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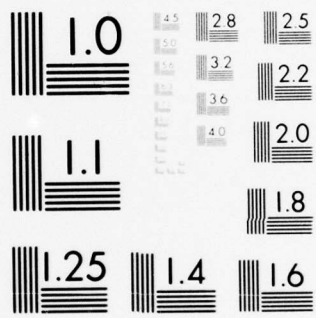
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# WATERBORNE COATINGS FOR AIRCRAFT

*NORTH DAKOTA STATE UNIVERSITY  
FARGO, NORTH DAKOTA 58102*

MAY 1978

TECHNICAL REPORT AFML-TR-78-44  
Report for Period 1 June 1977 - 31 December 1977

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FOR THE COMMANDER

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The purpose of this work was to determine the potential of waterborne polymers for use in high performance coatings for aircraft. The impetus for replacing current solvent-borne aircraft topcoats and primers is to reduce air pollution associated with solvent emissions. The approach was to obtain information on current waterborne technology by carrying out a literature search and by consultations with coatings scientists from coatings companies, raw materials suppliers, and institutes. The information		

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obtained was evaluated with regard to suitability of various waterborne coatings for use under conditions required in aircraft coating procedures such as spray application and ambient-temperature cure.

It was concluded that none of the currently available waterborne systems are suitable for replacement of current Air Force topcoats and primers without additional research and development. Waterborne replacements under current development were ranked according to potential for achieving the high performance required of aircraft coatings, and some of the problems anticipated for each type were identified.

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## FOREWORD

This report was prepared by Loren W. Hill, North Dakota State University, during participation as a Visiting Scientist under appointment on Task 12, F33615-77-C-5003, Contributive Research/Resident Scientists Program, administered by Southeastern Center for Electrical Engineering Education (SCEEE), Auburn, Alabama for the Air Force Materials Laboratory. The contract was initiated under Project Number 2422, "Protective Coatings and Materials", Task Number 242202, "Nonmetallic Coatings and Erosion Behavior". The work was administered under the direction of the Elastomers and Coatings Branch (AFML/MBE), Nonmetallic Materials Division, Air Force Materials Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio 45433. Mr. Michael J. Moscynski served as Project Engineer. This report covers work from 1 June 1977 through 31 December 1977.

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## SECTION I

### INTRODUCTION

Exterior aircraft coatings in current use (primer MIL-P-23377C and topcoat MIL-C-83286B) (1,2) contribute to pollution by emission of volatile organic compounds that are present as solvents. In the presence of sunlight and oxides of nitrogen emitted in automobile exhaust, volatile organic compounds contribute to photochemical smog production (3,4). A three-phase program for reduction of this source of pollution consists of 1. replacing air spray application by airless *electrostatic spray*, 2. use of high solids coatings, and 3. development of waterborne coatings for aircraft. The first phase has become operational by introduction of airless electrostatic spray equipment at the Air Logistics Centers (ALCs). An AFML contractual program (F33615-77-C-5101) for formulation of high solids coatings (65% volume solids) has been awarded to DeSoto, Inc. High solids coatings are considered to be an interim approach allowing for substantial reduction of solvent emissions.

Waterborne coatings are potentially more advantageous than high solids coatings because pollution, fire and health hazards, and wasteful use of costly organic solvents are greatly reduced. However, at the time of initiation of this visiting scientist program, commercial waterborne technology had not produced coatings having the high

performance required for aircraft exteriors. Therefore, survey and ranking of the potential of current and newly emerging waterborne systems for aircraft became part of this program.

## SECTION II

### BACKGROUND

#### 1. COMMERCIAL WATERBORNE SYSTEMS

Current commercial waterborne industrial coatings are not suitable for use on aircraft exteriors for one or more of the following reasons: 1. the method of application is impractical for aircraft, 2. high temperature cure is required whereas aircraft coatings must cure at ambient temperature, and/or 3. coatings performance is inadequate. A large current use of waterborne systems is for electro-deposition, but the complete immersion required clearly makes this approach impractical for completely assembled aircraft. Spray applied one-package thermosetting waterborne systems are widely used, and their use is growing rapidly; however, modification of such systems to achieve ambient cure would require remarkable advances. One-package air-drying waterborne systems that cure by ambient autoxidation involving double bonds in fatty acid residues do not show promise of achieving the required performance properties. Although industrial latex paints are being improved at a rapid rate, the possibility of achieving adequate resistance to liquids, such as hydraulic fluid, is open to question.

