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WATERBORNE POLYMERIC FILMS

A.J. Tortorello and M.A. Kinsella

DeSoto, Incorporated
Research and Development Center
1700 South Mount Prospect Road
Des Plaines, Illinois 60018



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MICHAEL HALLIWELL
Project Engineer
Coatings & Thermal Protective
Materials Branch



WILLIAM C. KESSLER, Chief
Coatings & Thermal Protective Materials
Branch
Nonmetallic Materials Division

FOR THE COMMANDER



F.D. CHERRY, Chief
Nonmetallic Materials Division

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a polyurethane of toluene diisocyanate and a hydantoin diol as displaying excellent fluid resistance but poor flexibility. Evaluation of several hydroxy-terminated prepolymers for introduction of flexibility into this fluid resistant urethane provided a caprolactone polyester as the prepolymer of choice.

Formulation of this urethane copolymer with a blend of crosslinking epoxy resins produced a clear coating displaying excellent flexibility and resistance to all fluids except Skydrol 500B. Pigmentation of this clear formulation resulted in a loss of water resistance.

Examination of several branched polyurethanes to upgrade fluid resistance has identified a triol having an isocyanurate ring structure. The urethane copolymer employing this triol has produced a pigmented formulation displaying good flexibility and resistance to all fluids except Skydrol 500B.

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PREFACE

This report is the final report for Contract F33615-78-C-5096 awarded by the Materials Laboratory, Wright-Patterson AFB, Ohio. The time frame covered extends from 15 September 1980 to 15 September 1981. The contract entitled, Waterborne Polymeric Films, was initiated under Project Number 2422, Task Number 242202.

The objective of the program is the development of water-based polymers which, under ambient conditions, will form high performance films suitable for formulation as an aircraft primer and/or topcoat. The Project Engineer is Mr Michael J. Halliwell (AFWAL/MLBE). This report was released by the authors in October, 1981.

The authors express appreciation to the Aerospace Department of DeSoto, Incorporated particularly R. W. Byrd, F. D. Hawker and A. E. Dorr for their guidance and discussion of the formulating aspects of coatings research. We also thank Ms Mary Meinert for her part in preparing this manuscript.

The technology, analysis and solubility parameter approach developed in this program will be transferred to aircraft resin developers. Due to the greatly increased interest by coating and resin manufacturers in the Air Force waterborne coating needs, the AFWAL/Materials Laboratory effort will currently be to evaluate submitted coatings that will address Air Force waterborne coating needs.

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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 aircraft topcoat and/or primer. As originally planned, the effort was scheduled to occur in three phases. The activity for the initial two phases was concerned with evaluating commercially available aqueous polymers. This study is summarized in an interim annual report.

Activity scheduled for the third phase of effort concerned synthesis and formulation of novel aqueous polymers. The design of these synthetic polymers is the subject of a second interim annual report. Formulation of these synthetic polymers into pigmented aqueous coatings constitutes the subject of this final report.

The study began with a selection of the preferred polymer (urethane) and dispersion (cationic) classification. This selection was followed by a brief study designed to evaluate various hydroxy-terminated prepolymers. The study was intended to identify a candidate capable of providing the combined effect of good fluid resistance and flexibility. While no single material was identified, Niax PCP-0200 was selected as the prepolymer of choice for further study.

The next study attempted to raise the solubility parameter value of the polyurethane based on Niax PCP-0200 in order to provide enhanced fluid resistance. A hydantoin diol, Dantocol DHE, was used for this purpose. The study determined that a considerable gap between acceptable fluid resistance and flexibility existed for polyurethanes based on Niax PCP-0200 and Dantocol DHE.

Attempts to bridge this gap with the use of additive crosslinking agents provided one clear-film formulation which displayed good resistance to all fluids except Skydrol 500B and excellent flexibility. However, pigmentation of this formulation with rutile titanium dioxide resulted in a loss of water resistance.

Use of alternate pigments and primary pigment dispersants were unsuccessful in restoring water resistance to acceptable levels.

Polymeric design then proceeded to the use of branched structures to upgrade fluid resistance. One formulation based on a branched polyurethane displayed acceptable resistance to all fluids except Skydrol 500B while maintaining excellent flexibility.

An attempt to upgrade Skydrol 500B resistance while maintaining other properties was made. Variations in composition and concentration of the crosslinking agent component were evaluated. None of the formulations provided adequate resistance to Skydrol 500B.

I. Introduction

The use of aqueous coatings in industrial applications has experienced a dramatic increase since the enactment of Rule 66 by Los Angeles County. Prior to this legislation, water-based industrial coatings were essentially limited to use 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 changes required that any newly developed water-based coating contain not more than 20 percent volatile organic compounds on a volume basis.²

Such legislative stimuli coupled with economic pressure associated with the cost and availability of conventional solvents led to a surprising reassessment of the commercial market place for industrial coatings. Some early projections estimated water-borne coatings to capture as much as 30 percent of the total market by 1980.³ More recent projections estimate aqueous coatings to hold 25 percent (a small majority) of the industrial market in America⁴ and Europe⁵ by 1990.

More specific to the aerospace industry the South Coast Air Quality Management District recently proposed Rule 1124.⁶ This piece of legislation not only defines the limits on volatile organic materials allowed in a coating but also proposes a schedule to reduce these limits.

A. Historical Background

The refinishing of U.S. Air Force service aircraft is accomplished at Air Logistics Centers (ALCs) throughout the nation. Coating restrictions which apply to private industry apply equally to these centers.

The Air Force recognized the onset of technology change and has,

since the early 1970's, sponsored research to attain compliance with federal emission guidelines.^{7,8,9} 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 an aqueous polymer system to function as the pigment binding vehicle component of a prospective aircraft primer and/or topcoat. As originally proposed, the intended approach was to occur in three phases of effort.

B. Phase One: Commercial Aqueous Polymers

The initial phase activity was intended as a screening effort. Test procedures and performance parameters were established. And samples of a number of commercially available aqueous polymers were compiled. These state-of-the-art (SOTA) resins were grouped according to generic polymer type and formulated to evaluate the clear-film (no pigmentation) performance against the established criteria.

The obvious purpose of this study was twofold: 1) to find a successful candidate among the class of commercial aqueous polymers and, failing this; 2) to determine if any specific generic type offered a greater potential for success than the other types. This preliminary study failed to identify a polymer totally satisfying all performance requirements and furthermore revealed no single generic class to be outstanding from the others. However, while no single polymer was found to be completely acceptable, a number of candidates met nearly all requirements and warranted closer scrutiny.

C. Phase Two: Pigmentation

The second phase activity was devoted to pigmentation studies. The

aqueous polymers identified in phase one as displaying near acceptable clear-film performance were pigmented to function as a topcoat and as a primer. These prospective coatings were then evaluated against the performance criteria established in phase one.

As was the case with the clear-film study, no single polymer was identified as totally satisfying all performance requirements.

The results of the study comprising the combined effort of phases one and two were reported in an interim annual report.¹⁰ The study revealed that a general-purpose industrial resin would not be capable of meeting the needs of such a high performance application. A specialty polymer would be required. Polymer synthesis characterized the remainder of the activity for phase three of the contract.

D. Phase Three: Novel Polymers

In considering the performance expected of a specialty resin, the combination of excellent fluid resistance and flexibility was believed to be particularly challenging because chemical resistance is normally achieved by crosslinking in the applied film and crosslinking usually causes film embrittlement.

Extending this reasoning, any polymer displaying inherent chemical resistance in the linear state could be expected to meet the fluid resistance requirement with minimal crosslinking. And the prospect of achieving the required flexibility with this polymer would be improved. Thus the critical performance requirement was judged to be chemical (fluid) resistance.

The study from phases one and two revealed that fluid resistance is not a function of generic polymer type. Clearly something more funda-

mental is operative. One variable expressing the relationship between polymers and solvents (fluids) is the solubility parameter concept.¹¹

Fortunately, the solubility parameter concept is useful in the design of synthetically novel polymers as atomic groups comprising the molecular structure can be summed to result in any desired solubility parameter.¹² The intriguing feature of this concept is that, if applicable, fluid resistance performance should be independent of polymer type. That is acrylics, urethanes, and polyesters of similar solubility parameter value should display similar fluid resistance.

Using the method suggested by Fedors¹³ acrylic copolymers and urethane copolymers having desired solubility parameter values were designed. The polymers were then synthesized in organic solvents and dispersed into aqueous medium as anionic and as cationic dispersions. The dispersions were then formulated for evaluation of clear-film performance against the established fluid resistance and flexibility requirements.

The results of this synthetic study are the subject of a second interim annual report.¹⁴ The report details that the solubility parameter concept can be successfully employed to guide the design of synthetically novel polymers. Furthermore, the correlation between predicted fluid resistance and that experimentally observed is very good. Also, the solubility parameter concept is useful in selecting alternates for polymers serving a particular application.

While the synthetic study provided some very interesting and practical information, a single polymer displaying good flexibility while maintaining resistance to all the test fluids was still not identified.

The remainder of phase three activity was devoted to the attempt to synthesize this polymer and to prepare a prospective coating from it. The following report describes the result of this effort.

II. Results and Discussion

The study examining the validity of the solubility parameter concept as a guide in polymer synthesis identified a useful range of solubility parameter values. Acrylic copolymers of solubility parameter greater than about 11.5 Hildebrand units¹⁸ can be expected to resist all the organic test fluids. For urethane copolymers, the onset of fluid resistance occurs above the value of about 12.0 to 12.5 Hildebrand units.

The same study incidentally provided a means of introducing flexibility. In the case of urethanes, flexibility is attained using hydroxy-terminated prepolymers as one of the reactive components.

With this information, the search for a single polymer displaying both mechanical flexibility and chemical resistance was begun. Since the use of prepolymers appeared to be the most direct method of introducing flexibility and since most commercial prepolymers are unreactive with acrylics, the search was limited to the class of polyurethanes. Furthermore, since the supply and safety of polyfunctional aziridine resins as crosslinking agents for carboxy-functional polymers was questionable, the dispersion type was limited to cationics for use with epoxy crosslinking agents.

Given these conclusions, the synthesis of a flexible cationic aqueous polyurethane dispersion of solubility parameter value approximately 12 Hildebrand units was begun.

