.0	MAX	MAX
2722-187	12.2	2.0	MAX	MAX
2722-162	12.8	4.0	MAX	MAX
Cationic urethanes:				
2722-108	9.7	4.0	MAX	MAX
2722-144	10.1	4.0	MAX	MAX
2722-120	10.4	5.5	0.0	5.5
2722-137	11.3	5.0	MAX	MAX
2722-153	11.3	4.0	MAX	MAX
2722-183	12.0	4.0	MAX	MAX
2722-158	12.9	4.0	MAX	MAX
Cationic acrylics:				
2830-06	9.7	4.0	MAX	MAX
2722-198	11.2	4.0	MAX	MAX
2830-19	12.0	4.0	MAX	MAX
2830-13	12.4	5.5	MAX	MAX

Table A-6

Baked Resin Resistance to H5606 Hydraulic Fluid (δ,7)

	δ	Original Rating	Immersed Rating	Decrease
Anionic acrylics:				
2722-37	11.4	4.0	5.0	0
2722-82	11.4	4.5	4.5	0
2722-54	12.0	4.0	4.0	0
2722-70	12.8	5.5	6.0	0
2722-75	13.8	5.0	5.0	0
Anionic urethanes:				
2524-130	9.9	4.0	5.0	0
2722-177	10.8	4.0	4.0	0
2722-166	11.2	4.5	4.0	0.5
2722-171	11.5	4.5	4.0	0.5
2722-187	12.2	5.5	4.5	1.0
2722-162	12.8	4.5	4.5	0
Cationic urethanes:				
2722-108	9.7	5.5	5.0	0.5
2722-144	10.1	4.0	4.0	0
2722-120	10.4	5.5	6.0	0
2722-137	11.3	6.0	6.0	0
2722-153	11.3	5.5	5.0	0.5
2722-183	12.0	6.0	6.0	0
2722-158	12.9	6.0	7.0	0
Cationic acrylics:				
2830-06	9.7	4.0	4.0	0
2722-198	11.2	5.5	6.0	0
2830-19	12.0	4.5	5.0	0
2830-13	12.4	6.0	5.5	0.5

Table A-7

Baked Resin Resistance to TT-S-35 Hydrocarbon (δ, 7.5)

	δ	Original Rating	Immersed Rating	Decrease
Anionic acrylics:				
2722-37	11.4	4.0	4.5	0
2722-82	11.4	4.5	5.0	0
2722-54	12.0	4.0	4.0	0
2722-70	12.8	5.5	6.0	0
2722-75	13.8	5.0	4.5	0.5
Anionic urethanes:				
2524-130	9.9	4.0	5.0	0
2722-177	10.8	4.0	4.0	0
2722-166	11.2	4.5	5.0	0
2722-171	11.5	4.5	4.5	0
2722-187	12.2	5.5	5.0	0.5
2722-162	12.8	4.5	4.5	0
Cationic urethanes:				
2722-108	9.7	5.5	5.0	0.5
2722-144	10.1	4.0	MAX	MAX
2722-120	10.4	5.5	4.0	1.5
2722-137	11.3	6.0	5.0	1.0
2722-153	11.3	5.5	4.5	1.0
2722-183	12.0	6.0	6.0	0
2722-158	12.9	6.0	6.5	0
Cationic acrylics:				
2830-06	9.7	4.0	MAX	MAX
2722-198	11.2	5.5	5.5	0
2930-19	12.0	4.5	5.5	0
2830-13	12.4	6.0	6.5	0

Table A-8

Baked Resin Resistance to Lubricating Oil (δ, 8)

	δ	Original Rating	Immersed Rating	Decrease
Anionic acrylics:				
2722-37	11.4	4.0	5.5	0
2722-82	11.4	4.5	4.0	0.5
2722-54	12.0	4.5	4.5	0
2722-70	12.8	5.5	6.0	0
2722-75	13.8	5.0	5.5	0
Anionic urethanes:				
2524-130	9.9	4.0	4.0	0
2722-177	10.8	4.0	MAX	MAX
2722-166	11.2	4.5	4.5	0
2722-171	11.5	4.5	5.0	0
2722-187	12.2	5.5	6.0	0
2722-162	12.8	4.5	6.0	0
Cationic urethanes:				
2722-108	9.7	5.5	4.0	1.5
2722-144	10.1	4.0	MAX	MAX
2722-120	10.4	5.5	4.0	1.5
2722-137	11.3	6.0	5.5	0.5
2722-153	11.3	5.5	4.5	1.0
2722-183	12.0	6.0	6.0	0
2722-158	12.9	6.0	7.5	0
Cationic acrylics:				
2830-06	9.7	4.0	MAX	MAX
2722-198	11.2	5.5	6.0	0
2830-19	12.0	4.5	5.0	0
2730-13	12.4	6.0	7.0	0

Table A-9

Baked Resin Resistance to Skydrol 500B (δ,11)

	δ	Original Rating	Immersed Rating	Decrease
Anionic acrylics:				
2722-37	11.4	4.0	MAX	MAX
2722-82	11.4	4.5	5.5	0
2722-54	12.0	4.0	4.0	0
2722-70	12.8	5.5	7.0	0
2722-75	13.8	5.0	5.0	0
Anionic urethanes:				
2524-130	9.9	4.0	MAX	MAX
2722-177	10.8	4.0	MAX	MAX
2722-166	11.2	4.5	MAX	MAX
2722-171	11.5	4.5	MAX	MAX
2722-187	12.2	5.5	MAX	MAX
2722-162	12.8	4.5	4.0	0.5
Cationic urethanes:				
2722-108	9.7	5.5	MAX	MAX
2722-144	10.1	4.0	MAX	MAX
2722-137	10.4	5.5	MAX	MAX
2722-153	11.3	6.0	MAX	MAX
2722-183	11.3	5.5	MAX	MAX
2722-158	12.0	6.0	MAX	MAX
	12.9	6.0	7.0	0
Cationic acrylics:				
2830-06	9.7	4.0	MAX	MAX
2722-198	11.2	5.5	5.5	0
2830-19	12.0	4.5	4.0	0.5
2830-13	12.4	6.0	5.5	0.5

Table A-10

Baked Resin Resistance to Water (δ,23)

	δ	Original Rating	Immersed Rating	Decrease
Anionic acrylics:				
2722-37	11.4	4.0	MAX	MAX
2722-82	11.4	4.5	MAX	MAX
2722-54	12.0	4.0	2.0	2.0
2722-70	12.8	5.5	MAX	MAX
2722-75	13.8	5.0	MAX	MAX
Anionic urethanes:				
2524-130	9.9	4.0	MAX	MAX
2722-177	10.8	4.0	3.0	1.0
2722-166	11.2	4.5	MAX	MAX
2722-171	11.5	4.5	MAX	MAX
2722-187	12.2	5.5	MAX	MAX
2722-162	12.8	4.5	MAX	MAX
Cationic urethanes:				
2722-108	9.7	5.5	3.5	2.0
2722-144	10.1	4.0	0.0	4.0
2722-120	10.4	5.5	1.5	4.0
2722-137	11.3	6.0	5.5	0.5
2722-153	11.3	5.5	1.0	4.5
2722-183	12.0	6.0	MAX	MAX
2722-158	12.9	6.0	MAX	MAX
Cationic acrylics:				
2830-06	9.7	4.0	4.0	0
2722-198	11.2	5.5	1.0	4.5
2830-19	12.0	4.5	MAX	MAX
2830-13	12.4	6.0	4.0	2.0

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