## 2. AIRCRAFT COATING REQUIREMENTS

The main function of aircraft coatings is to minimize corrosion and resulting high maintenance costs. High level performance specifications are required to insure that the coating system remains intact so that it can maintain its protective function. One combination of properties that is difficult to achieve is flexibility and resistance to organic liquids used in aircraft. Flexibility must be maintained at low temperatures and in impact. Aircraft coatings must be resistant to hydraulic fluids, lubricating oils and hydrocarbons. In most cases changes that increase flexibility of coatings, such as decreasing the extent of cross-linking, cause a decrease in resistance to the organic liquids. Thus, the combination of flexibility and organic liquid resistance, obtained with the current urethane topcoat, is unusual.

In order to prolong the useful lifetime of aircraft, Air Force practice involves complete paint stripping followed by metal pretreatment and recoating with primer and topcoat on a three to five year cycle. Thus, strippability is an important requirement which is in conflict with good adhesion and resistance to organic liquids.

Although resistance to softening on water immersion has not been difficult to achieve for solvent borne aircraft coatings, adequate performance of waterborne systems in water immersion tests may be more difficult to achieve.

### 3. PREVIOUS AFML CONTRACTURAL EFFORT

Since development of a completely new system that matches the unusual combination of flexibility and liquid resistance of the current urethane would be a challenging problem, the alternative of modification of the current system to make it waterborne appears attractive. In pursuing this alternative, acceptance of two-package systems for current coatings applications at ALCs is a substantial advantage. In the coatings industry the potential of two-package waterborne systems has not been as thoroughly investigated as is the case for one-package *thermosetting or air-drying* systems.

The modification of current systems to arrive at waterborne variations was attempted in an AFML supported study at Lehigh (5). For replacement of the epoxy-polyamide primer (MIL-P-23377C), the approach was to prepare aqueous emulsions of each component separately and to mix the two emulsions shortly before application as with the conventional two-package solvent system. The main problems with the primer were slow cure rates, preferential reaction at the interface between epoxy resin particles and curing agent particles, and pigment flocculation. For the aliphatic isocyanate topcoat (MIL-C-83286B), direct emulsification of the isocyanate component was not possible because isocyanate groups react with water. Therefore, the isocyanate groups were pre-reacted with polyols to form adducts. The adducts

formed films, but additional modifications for improvement of properties were recommended. Another undesirable feature of this emulsification approach was that ultrasonic irradiation or mechanical homogenization are required to obtain the small particle sizes required for stable emulsions. The effect of surfactants on film properties was not elucidated (5).

SECTION III  
SURVEY SUMMARY

Technical consultations were held with coatings scientists to obtain information concerning development of waterborne coatings. The dates of these meetings and companies (or institute) involved were as follows:

July 1	DeSoto, Inc. Des Plaines, Illinois
July 1	The Sherwin-Williams Co. Chicago, Illinois
July 26	3M Co. St. Paul, Minnesota
July 26	General Mills Chemicals* Minneapolis, Minnesota
July 27	Valspar Corp. Minneapolis, Minnesota
Aug. 1	Inmont Corp.** Automotive Development Center Whitehouse, Ohio
Aug. 9	Dow Corning Corp.***
Aug. 10	W. R. Grace and Co.***
Aug. 11	Polyvinyl Chemical Industries Wilmington, Mass.

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\*The Chemical Division of General Mills has recently been acquired by Henkle, A German Corporation.

\*\*Inmont Corp. has recently been acquired by Carrier Corp.