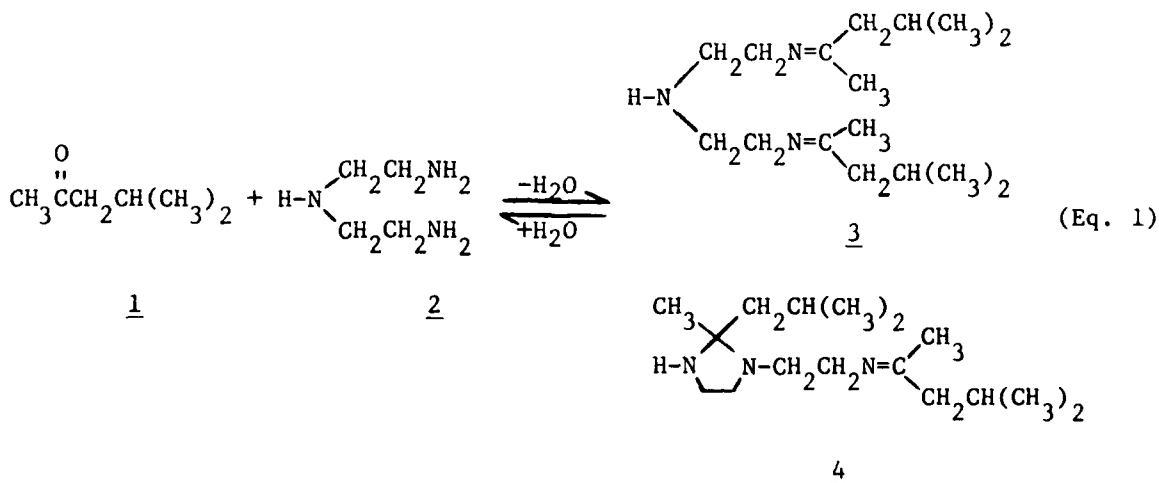
A. Cationic Aqueous Polyurethanes

In considering the design of cationic urethane dispersions, the initial concern must be the technique of introducing amine functionality into a polyurethane backbone. Since amines are well known crosslinking agents for isocyanate-terminated prepolymers, the prospect of using polyfunctional amines as coreactants in the polyurethane synthesis is remote. Therefore, an indirect method must be resorted to.

Literature techniques¹⁵ 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 modification of this technology has been successfully employed in our previous study.¹⁴

1. Ketimine-blocked Amine Sequence of Cationic Dispersion

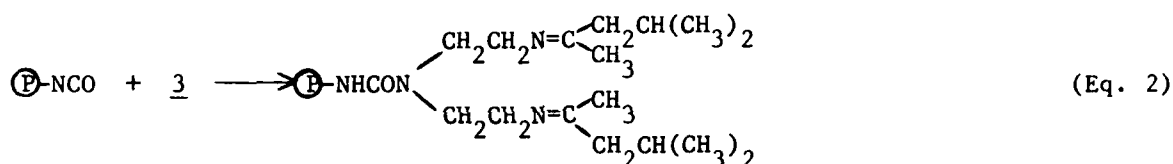
The indirect introduction of primary amine functionality pendant to a polyurethane backbone begins with the protection of the primary amine groups of diethylenetriamine (2) as the ketimine (3) of methyl isobutyl ketone (1). The reaction is given in equation 1.



As indicated, the reaction proceeds to an equilibrium. This is a fortunate circumstance as the equilibrium provides a means of introducing latent amine functionality for subsequent crosslinking with epoxy resins.

The equation also indicates the possibility of two isomeric products: the desired ketimine, 3 and the less desired imidazolidine, 4. Carbon and proton nuclear magnetic resonance spectroscopy can identify only isomer 3 as the isolated product. However, the use of less hindered ketones such as methyl ethyl ketone and cyclohexanone results in product mixtures containing both isomers.

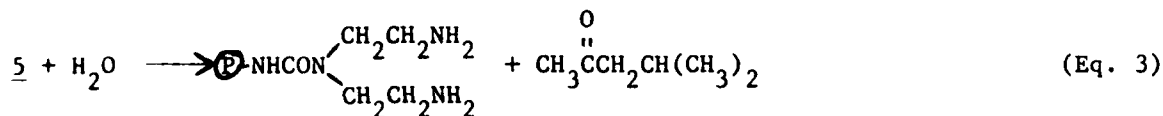
The sequence resulting in cationic dispersion of a polyurethane is continued by addition of the above ketimine (3) to an isocyanate-terminated prepolymer. This reaction is given in equation 2.



5

The resultant adduct (5) is a polyurethane with pendant urea and latent primary amine functionality.

Dispersion into aqueous medium is lastly accomplished by reaction of adduct 5 with volatile acid in the presence of excess water. The reaction is given in equation 3.



The liberated amines are neutralized by the volatile acid forming ammonium cations which stabilize the dispersion against flocculation.

The mechanism of stabilization is electrostatic repulsion of like charges associated with the surface of the colloidal particle. Upon film formation, the acid evaporates along with the other volatile components leaving the free primary amine for the crosslinking reaction with epoxy resins.

Applying the sequence to isomer 4 from equation 1 results in a product with primary and secondary amine functionality. Because of steric hindrance, secondary amines react slower with epoxides than primary amines. Consequently, isomer 4 is less desirable than isomer 3 for this ambient cure application. Fortunately, as indicated previously, isomer 3 is the only isolated product.

2. Combined Fluid Resistance and Flexibility

Having established the procedure for preparing cationic dispersions, the next concern addressed was the synthesis of flexible isocyanate-terminated polyurethanes having a solubility parameter value of approximately 12 Hildebrand units. In order to achieve this high value, the use of toluene diisocyanate (TDI) was necessitated. Given this restriction, application of this type of polymer as a coating vehicle appears to be more suited to a primer than a topcoat due to anticipated shortcomings in exterior durability.

Furthermore, the previous study¹⁴ identified the most direct means of introducing flexibility into a polyurethane as employing a hydroxy-terminated prepolymer as one of the reactants. Therefore, the synthesis of candidate polyurethanes based on toluene diisocyanate and a hydroxy-terminated prepolymer was begun.

a. Evaluation of Hydroxy-terminated Prepolymers

The polyurethane prepared from toluene diisocyanate and bis(2-hydroxyethyl) dimethylhydantoin (Dantocol DHE; Glyco Chem. Co.; Greenwich, Conn.) has a solubility parameter value of 12.9 H, displays excellent fluid resistance, but is sorely lacking in flexibility. This brief synthetic effort began with a screening of several hydroxy-terminated prepolymers to identify the ones best suited for incorporation into the TDI-Dantocol polyurethane.

Table 1 lists some of the physical properties of the prepolymers evaluated in this screening.

Table 1
Physical Properties of Hydroxy-terminated Prepolymers*

Polyol Code	Triethylene Glycol EG-3	Tetraethylene Glycol EG-4	Niax PPG-425 PPG	Polymeg Q-650 Q-650	Niax PCP-0200 PCP
Repeat unit	ethylene oxide	ethylene oxide	propylene oxide	butylene oxide	caprolactone
Hydroxyl value	747	578	265	174	212
Molecular weight	150	194	425	650	529

*Polymeg Q650 available from Quaker Oats Corp., Chemicals Div.; others available from Union Carbide Corp.

Selection of the candidate polyols was based on the ability to maintain a relatively high solubility parameter value in the subsequent polyurethane. Each candidate was then reacted with toluene diisocyanate to prepare a polyurethane in water-miscible organic solvent. The polyurethanes were reacted with the ketimine of diethylenetriamine and methylisobutyl ketone (3) for amine functionality. This adduct was then dispersed into water and formulated for clear-film evaluation.

Table 2 presents some of the properties of the formulations prepared.

Table 2
Cationic Polyurethane Formulation^a Characteristics

	<u>2830-63</u>	<u>2830-69</u>	<u>2830-75</u>	<u>2830-81</u>	<u>2830-87</u>
Polymer No.	2830-59	2830-65	2830-71	2830-77	2830-83
Polyol code	EG-3	PCP	Q-650	EG-4	PPG
Solubility parameter	11.0	10.1	9.3	10.7	9.5
Amine eq.wt.	2000	2000	2000	2000	2000
Solids, percent	29.1	26.9	22.6	29.6	37.9
pH	5.5	5.2	5.7	5.6	5.8
Visc., sec #22	18	24	29	27	32
VOC ^b	13.9	7.8	27.6	6.9	9.5

a. All formulations have stoichiometric equivalence of DER 331 epoxy crosslinking agent; b. Volatile organics as a weight percent of total formulation.

The most prominent feature presented in the table is the effect on the resin solubility parameter. To maintain a high value, the ethylene glycol derivatives with relatively few repeat units are preferred.

The formulations listed in Table 2 were spray applied to aluminum allowed to cure seven days under ambient and then tested. The same evaluations were then extended to coatings given a seven day ambient cure followed by a bake of 250^oF for 60 minutes.

A complete description of the applied film requirements has been given previously¹⁰ and need not be detailed here. In any case, only those tests related to fluid resistance and flexibility are pertinent in a screening such as this.

Table 3 presents the fluid resistance of the coatings evaluated. Fluid resistance is recorded in terms of decrease from original pencil hardness rating after immersion in the fluid of interest for the required time.

Table 3
Fluid Resistance of Cationic Polyurethane Coatings

<u>Formulation(6)</u>	<u>Film Thickness, mil</u>	<u>Original Hardness</u>	<u>Lubricating Oil(6,8)</u>	<u>Water (6,23)</u>	<u>H5606 (6,7)</u>	<u>Skydrol 500B(6,11)</u>	<u>TT-S-735 (6,7.5)</u>
2830-63(11.0)	0.7-0.9	HB(F)	F(F)	<4B(<4B)	HB(HB)	DF(<4B)	HB(F)
2830-69(10.1)	0.6-0.9	HB(HB)	HB(HB)	<4B(HB)	HB(HB)	<4B(<4B)	HB(HB)
2830-75(9.3)	0.4-0.8	HB(HB)	<4B(<4B)	<4B(4B)	HB(HB)	<4B(<4B)	<4B(<4B)
2830-81(10.7)	0.6-1.1	HB(HB)	HB(HB)	<4B(2B)	HB(HB)	<4B(<4B)	HB(HB)
2830-87(9.5)	1.2-1.7	3B(2B)	<4B(<4B)	<4B(<4B)	B(B)	<4B(<4B)	<4B(<4B)

The pencil hardness values presented in parentheses refer to evaluations in which the coatings were given the described bake after curing under ambient conditions. From the tabulated data, PCP-0200 (2830-69) appears to have the least adverse affect on fluid resistance. All the coatings were attacked by Skydrol but 2830-69 was the only one found to maintain all other properties while enhancing water resistance (in the baked film).

The same coatings were evaluated for flexibility as this is the feature of greatest interest which directs the use of these polyols. Table 4 lists the flexibility performance of these cationic polyurethanes.

Reverse impact flexibility is recorded in units of percent elongation when evaluated with a G.E. model impact tester according to FTMS 141, method 6222. Low temperature flexibility is recorded as a pass/fail test using a straight mandrel of the indicated diameter on substrate maintained at -65°F (-54°C).

Table 4
Flexibility of Cationic Polyurethane Coatings

<u>Formulation</u>	<u>Film Thickness, mil</u>	<u>Ambient Impact</u>	<u>High Temp. Impact</u>	<u>Low Temp. Mandrel</u>
2830-63	0.7-1.0	0.5	0.5	fail 1 inch
2830-69	0.6-1.0	60	60	pass 3/8 inch
2830-75	0.4-0.7	60	60	pass 3/8 inch
2830-81	0.5-0.9	1.0	1.0	fail 1 inch
2830-87	0.8-1.6	60	60	fail 1 inch

Flexibility testing was performed on coatings allowed to cure under ambient conditions only i.e. the coatings were not baked after ambient drying as with some of the fluid resistance tests.

The results identify three materials of potential use for introducing flexibility: PCP-0200(2830-69), Polymeg Q-650 (2830-75), and PPG-425 (2830-87). Among the three, PCP-0200 appears to be the choice based on its contribution to fluid resistance.

b. Niax PCP-0200 Series Polyurethanes

As discussed earlier, the polymer based on toluene diisocyanate and Dantocol DHE having a solubility parameter value around 12.9H displays excellent chemical resistance but poor flexibility. Using the results generated in the study on flexibility screening, the next sequence attempted to incorporate flexibility into the TDI-Dantocol polymer without

adversely affecting fluid resistance.

This study began with the design of a brief series of polymers in which PCP-0200 was copolymerized into the TDI-Dantocol backbone. These polymers were dispersed into water in the usual manner and then evaluated for clear-film performance. Table 5 lists some of the characteristics of these formulations.

Table 5

Niax PCP-0200 Series Polyurethanes; Formulation^a Properties

	<u>2830-33</u>	<u>2830-42</u>	<u>2830-27</u>	<u>2830-48</u>
Polymer No.	2830-29	2830-38	2830-23	2830-44
Dantocol/PCP ^b	100/0	97.5/2.5	95/5	90/10
Solubility param. ^c	12.9	12.7	12.6	12.4
Amine eq. wgt.	2000	2000	2000	2000
Solids, percent	18.5	32.0	29.5	31.9
pH	5.3	5.5	5.8	5.3
Visc., sec #22	30	29	22	30
VOC ^d	9.9	10.8	18.6	7.5

a. All formulations include stoichiometric equivalence of DER 331 epoxy crosslinking agent; b. Percent by weight; c. All polymers prepared with toluene diisocyanate; d. Volatile organics as percent by weight of total formulation.

The most apparent feature comparing the above formulations is the effect on the polymeric solubility parameter. Increasing the amount of PCP-0200 in the copolymer clearly lowers the value.

These formulations were then tested for fluid resistance and flexibility. Fluid resistance tests were performed under two types of cure

conditions: ambient for seven days and seven day ambient followed by a 250°F bake for 60 minutes. Table 6 describes the fluid resistance performance.

Table 6
Fluid Resistance of PCP-0200 Series Coatings

<u>Formulation(δ)</u>	<u>Film Thickness,mil</u>	<u>Original Hardness</u>	<u>Lubricating Oil(δ,8)</u>	<u>Water (δ,7)</u>	<u>H5606 (δ,7)</u>	<u>Skydrol 500B(δ,11)</u>	<u>TT-S-735 (δ,7.5)</u>
2830-33(12.9)	0.5-0.7	HB(F)	H(H)	<4B(<4B)	F(F)	DF(F)	F(H)
2830-42(12.7)	1.3-1.9	F(H)	F(F)	3B(<4B)	F(H)	DF(H)	F(H)
2830-27(12.6)	1.1-1.5	HB(H)	2H(H)	<4B(<4B)	HB(F)	DF(<4B)	HB(H)
2830-48(12.4)	0.8-1.3	HB(F)	F(F)	<4B(<4B)	H(H)	DF(<4B)	H(2H)

Examination of the table reveals that under ambient conditions alone none of the samples meet acceptable Skydrol and water resistance. Skydrol resistance can be achieved if the cure is accelerated as indicated by the baked-film performance. But Skydrol resistance is rapidly lost below a solubility parameter value of 12.7H. The effect of maintaining Skydrol resistance is lost as the amount of PCP-0200 in the copolymer is increased from 2.5 to 5.0 percent.

Table 7 lists the flexibility performance of the coatings in Table 5.

Table 7
Flexibility of PCP-0200 Series Coatings

<u>Formulation</u>	<u>Film Thickness,mil</u>	<u>Ambient Impact</u>	<u>High Temp. Impact</u>	<u>Low Temp. Mandrel</u>
2830-33	0.4-1.0	< 0.5	<0.5	fail 1 inch
2830-42	1.1-1.8	< 0.5	<0.5	fail 1 inch
2830-27	0.9-1.6	< 0.5	<0.5	fail 1 inch
2830-48	0.5-1.5	< 0.5	<0.5	fail 1 inch

Results of flexibility testing clearly show that levels of PCP-0200

greater than 10 weight percent are required for acceptable flexibility. However, reviewing the fluid resistance results, levels greater than 2.5 percent result in attack by Skydrol. The result appears to be mutually antagonistic performance.

c. Dantocol DHE Series Polyurethanes

Since the loss of Skydrol resistance occurred before the onset of flexibility an alternate approach was required. Beginning with a flexible polymer an attempt was made to incorporate Skydrol resistance. This attempt was based on increasing the solubility parameter of the polymer by incorporation of Dantocol DHE (the most likely diol available for raising δ) into the TDI-PCPO200 backbone.

However, expecting successful fluid resistance and flexibility from this approach clearly is limited. Previous results on the TDI-Dantocol polymer have already shown the loss of Skydrol resistance before flexibility is achieved.

Consequently, an attempt to increase the solubility parameter of the coating by increasing the number of crosslinking bonds (i.e. crosslink density) was tried. In total this new approach required two changes: reducing the equivalent weight of the TDI-PCPO200 polymers for increased crosslink density and incorporation of Dantocol DHE to raise the solubility parameter slightly without sacrificing flexibility.

Table 8 lists some of the properties of the formulations evaluated in this series of tests.

Table 8

Dantocol DHE Series Polyurethanes; Formulation^a Properties

	<u>2830-99</u>	<u>2830-113</u>	<u>2830-123</u>	<u>2830-145</u>
Polymer No.	2830-95	2830-109	2830-119	2830-141
PCP/Dantocol ^b	100/0	80/20	60/40	40/60
Solubility param. ^c	10.1	10.4	10.8	11.2
Amine eq. wgt.	1000	1000	1000	1000
Solids, percent	24.3	35.6	27.3	35.7
pH	5.5	5.6	5.6	5.2
Visc., sec #2Z	28	25	17	28
VOC ^d	7.0	11.3	9.2	8.3

- a. All formulations include stoichiometric equivalence of DER 331 crosslinking agent; b. Percent by weight; c. All polymers prepared with toluene diisocyanate; d. Volatile organics as weight percent of total formulation.

All polymers were dispersed into water by acidification of amine functionality which was introduced using the ketimine of diethylene-triamine and methylisobutyl ketone referred to previously. Two features are most prominent in the table: the resin equivalent weight has been reduced to half the previous value and the resin solubility parameter values do not nearly approach the value (12.6H) previously shown to result in Skydrol resistance.

These formulations were evaluated for fluid resistance and flexibility. Fluid resistance was tested under two sets of cure conditions: seven days ambient and seven days ambient followed by 60 minutes at 250^oF.

Table 9 describes the results of the fluid resistance tests. Values displayed in parentheses refer to coatings cured with a thermal assistance.

Table 9

Fluid Resistance of Dantocol DHE Series Coatings

<u>Formulation(δ)</u>	<u>Film Thickness, mil</u>	<u>Original Hardness</u>	<u>Lubricating Oil(δ,8)</u>	<u>Water (δ,23)</u>	<u>H5606 (δ,7)</u>	<u>Skydrol 500B(δ,11)</u>	<u>TT-S-735 (δ,7.5)</u>
2830-99(10.1)	0.8-1.2	HB(HB)	HB(HB)	<4B(2B)	HB(HB)	<4B(<4B)	3B(<4B)
2830-113(10.4)	1.0-1.6	2B(2B)	B(B)	<4B(<4B)	3B(3B)	<4B(<4B)	HB(2B)
2830-123(10.8)	0.7-1.2	H3(HB)	HB(HB)	<4B(B)	HB(HB)	<4B(<4B)	2B(2B)
2830-145(11.2)	1.5-2.1	HB(F)	HB(F)	<4B(<4B)	HB(F)	DF(<4B)	2B(HB)

The table reveals that some resistance to water can be achieved in the case of accelerated cures but resistance to Skydrol is lacking in all cases.

Flexibility results are displayed in Table 10.

Table 10

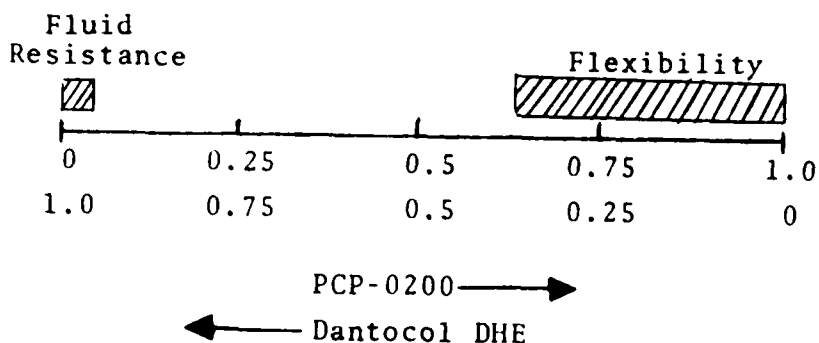
Flexibility of Dantocol DHE Series Polyurethanes

<u>Formulation</u>	<u>Film Thickness, mil</u>	<u>Ambient Impact</u>	<u>High Temp. Impact</u>	<u>Low Temp. Mandrel</u>
2830-99	0.6-1.0	60	60	pass 3/8 inch
2830-113	0.8-1.3	60	60	pass 3/8 inch
2830-123	0.7-1.2	60	60	pass 3/8 inch
2830-145	1.4-1.8	2.5	2.5	fail 1 inch

Examination of the results reveals that incorporation of Dantocol causes a loss in flexibility as the level of PCP-0200 is decreased from 60 percent to 40 percent.