\*\*\*Meeting held at AFML, W-PAFB, Ohio

Aug. 11	Hughson Chemicals Lord Corporation Erie, Pennsylvania
Aug. 12	Mobay Chemical Corp. Pittsburgh, Pennsylvania
Aug. 12	Westinghouse Electric Corp. Research and Development Center Pittsburgh, Pennsylvania
Aug. 18	Battelle Memorial Institute Columbus Laboratories Columbus, Ohio

Selection of companies for consultations was based on identification of potential waterborne products in technical and trade literature, demonstrated previous interest in aircraft coatings, and existence of personal contacts at companies.

An outline of the approach and a list of questions used in consultations are given in the appendix. Several companies indicated that they would submit a proposal in response to a request of a contractual program directed at development of a waterborne replacement for the current topcoat (Question 1.).

Three companies indicated that they were well along in development of systems that had potential for matching performance properties of current aircraft topcoats. As expected, details of these systems were considered proprietary; however, it appeared that all three systems involved reactions included in the discussion presented in the next section. In some cases, potential toxic hazards were discussed. An

additional six companies indicated that they had developed water systems for other applications that included many of the performance requirements specified for aircraft.

When asked to predict which type of waterborne system had the greatest potential for urethane topcoat replacement, coatings scientists, in most cases, did not make a direct response. A frequent response was to emphasize the need to carefully compare the relative environmental advantages of high solids systems and waterborne systems. In several cases dispersions were considered superior to water soluble types and latex systems. (These terms are defined in the next section.)

Five companies indicated that they had investigated the use of urethane dispersions or closely related products. Of these five, two companies had developed their own products of this type while the others had used commercially available products. The polyfunctional aziridine cross-linkers, sometimes used in combination with polyurethane dispersions, were recognized as potential health hazards. One company is continuing toxicological testing of the cross-linkers, and they express optimism about the possibility of safe use of low levels of cross-linker under carefully controlled conditions.

All of the companies indicating an interest in submission of a proposal for topcoat replacement, expressed preference for considering development of a complete primer/topcoat system. The consensus

was that primer replacement would be less challenging than topcoat replacement. Several variations of two-package systems were discussed in which the cross-linker is water soluble and possesses surfactant-like properties such that epoxy resins can be readily emulsified prior to application. Possibly part of the optimism about primer replacement is related to less demanding flexibility requirements in the primer specifications (1), in comparison to the topcoat specifications (2). In most of the consultations, one or more company or institute representatives were knowledgeable concerning aircraft coating specifications.

## SECTION IV

### DISCUSSION

#### 1. PROCEDURES AND SPECIFICATIONS

Before assessing the potential of waterborne coatings for replacement of current aircraft coatings, it is necessary to establish ground rules related to Air Force coating procedures. Judgements will be based on the assumption that the following procedures will not be modified: 1. application by spray, preferably airless electrostatic spray, 2. ambient temperature cure, and 3. strip and recoat on a three to five year cycle. The size and irregular shape of aircraft make most application methods, other than spray, impractical. The size also eliminates high temperature cure, and the irregular shape eliminates UV cure, at least by current UV technology. It is doubtful that the replacement coatings will be good enough to eliminate the need for stripping and recoating.

It is also necessary to consider coating performance requirements in detail. It is tempting to simply state that the waterborne replacements must meet the specifications of the current primer (1) and topcoat (2). The danger in this approach is that current specifications may have been established on the basis of performance of the current systems in paint test methods rather than on the basis of properties required for successful performance of coatings on aircraft. Thus,

demanding that replacements meet requirements of current specifications might be too restrictive, resulting in unjustified elimination of certain potential waterborne systems. Unfortunately, the requirements for successful performance on aircraft are not well established. Thus, it is not possible to know which requirements could be made less stringent.

At least some modification of requirements in the current topcoat specifications will be necessary for waterborne replacements. For instance,

"3.5.6 Moisture Content Component I of the gloss coating material shall not contain more than 0.50 percent by volume of water...."

Obviously this low level of water in a waterborne component is impossible. Other examples of requirements that were written with solvent borne urethane systems in mind are 3.5.4 Nonphotochemically reactive solvent and 3.6.6 Free diisocyanate.