A review of the information gathered to this point indicates a gap between acceptable fluid resistance and flexibility for the TDI-Dantocol-PCP copolymer. This gap occurs somewhere between 5 and 60 percent PCP-0200

and can be illustrated graphically:



d. Alternate Crosslinking Agents

Within this polymer system the prospect of obtaining a successful coating does not appear very promising. The gap between acceptable fluid resistance and flexibility must be filled.

One method of accomplishing this task is with the use of an additional crosslinking agent. Previous results¹⁰ have identified an epoxy-silane, normally considered an adhesion promoter, which enhances fluid resistance in a film cured under ambient conditions. The material is a product of Dow Corning Corp. designated as Z6040 silane.

1. Z6040 Silane and DER 331 Epoxy Resin

Formulations analogous to those listed in Table 8 were prepared. These new formulations, however, were composed of an alternate crosslinking system consisting of a combination of Z6040 silane and DER 331 epoxy.

The clear coatings were spray applied and evaluated for fluid resistance and flexibility. As before, fluid resistance was evaluated using cure conditions of solely ambient and ambient followed by an assisting bake of 60 minutes at 250°F. Table 11 summarizes the properties of these formulations.

Table 11

Crosslinker Series Cationic Polyurethanes; Formulation Properties

	<u>2830-107</u>	<u>2830-133</u>	<u>2830-139</u>
Polymer No.	2830-103	2830-129	2830-135
PCP/Dantocol ^a	100/0	80/20	60/40
Solubility param. ^b	10.1	10.4	10.8
Amine eq. wgt.	2000	2000	2000
Crosslink agents	331/6040	331/6040	331/6040
Solids, percent	27.4	22.9	22.1
pH	5.8	5.4	5.4
Visc., #2Z	25	28	25
VOC ^c	9.0	5.3	9.3

a. Percent by weight; b. All polymers prepared with toluene diisocyanate; c. Volatile organics as a weight percent of the total formulation.

The formulations displayed in Table 11 employ blends of DER 331 and Z6040 in which the total epoxide equivalents were calculated to equal the total amine equivalents of the resin. And as previously the resin was a copolymer of PCP-0200 and Dantocol DHE with toluene diisocyanate. Variations in the PCP/Dantocol ratio result in different solubility parameter values.

Table 12 displays the fluid resistance performance of these formulations. Values in parentheses refer to cure conditions in which an accelerating bake was applied.

Table 12

Fluid Resistance of Crosslinker Series Formulations

<u>Formulation(6)</u>	<u>Film Thickness,mil</u>	<u>Original Hardness</u>	<u>Lubricating Oil(6,8)</u>	<u>Water (6,23)</u>	<u>HS606 (6,7)</u>	<u>Skydrol 500B(6,11)</u>	<u>T1 S-735 (6,7,5)</u>
2830-107(10.1)	1.0-1.4	HB(HB)	HB(HB)	HB(HB)	HB(HB)	<4B(<4B)	HB(HB)
2830-133(10.4)	1.0-1.4	B(B)	B(B)	<4B(B)	B(HB)	<4B(<4B)	HB(B)
2830-139(10.8)	0.7-1.0	B(HB)	HB(HB)	2B(HB)	HB(HB)	<4B(<4B)	HB(HB)

The table reveals that incorporation of the additional silane cross-linking agent enhances fluid resistance. While Skydrol resistance was not achieved, water resistance was improved and resistance to all the other fluids was maintained.

Table 13 displays the flexibility of these formulations.

Table 13

Flexibility of Crosslinker Series Polyurethanes

<u>Formulation</u>	<u>Film Thickness,mil</u>	<u>Ambient Impact</u>	<u>High Temp. Impact</u>	<u>Low Temp. Mandrel</u>
2830-107	1.0-1.4	60	60	pass 3/8 inch
2830-133	1.0-1.3	60	60	pass 3/8 inch
2830-139	0.7-0.9	60	60	pass 3/8 inch

All formulations are found to display fully acceptable flexibility. The use of the added crosslinking agent has had no effect on film extensibility.

2. Z6040 Silane and PGAX Epoxy Resin

Although still lacking in Skydrol resistance, the use of epoxy-silane has demonstrated generally improved fluid resistance when combined with DER 331 as a crosslinking system. In an attempt to further upgrade fluid resistance, replacement of the difunctional DER 331 with a multifunctional epoxide was considered.

The candidate material is a tetrafunctional epoxide known as the tetraglycidyl amine of meta-xylylenediamine. The material designation is PGAX available from the Sherwin Williams Company.

The intention of using a multifunctional material is to increase the crosslink density to such an extent that Skydrol permeation into the film is appreciably slowed.

A series of cationic polyurethanes employing PGAX combined with Z6040 silane as the crosslink agent system was prepared. The polymers were similar in solubility parameter to those previously evaluated. The properties of the coatings are summarized in Table 14.

Table 14

PGAX Series Cationic Polyurethanes; Formulation Properties

	<u>2830-186</u>	<u>2830-182</u>	<u>2830-184</u>
Polymer No.	2830-170	2830-161	2830-135
PCP/DAN ^a	40/60	50/50	60/40
Solubility Param. ^b	11.2	11.0	10.8
Amine Eq. Wgt.	2000	2000	2000
Crosslink Agents	PGAX/Z6040	PGAX/Z6040	PGAX/Z6040
Solids, percent	20.4	30.4	16.3
pH	5.6	5.5	5.5
Visc., #2Z (sec.)	30	26	29
VOC ^c	5.4	5.7	8.8

- a. Molar ratio; b. All polymers prepared with TDI;
c. Volatile organics as a weight percent of the total formulation

In all cases, total epoxide equivalents introduced as PGAX and Z6040

were equal to total resin amine equivalents present.

Table 15 displays the fluid resistance properties of clear films prepared from the PGAX formulations. Values in parentheses refer to cure conditions in which an accelerating bake was applied.

Table 15

Fluid Resistance of PGAX Series Formulations

<u>Formulation (5)</u>	<u>Film Thickness, mil</u>	<u>Original Hardness</u>	<u>Lubricating Oil (6,8)</u>	<u>Water (6,23)</u>	<u>h5606 (6,7)</u>	<u>Skydrol 500B (6,11)</u>	<u>TT-S-735 (6,7,5)</u>
2830-186(11.2)	0.9-1.2	HB(HB)	HB(HB)	<4B(2B)	F(F)	<4B(<4B)	2B(B)
2830-182(11.0)	1.0-1.5	B(HB)	B(B)	<4B(2B)	HB(HB)	<4B(<4B)	3B(2B)
2830-184(10.8)	0.5-0.7	2B,B(2B,B)	HB(HB)	2B(HB)	HB(HB)	<4B(<4B)	HB(HB)

The table indicates that resistance to water is marginal at best and resistance to Skydrol is poor. Formulation 2830-184 appears to display the best overall resistance but the initial film hardness is somewhat soft.

Table 16 displays associated flexibility.

Table 16

Flexibility of PGAX Series Formulations

<u>Formulation</u>	<u>Film Thickness, mil</u>	<u>Ambient Impact</u>	<u>High Temp. Impact</u>	<u>Low Temp. Mandrel</u>
2830-180	0.8-1.2	60%	1%	pass 3/8"
2830-182	1.1-1.4	60%	60%	pass 3/8"
2830-184	0.5-0.8	60%	60%	pass 3/8"

Results in the table indicate that replacement of DER 331 epoxy with PGAX epoxy has little effect on flexibility. In agreement with previous results, flexibility is found to decrease as the level of PCP-0200 is lowered to 40 percent. However, this study extends slightly the previous study summarized in table 8. Acceptable flexibility is found to be maintained at compositions in which equal amounts of PCP-0200 and Dantocol DHE are employed.

This brief study thus indicates that, while inclusion of a poly-functional epoxide crosslinking agent has no adverse effect on flexibility, the expected improvement in Skydrol resistance is not realized.

e. Blend with Fluid Resistant Acrylic Copolymer

Since attempting to change the crosslink density resulted in no significant improvement in overall fluid resistance, an alternate approach of blending the flexible urethane with a fluid resistant acrylic copolymer was attempted. The obvious purpose of this study was to determine if the film resulting from such a blend would exhibit the favorable characteristics of each component.

The acrylic resin chosen, 2830-19, previously¹⁴ demonstrated excellent Skydrol resistance but was deficient in flexibility and water resistance.

Following established procedures, the polymers were first synthesized separately in organic solvent and then treated with imine 3 to produce adducts possessing the latent amine functionality. Properties of the two adducts are listed in Table 17.

Table 17

Acrylic-Urethane Blend; Component Adduct Properties

	<u>2911-15</u>	<u>2911-08</u>
Resin type	acrylic	urethane
Resin composition	AN/BA/GMA ^a	TDI/DAN/PCP-0200 ^b
Solubility param.	12.0	10.8
Amine equiv. wgt.	1119	1873
Solids, percent	39.8	49.3
Brookfield visc., cps ^c	4700	2570

a. acrylonitrile (AN), butyl acrylate (BA), glycidyl methacrylate (GMA); b. molar ratio PCP: DAN=60:40; c. Recorded with spindle #3 at 20 rpm on model RVT.

The adducts were then dispersed separately. Dispersion properties are listed in Table 18.

Table 18

Acrylic-Urethane Blend; Component Dispersion Properties

	<u>2911-16</u>	<u>2911-09R1</u>
Polymer No.	2911-15	2911-08
Solids, percent	16.0	33.5
pH	5.2	5.3
Density, lbs/gal	8.47	8.85
Brookfield visc, cps	22840 ^a	4185 ^b

a. Recorded with spindle #3 at 2.5 rpm on model KVT

b. Recorded with spindle #3 at 20 rpm

Two blends of these dispersions were prepared and formulated with crosslinking agents. Formulation properties are listed in Table 19.

Table 19

Acrylic-Urethane Blend Formulation Properties

	<u>2911-18</u>	<u>2911-20</u>
Acrylic/urethane ^a	10/90	25/75
Crosslink agents	DER 331/Z6040	DER 331/Z6040
Solids, percent	27.1	24.1
pH	5.2	5.3
Visc., #2Z (sec)	30	30
VOC ^b	6.8	10.2

a. Weight ratio of resin solids b. Volatile organics as
a weight percent of the total formulation

Total crosslinking epoxide equivalents were equal to total resin amine equivalents present in each case.

Fluid resistance performance is presented in Table 20. Baked film performance is listed in parentheses.

Table 20

Fluid Resistance of Acrylic-Urethane Blends

<u>Formulation</u>	<u>Film Thickness, mil</u>	<u>Original Hardness</u>	<u>Lubricating Oil(δ,8)</u>	<u>Water (δ,23)</u>	<u>H5606 (δ,7)</u>	<u>Skydrol 500B(δ,11)</u>	<u>TT-S-735 (δ,7.5)</u>
2911-18	1.5-2.0	2B(2B)	2B(B)	<4B(<4B)	2B(2B)	<4B(<4B)	2B(2B)
2911-20	1.5-1.9	2B(B,HB)	HB(HB)	<4B(<4B)	HB(HB)	<4B(<4B)	3B(3B)

Introduction of the acrylic resin at levels being considered does not result in a significant improvement in Skydrol resistance. Furthermore resistance to water is adversely affected in both cases.

Table 21 summarizes the flexibility performance of these blends.

Table 21

Flexibility of Acrylic-Urethane Blends

<u>Formulation</u>	<u>Film Thickness, mil</u>	<u>Ambient Impact</u>	<u>High Temp. Impact</u>	<u>Low Temp. Mandrel</u>
2911-18	1.3-1.7	60%	60%	pass 1"
2911-20	1.4-1.8	60%	60%	pass 1"

Low temperature flexibility is somewhat decreased in both cases.

Apparently higher levels of acrylic must be present in the blends if Skydrol resistance is to be achieved. However, this would undoubtedly result in a further loss of flexibility, particularly at low temperatures. In addition, water resistance is already unacceptable at the levels of acrylic present in the formulations evaluated. Thus, further work with this polymer blend is not warranted.

B. Preliminary Pigmentation Studies

Results¹⁰ from previous work on SOTA resins had indicated that Skydrol resistance was generally improved for pigmented films relative to corresponding clear films. Since no resin system possessing both flexibility and clear-film resistance to all test fluids under consideration had been

identified, clear-film evaluations were abandoned in favor of pursuing studies involving pigmented films.

1. Rutile Titanium Dioxide

To determine if Skydrol resistance could be measurably improved for a TDI-PCP-DAN resin system by pigmentation alone, preliminary pigmentation studies on such a polymer system were initiated. Preparation of a 60/40 PCP/DAN/TDI polymer (amine equiv. wgt. - 2000) was first scaled up to one gallon quantities (2911-07). The polymer was then made imine functional, dispersed into water (2911-09) and pigmented with rutile titanium dioxide. The pigmented dispersions were then formulated with crosslinking agents and evaluated.

Pigmented formulation properties are listed in Table 22.

Table 22

Pigmented^a Formulation Properties from Polymer 2911-07

	<u>2911-11</u>	<u>2911-22</u>	<u>2911-26</u>
P/B ^b	0.5	0.3	0.7
Solids, percent	33.4	29.1	34.7
pH	5.6	5.3	5.4
Visc., #2% (sec)	30	30	27
VOC ^c	5.2	4.7	4.2

- a. The pigment used in all cases was Ti Pure R960.09; (DuPont)
- b. Mass ratio of pigment to resin solids;
- c. Volatile organics as a weight percent of total formulation.

The crosslinking system used in each case was DER 331/Z6040. Epoxide equivalents introduced were equal to amine equivalents present.

Fluid resistance performance and film properties are listed in Table 23.

Table 23

Fluid Resistance of Pigmented Films

<u>Formulation</u>	<u>Film Thickness, mil</u>	<u>Gloss, 60°</u>	<u>Original Hardness</u>	<u>Lubricating Oil (6,8)</u>	<u>Water (6,23)</u>	<u>H5606 (6,7)</u>	<u>Skydrol 500B(6,11)</u>	<u>Ti-S-735 (6,7.5)</u>
2911-11	1.3-1.8	96.3-96.8	2B,3B(2B)	B(B,2B)	<4B(<4B)	B-HB(HB)	<4B(<4B)	HB(HB)
2911-22	1.3-1.7	97.2-97.5	2B(HB)	2B(2B)	<4B(<4B)	B(B)	<4B(<4B)	2B(E)
2911-26	0.8-1.1	91.9-93.0	HB(HB)	HB(HB)	<4B(<4B)	HB(HB)	<4B(<4B)	B(B)

Skydrol resistance is not achieved at any of the levels of added pigment evaluated. Performance in water is also poor. This loss of water resistance could indicate incomplete crosslinking caused by an acid-base type interaction between the titanium dioxide pigment and resin amine groups. Such an interaction would result in the amine groups being unavailable for reaction with the crosslinking epoxide component. Thus water sensitive sites would remain in the resultant film. This type of situation would undoubtedly affect resistance to other fluids as well.

Flexibility performance of the pigmented films is indicated in Table 24.

Table 24

Flexibility of Pigmented Films

<u>Formulation</u>	<u>Film Thickness, mil</u>	<u>Ambient Impact</u>	<u>High Temp. Impact</u>	<u>Low Temp. Mandrel</u>
2911-11	1.2-1.6	60%	60%	pass 3/8"
2911-22	1.0-1.4	60%	60%	pass 3/8"
2911-26	0.9-1.3	60%	60%	pass 3/8"

Pigmentation does not appear to adversely affect flexibility as performance remains at acceptable levels in all cases. However, incomplete crosslinking may also be a factor contributing to the unaffected flexibility.

Only formulation 2911-11 has been evaluated to date for corrosion resistance and exterior durability. The coating successfully resisted 500 hours of 5 percent salt fog and 720 hours of 100 percent humidity. However 500 hours of exposure in a self-contained weathering machine resulted in poor gloss retention (53.7 (60°) vs 96.0(60°) initially) and yellowing of the film. This behavior was expected based on the inclusion of an aromatic isocyanate (TDI) in the resin system. For this reason the resin in question is probably better suited for application as a primer rather than as a topcoat.

2. Primary Pigment Dispersant XD-7080

As discussed, the unexpected decrease in fluid resistance performance observed upon pigmentation of the TDI-PCP-DAN copolymer (2830-135 and 2911-07) was believed to be attributed to incomplete crosslinking caused by an acid-base type interaction between the pigment and polymer. To minimize this interaction an attempt was made to disperse the pigment in a small amount (5% of total resin mass) of an amine functional acrylic copolymer as the primary dispersant.

In this manner the pigment would be expected to complex preferentially with the acrylic amine allowing the urethane to crosslink normally. The effect of any unreacted amine groups still left in the film would be minimized by the increased crosslink density.

The acrylic chosen was previously evaluated in phase one¹⁰ and is a product of the Dow Chemical Company designated as XD-7080. The pigment was ground to the desired Hegman fineness in XD-7080 and let down into the urethane dispersion. The pigmented dispersion was then formulated with the DER 331/Z6040 crosslinker system and evaluated. Properties of

the formulation are summarized in Table 25.

Table 25

Pigmented^a Formulation Properties; 2911-07 and XD-7080

	<u>2911-96</u>
P/B ^b	0.5
Solids, percent	35.5
pH	5.20
Visc., #2Z (sec.)	18
VOC ^c	4.6

a. Ti Pure R960.09 (DuPont); b. Mass ratio of pigment to resin solids; c. Volatile organics as a weight percent of total formulation.

Fluid resistance performance and film properties are listed in Table 26. Baked film performance is given in parentheses.

Table 26

Fluid Resistance of 2911-96

Film Thickness, mil	Gloss, 60°	Original Hardness	Fluid Resistance of 2911-96				
			Lubricating Oil (6,8)	Water (6,23)	H5606 (6,7)	Skydrol 500B (6,11)	TT-S-735 (6,7.5)
0.8-1.7	97.3-99.0	2B(B)	B-HB(B-HB)	<4B(<4B)	B(B,HB)	<4B(<4B)	2B(2B)

Water resistance is not measurably improved by this procedure. Apparently enough unreacted amine remains in the film after curing to allow for substantial water attack. In addition, resistance to Skydrol remains unacceptable.

Flexibility performance is given in Table 27.

Table 27

Flexibility of 2911-96

<u>Film Thickness, mil</u>	<u>Ambient Impact</u>	<u>High Temp. Impact</u>	<u>Low Temp. Mandrel</u>
0.9-1.2	60%	40-60%	pass 3/8"

Flexibility is not markedly altered by the presence of XD-7080 in the film.

Use of an additional amine as a pigment surfactant does not appear to circumvent the difficulties introduced by pigmentation in this case. The level of crosslinking present is not sufficient to counteract the water sensitivity introduced by the unreacted amine functionality.

3. Use of an Alternate Pigment

Another procedure implemented to improve pigmented-film water resistance involved use of an alternate pigment. In an effort to reduce interaction with resin amine, titanium dioxide was replaced with zinc oxide as the pigment in a formulation prepared from polymer 2911-07.

Formulation properties are listed in Table 28.

Table 28

Pigmented Formulation Properties; 2911-07 with Zinc Oxide^a

	<u>2911-72</u>
P/B ^b	0.5
Solids, percent	44.7
pH	6.55
Visc., #2Z (sec.)	25
VOC ^c	5.9

a. Kadox 515 (New Jersey Zinc Co.); b. Mass ratio of pigment to resin solids; c. Volatile organics as a weight percent of total formulation.

Fluid resistance performance is given in Table 29. Values in parentheses refer to baked film performance.

Table 29

Fluid Resistance of 2911-72

<u>Film Thickness, mil</u>	<u>Gloss, 60°</u>	<u>Original Hardness</u>	<u>Lubricating Oil (δ,8)</u>	<u>Water (δ,23)</u>	<u>H5606 (δ,7)</u>	<u>Skydrol 500B (δ,11)</u>	<u>TT-S-735 (δ,7.5)</u>
2.0-2.6	97.4-98.4	2B(2B)	<4B(<4B)	<4B(<4B)	2B(2B)	<4B(<4B)	B(<4B)

In addition to showing no improvement in water resistance, films pigmented with zinc oxide exhibit a decreased level of overall fluid resistance. The need for further work with zinc oxide as a pigment in this system is not indicated.

C. Selection of the Final Formulation

Numerous and varied attempts to upgrade water and Skydrol resistance in the pigmented-film based on urethane copolymer 2830-135 and its analog 2911-07 have been unsuccessful. The best candidate can be described as displaying acceptable water resistance as a clear-film but poor water and Skydrol resistance as a pigmented film. In addition to these deficiencies, the original hardness of some of the films has been somewhat soft (B-2B).

Prior to selection of the final formulation another approach to providing the combination of Skydrol and water resistance was attempted.

All the previous studies have been based on a linear copolymer of solubility parameter 10.8 Hildebrand units. When formulated with the optimum crosslinking agents, this polymer undergoes network formation associated with the epoxy-amine reaction. This sequence of events occurs under ambient conditions. As a result of the deficiencies in fluid resistance performance, the extent of network formation under these con-

ditions must be suspect.

An alternate approach is to supplement network formation in the applied film by beginning with a branched or even partially crosslinked copolymer.