Requirement 3.6.2 (Drying time) appears to be unnecessarily restrictive. It requires a set-to-touch time of 2 hours or less and a dry-to-recoat condition of 1 hour or less. Since the rate of water loss from coatings is lower than loss rates of most organic solvents used in coatings, acceptance of less stringent drying times may be necessary. Modifications in coating procedures to accommodate longer drying times

would appear to be a minor inconvenience compared to the potential advantages of water systems. The effect of variations in relative humidity in ALCs on water loss rates will be an important consideration (6).

## 2. TERMINOLOGY AND CLASSIFICATION

It is generally agreed that, in addition to emulsions (Section II 3.), there are three types of waterborne systems which can be classified according to appearance, molecular weight of the polymeric component, and the particle size of the dispersed phase. However, there is considerable variation in terminology used to identify each type and in the specification of dividing lines between types. A classification consistent with common current terminology (7, 8, 9) is given in Table 1.

TABLE 1  
CLASSIFICATION OF POLYMERS FOR WATERBORNE COATINGS

	<u>Water Soluble</u>	<u>Aqueous Dispersion</u>	<u>Latex</u>
Appearance	Clear	Translucent	Opaque
Particle Size (micrometers)	0.001 to 0.01	0.01 to 0.1	0.1 to 1.0
Molecular Weight	5000 to 20,000	20,000 to 50,000	Approximately 1,000,000

Several sources of confusion exist in use of the terms in Table 1. The systems called "water soluble" are usually not soluble in water

unless an organic cosolvent is also present, and frequently aggregation of polymer molecules occurs so that particle size is variable depending on polymer concentration and water/cosolvent ratio (10). As used in Table 1, "aqueous dispersion" has a fairly specific meaning whereas in general usage dispersion has a broader meaning encompassing any system consisting of a discontinuous phase and a continuous phase. The aggregation phenomenon, mentioned in connection with water soluble systems, is even more pronounced in aqueous dispersions; thus, particle size is again very dependent on polymer concentration and solvent composition. "Latex" is a better term than "emulsion" for the high molecular weight systems because by analogy to naturally occurring rubber latexes it accurately describes a dispersion of a noncross-linked high polymer in water. The term "emulsion" is too general in this context.

Several attempts have been made to compare performance and application properties characteristic of the types of systems listed in Table 1 (8,9). However, generalizations of this type are of limited value because performance and application properties depend strongly on the specific polymer used, formulation variations, and curing conditions such as high temperature versus ambient cure. Furthermore, rapid advances are being made so that problems identified with a given type of system may be eliminated in the near future.

### 3. RANKING OF WATERBORNE POLYMERS FOR USE IN AIRCRAFT COATINGS

Limiting waterborne replacement candidates by requiring spray application and ambient temperature cure (Section II 2.) results in a short list of possible coatings types:

1. Two-package, reactive coatings
2. One-package coatings that cure by air oxidation of fatty acid chains
3. One-package latex coatings

Coatings of types 1 and 2 are based on relatively low molecular weight waterborne resins such as described under water soluble or aqueous dispersions in the preceding section. To obtain resistance to organic liquids, types 1 and 2 would have to undergo chemical reaction after (or during) application. Such reactions increase the molecular weight and introduce cross-links both of which would increase resistance to organic liquids. Coatings of type 3 form films by coalescence of latex particles and would not undergo reaction during film formation. Even though the molecular weight of latexes is high, it appears unlikely that uncross-linked films would have adequate resistance to organic liquids. Other challenging problems for type 3 coatings are achieving high gloss and avoiding performance problems caused by surfactants and coalescing aids. For these reasons type 3 coatings are ranked below type 1.

Cross-linkable latexes are being developed, but ambient cure variations of this type are uncommon. Of course, use of a second

component for cross-linking, places cross-linked latexes within type 1.