1. THEIC Series Amine-functional Polyurethanes

Two procedures were implemented to affect the copolymer structure. The first procedure involved partial replacement of the difunctional alcohol component with a tri or tetrafunctional alcohol. Again, the primary consideration to maintaining a high solubility parameter value must be made. With this in mind, the best suited candidate from a structural viewpoint appeared to be tris(2-hydroxyethyl) isocyanurate, abbreviated as THEIC. This compound is a trifunctional alcohol with the isocyanurate ring structure and results in branched copolymers.

The second procedure concerned the isocyanate group on the polymer chain ends. These groups are normally reacted with the protected amine and thus converted to latent amine functionality prior to dispersion. In this alternate procedure, a fraction of the isocyanate groups are left intact. Subsequent reaction of these groups with water upon dispersion result in urea and biuret bonds between existing polymer chains. Polymeric molecular weight and branching can thus be further increased upon dispersion into water.¹⁶ In addition, the high solubility parameter value can be maintained and possibly increased by both the inclusion of THEIC and by the incorporation of urea and biuret groups.

A series of isocyanate-terminated polymers composed of TDI, Dantocol DHE, PCP-0200 and various amounts of THEIC were synthesized (NCO equivalent weight \approx 2000). The functional groups were then partially or fully con-

verted to potential amine functionality by treatment with imine 3. Properties of the amine functional polymers are given in Table 30.

Table 30

THEIC Series Amine-functional Polyurethane Properties

	<u>2911-50</u>	<u>2911-62</u>	<u>2911-77</u>	<u>2911-87</u>
PCP/DAN/THEIC ^a	57.6/38.4/4.0	57.6/38.4/4.0	55.8/37.2/7.0	54.0/36.0/10.0
Solubility Param. ^b	10.8	10.8	10.9	11.0
Solids, percent	50	50	50	50
NCO to Amine Conversion, percent	100	75	75	75
Amine Equiv. Weight	1035	1564	1823	1756

a. Ratio of hydroxyl equivalents; b. All polymers prepared with TDI.

Polymers 2911-50 and 2911-62 are similar in all respects except one; terminating isocyanate groups are completely converted to amine functionality in the first case but only 75% are converted in the second. Any differences in performance should be related to this difference in preparation.

The polymers were then dispersed into water, pigmented with titanium dioxide, formulated with Z6040/DER 331 and evaluated. Formulation properties are listed in Table 31.

Table 31

THEIC Series Cationic Urethanes; Pigmented^a Formulation Properties

	<u>2911-53</u>	<u>2911-65</u>	<u>2911-80</u>	<u>2911-92</u>
Polymer No.	2911-50	2911-62	2911-77	2911-87
P/B ^b	0.5	0.5	0.5	0.5
Solids, percent	46.3	40.4	42.3	43.9
pH	5.45	5.85	6.05	6.30
Visc., #2Z (sec)	33	22	30	30
VOC ^c	6.9	5.0	5.4	5.3

a. Ti Pure R960.09 (DuPont); b. Mass ratio of pigment to resin solids; c. Volatile organics as a weight percent of total formulation.

Fluid resistance performance is listed in Table 32. Baked film performance is given in parentheses.

Table 32

Fluid Resistance of THEIC Series Cationic Urethanes

Formulation	Film Thickness, mil	Gloss, 60°	Original Hardness	Lubricating Oil (6,8)	Water (6,23)	H5606 (6,7)	Skydrol 500B(6,11)	TT-S-735 (6,7,5)
2911-53	1.6-2.1	101.1-101.6	2B(B)	HB(HB)	<4B(<4B)	HB(HB)	<4B(<4B)	4B(4B)
2911-65	1.0-1.5	96.4-96.7	B(B)	B(B-HB)	2B(2B)	B(B)	<4B(<4B)	2B(2B-B)
2911-80	0.8-1.4	95.6-96.2	B(B)	B(B)	2B,3B(B,2B)	B(B,HB)	<4B(<4B)	B(2B)
2911-92	1.0-1.5	92.9-95.4	HB(HB)	HB,B(HB)	2B,3B(B)	B(B)	<4B(<4B)	B(B)

None of the resin systems evaluated showed improved Skydrol resistance. However water resistance is improved to acceptable or near acceptable levels in all but the first case. Since polymers 2911-50 and 2911-62 differ only in the extent of isocyanate to amine conversion, the improved water resistance observed for this series is probably related to the presence of urea/biuret linkages in the polymer backbone. Resistance to the other test fluids remains acceptable in most cases.

Flexibility performance is listed in Table 33.

Table 33

Flexibility Performance of THEIC Series Cationic Urethanes

Formulation	Film Thickness, mil	Ambient Impact	High Temp. Impact	Low Temp. Mandrel
2911-53	1.4-1.9	60%	60%	fail 1"
2911-65	1.0-1.3	60%	60%	pass 3/8"
2911-80	0.8-1.3	60%	60%	pass 3/8"
2911-92	1.2-1.5	60%	40-60%	pass 3/8"

Flexibility is good in all cases except that of 2911-53 at low temperatures. The unusual thickness of the film in this case may be related to this anomalous behavior.

While this brief study was unsuccessful in providing network films capable of resisting Skydrol, a method of improving water resistance was identified. More extensive application of these techniques is limited by the increasingly viscous nature of the solutions of branched polymers and by the difficulty encountered in dispersing partially amine-substituted polymers into water.

An additional attempt to provide combined water and Skydrol resistance in a branched copolymer was made. This trial concentrated on enhancing network formation in the applied film by increasing the level of crosslinking agent.

2. Variation in Crosslinking Agent Concentration

The novel synthetic polymer which has evolved from most of the previous results is an amine functional polyurethane. The material is composed of toluene diisocyanate, Dantocol DHE (36% of total hydroxyl equivalents), Niox PCP-0200 (54%), and tris (2-hydroxyethyl) isocyanurate (10%). When converted to an aqueous dispersion by neutralizing 75% of the amine groups and formulating with a combination of epoxy resins, the coating (2911-92) displays acceptable resistance to all fluids except Skydrol while maintaining good flexibility.

The polymer contains primary amine functionality which reacts with epoxy resins in crosslinking. The addition of a primary amine and an epoxide is a secondary amine which is capable of reacting with a second epoxide, usually at a rate slower than that of the first reaction. In the previous studies only the first reaction had been considered; epoxide equivalents have been introduced in amounts stoichiometrically equal to amine equivalents.

A brief study to examine the effect of increased epoxy resin concentration was planned. The additional epoxide groups should result in a more densely crosslinked film because of the epoxide-secondary amine addition.

To begin this study a polymer (2911-150) which differs slightly from that in use (2911-87) was designed. The polymer was synthesized in a solvent blend which contains a lower amount of the less volatile component (90% dimethoxyethane: 10% butyrolactone) than the conventional blend (85:15). In addition, only 65% of the isocyanate groups were converted to potential amine functionality compared to 75% for the previous polymer.

A series of pigmented coatings based on this alternate polyurethane dispersion (2911-152) but employing various concentrations and compositions of epoxy resin blends was formulated. The series is summarized in Table 34.

Table 34

Dispersion Properties of Crosslinking Agent Series Topcoat^a Formulations

	<u>2911-155</u>	<u>2911-158</u>	<u>2911-161</u>	<u>2911-164</u>	<u>2911-167</u>
Epoxy/amine ratio	1:1	1.5:1	2:1	1:1	1.5:1
DER 331/Z6040 ratio	3:2	3:2	3:2	1:4	1:4
P/B ^b	0.5	0.5	0.5	0.5	0.5
Solids, percent	42.9	43.6	43.4	44.2	44.7
Viscosity, sec(#22)	28	30	28	31	33
pH	5.70	5.75	5.75	5.70	5.70
Density, lbs/gal	9.73	9.72	9.60	9.82	9.79
VOC ^c	4.7	5.1	4.7	5.2	5.3

- a. TiPure R960.09 (DuPont); b. Mass ratio of pigment to resin solids;
c. Volatile organics as a weight percent of total formulation.

Comparison of the tabulated entries reveals that the epoxy levels varied from stoichiometric equivalence with primary amine functionality to 100 percent excess. As described, the excessive amount was calcu-

lated for reaction with all the available amine hydrogen atoms.

In addition to concentration, changes in the composition of the epoxy crosslinking agent blends were made. The ratio of epoxy resin to epoxy silane was varied from 3:2 to 1:4.

The fluid resistance performance of these prospective coatings is detailed in Table 35.

Table 35

Fluid Resistance of Crosslinker Series Formulations

<u>Formulation</u>	<u>Film Thickness, mil</u>	<u>Gloss 60°</u>	<u>Original Hardness</u>	<u>Lubricating Oil(δ,8)</u>	<u>Water (δ,23)</u>	<u>H5606 (δ,7)</u>	<u>Skydrol 500B(δ,11)</u>	<u>TT-S-735 (δ,7.5)</u>
2911-155	1.0-1.2	94.2-95.1	B(B)	HB(B,HB)	<4B(3B)	HB(HB)	<4B(<4B)	B(2B)
2911-158	1.0-1.3	93.8-95.4	B(B)	HB(HB)	<4B(3B)	B(HB)	<4B(<4B)	2B(2B)
2911-161	0.9-1.2	95.1-96.1	2B(B)	HB(HB)	<4B(2B)	B(B)	<4B(<4B)	2B(2B)
2911-164	0.8-1.1	94.0-94.8	2B(B)	HB,F(F)	<4B(2B)	B(B)	<4B(<4B)	2B(2B)
2911-167	0.6-1.1	94.3-95.3	2B(B)	HB(HB)	<4B(2B)	B(B)	<4B(<4B)	2B(2B)

Data compiled in the table reveal water resistance to be at best marginal and only in the case of accelerated cures. Skydrol resistance is still poor in all cases.

Comparison of formulations 2911-155, 2911-158, and 2911-161 reveals that increasing the concentration of epoxy resins does not provide the additional crosslinking as expected. In fact, enriching the epoxy content appears to reduce resistance to H5606 hydraulic fluid and TT-S-735 hydrocarbon.

Comparison of formulations 2911-155, 2911-164 and 2911-167 reveals that the effect of altering the epoxy resin composition is minimal.

Table 36 lists the flexibility of the crosslinking agent series formulation.

Table 36

Flexibility of Crosslinker Series Formulations

<u>Formulation</u>	<u>Film Thickness, mil</u>	<u>Ambient Impact</u>	<u>High Temp. Impact</u>	<u>Low Temp. Mandrel</u>
2911-155	0.7-1.1	60%	60%	pass 3/8 in.
2911-158	0.7-1.1	60%	60%	pass 3/8 in.
2911-161	0.6-0.9	60%	60%	pass 3/8 in.
2911-164	0.6-0.9	60%	60%	pass 3/8 in.
2911-167	0.7-1.0	60%	60%	pass 3/8 in.

The results described in the table indicate that flexibility is unaffected by the changes in crosslinking agent and is acceptable in all cases.

This last study provided no improvement over previously evaluated formulation 2911-92.

III. Experimental

This section will briefly describe the techniques used in the synthesis, dispersion and formulation of the products discussed in Section II, Results and Discussion. Since many materials were discussed, a general procedure for all materials will be described and the differences among the individual products will be given in tabular form according to material composition.

A. Synthesis

This section will describe the synthetic techniques and material composition of the products related to clear coatings discussed in Section II.

1. Ketimine-blocked Amine 2830-22(3)

Into a 2 liter single neck flask is weighed 47.7g of deithylenetriamine (2), 99.5g of methylisobutyl ketone (1), 0.25g of Dowex 50W-X8 ion exchange resin and enough benzene to make a final volume of 750 ml. The

flask is then equipped with a magnetic stirrer, Dean-Stark trap and reflux condenser (with drying tube).

The mixture is then heated to reflux with stirring and water is azeotropically removed. Reflux is continued until water is no longer collected (16.6g theory). The solution is then cooled to ambient temperature and the resin is filtered. The filtrate is then concentrated by rotary evaporation under vacuum.

The product is transferred to an amber bottle without further purification and stored under nitrogen in a refrigerator.

IR (cm^{-1}): 3350 (bd. singlet), N-H; 1660 (sharp singlet), C=N.

Proton and carbon magnetic resonance spectra confirm structure 3.

Literature¹⁷ report: 1,7-bis(1,3-dimethylbutylidene) diethylenetriamine; b.p. 138°C (1 mm Hg).

2. Linear Polyurethanes

The following general procedure describes the synthesis, adduct (5) formation and aqueous dispersion of the amine-functional linear polyurethanes referred to in Section II:

A four neck flask is equipped with mechanical stirrer, thermometer, reflux condenser (drying tube), dry nitrogen inlet, and dropping funnel. Into the flask is poured the solvent mixture and polyol reactants. The flask contents are heated to reaction temperature (80°C) and thermostated to $\pm 1^\circ\text{C}$. The catalyst solution is then added to the flask.

To this solution is then added the isocyanate component. Addition is made to occur dropwise over 1 hour at the reaction temperature. The isocyanate content of the mixture is monitored periodically until the theoretical value is attained.

The temperature of the mixture is then lowered to 60-70°C and a solution of 3 equivalents of ketimine 2830-22 (3) in the indicated solvent is added dropwise in 15-20 minutes. After addition, the isocyanate absorption in the infrared spectrum is monitored periodically. The temperature is maintained until the isocyanate is consumed (approximately 30 minutes). The solution is then cooled and poured into a glass jar.

Aqueous dispersion of the imine adduct (5) described above is then accomplished. The adduct is weighed into a stainless steel beaker and treated with an equivalent amount of acetic acid. Low shear agitation is then applied for a few minutes to ensure complete mixing. Agitation is then increased to high shear and deionized water is added slowly. Viscosity continues to rise until inversion is reached as evidenced by dramatic viscosity reduction. Addition of water to the desired concentration is continued.

The dilute dispersion is then transferred to a flask and the co-solvent is removed by rotary evaporation under vacuum. The concentration is adjusted by adding the calculated amount of deionized water.

a. Polyol Series Polyurethanes

The following section will detail the synthesis, dispersion and clear-film formulation of the polymers discussed in the section relating to evaluation of hydroxy-terminated prepolymers; Section II-A-2-a.

1. Polymer and Imine-adduct (5) Synthesis

The following table describes the material composition (in grams) of the polymers and imine-adducts designed to evaluate the effect of various prepolymers on flexibility.

<u>Polymer</u>	<u>2830-59</u>	<u>2830-65</u>	<u>2830-71</u>	<u>2830-77</u>	<u>2830-83</u>
<u>Adduct(5)</u>	<u>2830-60</u>	<u>2830-66</u>	<u>2830-72</u>	<u>2830-78</u>	<u>2830-84</u>
Toluene diisocyanate	174.7	84.7	72.4	154.6	94.9
Diol:					
Triethylene glycol	145.3				
Niax PCP-0200		235.3			
Polymeg Q-650			247.6		
Tetraethylene glycol				165.4	
Niax PPG-425					225.1
Solvent:					
1,2-Dimethoxyethane	272.0	272.0	272.0	272.0	272.0
Butyrolactone	48.0	48.0	48.0	48.0	48.0
Dibutyltindilaurate (1%)	1.2	0.6	0.5	1.0	0.6
2830-22(3)	19.2	19.2	18.8	22.6	24.5
1,2-Dimethoxyethane } mix	19.2	19.2	18.8	22.6	24.5

2. Aqueous Dispersion

The following table describes the material composition (in grams) of the cationic dispersions prepared from the imine-adducts described in the previous section.

	<u>2830-61</u>	<u>2830-67</u>	<u>2830-73</u>	<u>2830-79</u>	<u>2830-85</u>
<u>Adduct(5):</u>					
2830-60	181.5				
2830-66		224.2			
2830-72			177.6		
2830-78				194.1	
2830-84					260.7
1,2-Dimethoxyethane		47.6	31.9		
Butyrolactone		8.4	5.6		
Acetic acid, glacial	2.4	3.0	2.2	3.2	4.4
Deionized water	178.4	464.1	198.8	219.1	256.3
Solvent removed	51.8	314.2	22.9	131.0	169.4

3. Clear-film Formulation

The following table describes the material composition (in grams) of the clear-film formulations developed from the aqueous polyurethane dis-

persions listed in the previous section.

	<u>2830-63</u>	<u>2830-69</u>	<u>2830-75</u>	<u>2830-81</u>	<u>2830-87</u>
<u>Dispersion</u>					
2830-61	155.8				
2830-67		218.1			
2830-73			282.9		
2830-79				204.7	
2830-85					228.2
1,2-Dimethoxyethane } mix	4.0	5.0	5.0	8.0	10.0
DER 331	3.7	4.8	5.0	7.3	8.4
Fluorad FC170C (1% aq)	6.5	2.3	2.9	4.4	2.5
Deionized water				43.0	

b. Fluid Resistance and Flexibility Series Polyurethanes

The following section will list the synthesis, dispersion, and clear-film formulation characteristics of the polymers described in the sections relating to the combination of fluid resistance and flexibility; Sections II-A-2-b and II-A-2-c.

1. Polymer and Adduct (5) Synthesis

The following table describes the material composition (in grams) of the polymers and adducts designed to provide the combination of fluid resistance and flexibility.

<u>Polymer</u>	<u>2830-29</u>	<u>2830-38</u>	<u>2830-23</u>	<u>2830-44</u>	<u>2830-95</u>	<u>2830-109</u>	<u>2830-119</u>	<u>2830-141</u>
<u>Adduct (5)</u>	<u>2830-30</u>	<u>2830-39</u>	<u>2830-24</u>	<u>2830-45</u>	<u>2830-96</u>	<u>2830-110</u>	<u>2830-120</u>	<u>2830-142</u>
Toluene diisocyanate	146.2	143.4	140.7	134.0	89.4	96.6	105.3	116.0
Dantocol DHE	173.8	166.1	158.7	147.7		21.6	47.7	79.8
Niix PCP-0200		10.5	20.6	38.3	230.6	201.8	167.0	124.2
1,2-Dimethoxyethane	272.0	272.0	408.0	272.0	332.4	272.0	272.0	272.0
Butyrolactone	48.0	48.0	72.0	48.0	58.7	48.0	48.0	48.0
Dibutyltindilaurate (1%)	1.0	1.0	0.9	0.9	0.6	0.6	0.7	0.8
2830-22 (3) } mix	19.7	21.4	12.1	20.9	32.7	44.5	42.5	39.6
1,2-Dimethoxyethane	19.7	21.4	18.1	20.9	40.0	44.5	42.5	39.6

2. Aqueous Dispersion

The following table compares the material composition (in grams) of

aqueous cationic dispersions prepared from the amine-functional polymers described in the previous section.

	<u>2830-31</u>	<u>2830-40</u>	<u>2830-25</u>	<u>2830-46</u>	<u>2830-97</u>	<u>2830-111</u>	<u>2830-121</u>	<u>2830-143</u>
Adduct (5):								
2830-30	228.1							
2830-39		224.0						
2830-24			247.1					
2830-45				235.1				
2830-96					395.1			
2830-110						320.7		
2830-120							277.4	
2830-142								352.5
1,2-Dimethoxyethane							30.8	
Acetic acid, glacial	2.9	3.8	1.8	3.8	8.3	10.0	9.1	10.0
Deionized water	324.8	221.9	180.8	272.2	532.4	398.2	376.2	420.8
Solvent removed	76.6	76.8	89.5	129.6	330.1	320.1	145.7	352.5

3. Clear-film Formulation

The following table details the material composition (in grams) of the clear-film formulations developed from the cationic dispersions described in the previous section.

Cationic dispersion:	<u>2830-33</u>	<u>2830-42</u>	<u>2830-27</u>	<u>2830-48</u>	<u>2830-99</u>	<u>2830-113</u>	<u>2830-123</u>	<u>2830-145</u>
2830-31	320.4							
2830-40		282.6						
2830-25			273.8					
2830-46				256.0				
2830-97					270.2			
2830-111						165.1		
2830-121							211.4	
2830-143								137.9
DER 331	6.1	8.9	4.6	8.0	9.8	12.7	11.1	10.1
1,2-Dimethoxyethane } mix	7.0	10.0	7.0	8.0	10.0	15.0	12.0	7.0
Fluorad FC-170C (1% Aq.)	7.9	7.6	2.9	4.2	5.8	2.2	4.7	3.7
Deionized water	60.0				25.0	25.0		30.0

c. Crosslinking Agent Series Polyurethanes

The following section will describe the synthesis, dispersion and clear-film formulation of the amine-functional polyurethanes prepared to evaluate the effect of various epoxy resins on fluid resistance. The corresponding discussion section is II-A-2-d.

1. Polymer and Imine-adduct (5) Synthesis

The following table describes the material composition (in grams) of

the polymers and adducts designed to evaluate various crosslinking agents.

<u>Polymer</u>	<u>2830-103</u>	<u>2830-129</u>	<u>2830-135</u>	<u>2830-170</u>	<u>2830-161</u>	<u>2911-07</u>
<u>Adduct (5)</u>	<u>2830-104</u>	<u>2830-130</u>	<u>2830-136</u>	<u>2830-171</u>	<u>2830-162</u>	<u>2911-08</u>
Toluene diisocyanate	84.7	92.1	101.0	111.9	106.1	403.9
Dantocol DHE		22.0	48.7	81.4	64.1	194.6
Niax PCP-0200	253.3	205.9	170.4	126.7	149.7	681.5
1,2-Dimethoxyethane	272.0	272.0	272.0	272.0	272.0	1088.0
Butyrolactone	48.0	48.0	48.0	48.0	48.0	192.0
Dibutyltindilaurate (1%)	0.6	0.6	0.7	0.8	0.7	2.7
2830-22 (3)	15.8	22.5	22.1	21.8	22.5	88.6
1,2-Dimethoxyethane } mix	15.8	22.5	22.1	21.8	22.5	88.6

2. Cationic Aqueous Dispersion

The following table lists the material composition (in grams) of the aqueous dispersions prepared from the adducts described in the previous section.

	<u>2830-105</u>	<u>2830-131</u>	<u>2830-137</u>	<u>2830-172</u>	<u>2830-163</u>	<u>2911-09</u>
Adduct (5):						
2830-104	249.7					
2830-130		319.4				
2830-136			321.5			
2830-171				189.5		
2830-162					324.6	
2911-08						295.6
1,2-Dimethoxyethane	53.1					
Butyrolactone	9.4					
Acetic acid, glacial	3.0	5.2	4.9	3.0	5.4	4.7
Deionized water	309.1	406.0	356.5	219.4	375.7	362.6
Solvent removed	155.7	198.0	102.0	59.3	193.0	221.4

3. Clear-film Formulation

The following table details the material composition (in grams) of the clear-film formulations prepared from the aqueous dispersions listed in the previous section. Since dispersion 2911-09 was formulated with pigments only, no clear-film formulation will be listed. Instead, the pigmented formulations based on this dispersion will be described in the next section related to pigmentation.

Aqueous dispersion:	<u>2830-107</u>	<u>2830-133</u>	<u>2830-139</u>	<u>2830-186</u>	<u>2830-182</u>	<u>2830-184</u>
2830-105	354.0					
2830-131		199.0				
2830-137			328.2			237.1
2830-172				228.5		
2830-163					174.4	
DER 331	4.3	3.5	4.6			
PGAX				2.0	1.9	1.6
Z6040 Silane	3.6	3.0	3.9	3.2	2.9	2.6
1,2-Dimethoxyethane	10.0	5.0	6.0	2.0	2.0	2.0
Butyrolactone		1.0		1.0	1.0	1.0
Fluorad FC-170C (1% aq)		2.5	8.0	6.0	3.6	6.0
Deionized water		65.0	60.0	95.0	14.0	95.0

3. Branched Polyurethanes

The following section will relate, in tabular form, the synthesis and dispersion characteristics relating to the discussion of branched polyurethanes. The general synthetic procedure is identical to that detailed for linear polyurethanes in Section III-A-2 and will not be described here.

a. Polymer and Imine-adduct(5)

The following table lists the material composition (in grams) of the branched polyurethanes and their respective adducts.

<u>Polymer</u>	<u>2911-49</u>	<u>2911-61</u>	<u>2911-76</u>	<u>2911-86</u>	<u>2911-150</u>
<u>Adduct(5)</u>	<u>2911-50</u>	<u>2911-62</u>	<u>2911-77</u>	<u>2911-87</u>	<u>2911-151</u>
Toluene diisocyanate	106.8	106.8	108.0	109.1	218.3
Dantocol DHE	46.5	46.5	45.6	44.7	89.4
Niax PCP-0200	162.9	162.9	159.8	156.5	313.0
Tris(2-hydroxyethyl) isocyanurate	3.8	3.8	6.7	9.7	19.3
1,2-Dimethoxyethane	272.0	272.0	272.0	272.0	576.0
Butyrolactone	48.0	48.0	48.0	48.0	64.0
Dibutyltindilaurate (1%)	0.7	0.7	0.7	0.7	1.4
2830-22(3)	43.8	32.9	27.8	29.0	53.7
1,2-Dimethoxyethane } mix	43.8	32.9	27.8	29.0	53.7

b. Aqueous Dispersion

The following table summarizes the material composition (in grams) of the cationic aqueous dispersions prepared from the branched polyurethanes listed in the previous section.

	<u>2911-51</u>	<u>2911-63</u>	<u>2911-78</u>	<u>2911-88</u>	<u>2911-152</u>
Adduct (5):					
2911-50	311.7				
2911-62		275.8			
2911-77			358.9		
2911-87				251.7	
2911-151					1303.9
Acetic acid, glacial	8.2	5.3	5.9	4.3	22.3
Deionized water	284.7	260.3	450.9	316.0	1148.0
Solvent removed	245.0	153.7	314.3	226.8	724.3

B. Pigmentation

This section will describe the material composition of the pigmented coatings evaluated as topcoats and discussed in Section II.

1. Topcoat Formulations Based on Linear Polyurethanes

The following general procedure is used to prepare the pigmented topcoat formulations discussed in Section II:

The cationic aqueous dispersion is weighed directly into a 1 liter stainless steel beaker and mixed under low shear agitation. To the dispersion is then added defoamer, water (or solvent) and rutile titanium dioxide. The mixture is then stirred under high shear agitation for a few minutes to ensure pigment wetting. The slurry is then transferred to a pebble mill and ground to the desired Hegman fineness.

The pigmented grind is then transferred to a beaker and the mill yield is calculated. The letdown is prepared in a separate beaker and the pigment grind is added to the letdown with low shear agitation.

The final spray formulation is then prepared by adding the appropriate crosslinking agents, flow control aids and water (or diluents)

to the pigment base.

The following table lists the material composition (in grams) of the aqueous topcoats based on the linear polyurethanes as discussed in Section II-B.

	<u>2911-11</u>	<u>2911-22</u>	<u>2911-26</u>	<u>2911-96</u>	<u>2911-72</u>
Grind:					
Dispersion 2911-09	138.8	223.5	218.4		165.3
Dow XD7080				11.9	
Ti Pure R960.09	46.7	44.4	100.9	58.3	
Kadox 515					60.0
Surfynol 104A	0.1	0.2	0.2	0.2	0.1
Deionized water	18.9	14.6	40.5	58.1	
Grind to NS 7+					
Letdown:					
Dispersion 2911-09	138.8	223.5	218.4	332.6	165.3
Deionized water	56.8	43.8	121.5	38.9	9.2
Spray formulation:					
Pigment base	178.2	203.5	225.3	350.5	167.6
DER 331	2.5	3.3	2.8	5.1	3.0
Z6040 silane	2.1	2.8	2.3	4.3	2.5
1,2-Dimethoxyethane	4.0	4.0	3.0	5.0	3.0
Fluorad FC-170C (1% aq.)	3.7	4.3	7.0	7.2	5.3
Deionized water	10.0	45.0			

2. Topcoat Formulations Based on Branched Polyurethanes

The following table lists the material composition (in grams) of the topcoat formulations based on branched polyurethanes as discussed in Section II-C-1. The procedure used to prepare these formulations is similar to the general procedure described in the previous section.

	<u>2911-53</u>	<u>2911-65</u>	<u>2911-80</u>	<u>2911-92</u>
Grind:				
Dispersion 2911-51	150.7			
Dispersion 2911-63		148.1		
Dispersion 2911-78			145.3	
Dispersion 2911-88				168.3
Ti Pure R960.09	60.0	53.3	52.5	60.0
Surfynol 104A	0.1	0.1	0.1	0.1
Deionized water		25.2		
Grind to NS 7+				
Letdown:				
2911-51	150.7			
2911-63		148.1		
2911-78			145.3	
2911-88				168.3
Deionized water	38.5	25.2	6.9	3.4
Spray formulation:				
Pigment base	283.8	340.6	120.6	309.0
DER 331	9.2	6.5	2.2	5.9
Z6040 silane	7.8	5.5	1.9	5.0
1,2-Dimethoxyethane	6.0	5.0	2.0	5.0
Fluorad FC170C (1% aq.)	6.1	7.1	1.3	3.2
Deionized water			10.0	15.0

3. Topcoat Formulations Based on Polyurethane 2911-152

The following table lists the material composition (in grams) of the topcoat formulations based on aqueous polyurethane dispersion 2911-152. These formulations were designed to examine the effect of crosslinking agent composition and concentration on fluid resistance as discussed in Section II-C-2.

	Pigment Base				
	<u>2911-154</u>				
Grind:					
Dispersion 2911-152	329.6				
Ti Pure R960.09	128.0				
Surfynol 104A	0.2				
Grind to NS 7+					
Letdown:					
Dispersion 2911-152	329.6				
Deionized water	12.6				
Spray formulations:					
	<u>2911-155</u>	<u>2911-158</u>	<u>2911-161</u>	<u>2911-164</u>	<u>2911-167</u>
Pigment base 2911-154	201.2	162.8	176.1	169.3	154.8
DER 331	4.1	5.0	7.2	1.2	1.6
Z6040 silane	3.5	4.2	6.1	5.8	8.0
1,2-Dimethoxyethane	5.0	5.0	5.0	5.0	5.0
Fluorad FC-170C (1% aq.)	4.3	3.5	3.9	3.6	3.4
Deionized water	25.0	20.0	27.0	15.0	15.0

IV. Appendix

Table 37

Structural Identity of Polyurethane Formulation Components

<u>Designation</u>	<u>Name</u>	<u>Structure</u>
Isocyanate:		
TDI	Toluene diisocyanate: mixture of 2,4- and 2,6-isomers	
Polyol:		
EG-3(4)	Tri(tetra) ethylene glycol	$\text{HO} \left[\text{CH}_2 \text{CH}_2 \text{O} \right]_n \text{H}$ $n = 3, 4$
PPG-425	Polypropylene Glycol	$\text{HO} \left[\text{CH}_2 \text{CH}(\text{CH}_3) \text{O} \right]_n \text{H}$
Q-650	Polymeg 650	$\text{HO} \left[\text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{O} \right]_n \text{H}$
PCP-0200	Polycaprolactone	$\text{HO} \left[(\text{CH}_2)_5 \text{CO}_2 \right]_m \left[\text{CH}_2 \text{CH}_2 \text{O} \right]_n \text{H}$
Dantocol DHE	Bis (2-hydroxyethyl) dimethyl-hydantoin	
THEIC	Tris (2-hydroxyethyl)-isocyanurate	
Epoxy: Z6040 silane	γ - Glycidoxypropyl-trimethoxysilane	
PGA-X	Tetraglycidyl-meta-xylylenediamine	

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18. As suggested by Prof. R.B. Seymour at the Fall 1981 ACS meeting, the convention of designating the solubility parameter in terms of Hildebrand units will be used.