For type 2 coatings, the major problem is likely to be obtaining adequate mechanical properties. This problem is related to the rate of cross-link formation by air oxidation. Although some control of the rate is possible through catalyst variations, the initial rate is likely to be too slow to result in sufficient toughness and high modulus with reasonable drying times. This problem is more serious for multiple coat application as anticipated for aircraft coatings. Long term retention of flexibility may also be a problem because cross-linking will continue as long as air can diffuse into regions where double bonds are present. Many different waterborne polymers have been modified to contain fatty acid chains; thus, the range of polymers available for type 2 systems is broad. Although the seriousness of the problems identified will vary somewhat depending on the particular polymer chosen, it seems unlikely that such problems could be completely eliminated. Therefore coatings of type 2 are ranked below type 1 regarding potential for replacement of current aircraft coatings and approximately equal to coatings of type 3 in this regard.

Waterborne variations of type 1 are ranked highest as potential replacements for current aircraft coatings. The development of such coatings by industry has not reached an advanced stage. Therefore, a

danger exists that problems associated with type 1 coatings have not been as thoroughly identified as is the case for type 2 and type 3 both of which are quite widely used for current industrial coatings. An obvious potential problem is toxicity of components. If the two components have sufficient reactivity to cure effectively when mixed at room temperature, then the reactivity must be high. Since cross-linking reactions in most cases involve functional groups that are present in the human body, it is reasonable to expect that coatings components will be hazardous for personnel who are applying the coatings.

Polymer systems of type 1, under current development, include reactive emulsions and room temperature curing latexes and dispersions. For example, it is reported that aqueous urethane dispersions can be cross-linked at room temperature by polyfunctional aziridine cross-linkers (11). For the two-package emulsion approach, it is reported that a water soluble component can serve both as a cross-linking agent and as a surfactant so that the second component can be readily dispersed without use of other surfactants (12,13). It is anticipated that these systems are suitable starting points for research directed at development of waterborne replacements for current aircraft coatings.

#### 4. EXAMPLES OF TWO-PACKAGE, REACTIVE WATERBORNE SYSTEMS

Polyvinyl Chemical Industries' product, NeoRez R-960 is an example of a urethane dispersion (11). Although the precise structure of this resin has not been disclosed, it is known to contain "pre-reacted" urethane groups and ionic groups which assist in producing a stable dispersion. At least some of the ionic groups are carboxyl groups, and it is the carboxyl groups which react with the three-membered nitrogen containing ring present in polyfunctional aziridine cross-linkers (14). Polyfunctional aziridine cross-linkers are produced by Polyvinyl Chemical Industries (CX-100 and EX-228) and by Cordova Chemical (XAMA series).

An attractive feature of the aqueous urethane dispersion approach is that the unusual combination of flexibility and organic liquid resistance, exhibited by the current solvent borne urethane, might be retained in the waterborne variation. Preliminary tests at AFML/MBE on clear films of a R-960/CX-100 combination produced favorable results (15).

The main drawback of urethane dispersion systems is the potential toxic hazard of the aziridine cross-linkers. These dispersions form films on air drying without cross-linker, but the organic solvent resistance is poor (11). Low levels of cross-linker (approximately 2%) improve solvent resistance substantially. When mutagenic tendencies of the undiluted cross-linker were determined by the Ames test, positive

results were obtained (16). However, when recommended levels of cross-linker were used in dispersion/cross-linker combinations, negative results were obtained (16). In a letter dated 20 September 77, to Mr. Childers, AFML/MXA, Colonel G. D. Taylor of the USAF Occupational and Environmental Health Laboratory (AFSC) recommended that work on aziridine containing cross-linkers should continue and that simultaneously additional toxicological evaluation should be started.

Dow Chemical Company's product, XD-7080, is an example of a resin which acts both as a cross-linker and as a surface active agent for dispersion of a second component in a two-package reactive coating system (12,13). The polymer consists of an acrylic backbone with pendant amine groups. The amine groups are introduced by reaction of carboxyl containing acrylic copolymers with imine derivative (17,18). Water solubility is achieved by addition of an acid which converts amine groups to amine salts. The second component can be a liquid epoxy resin or a high solids solution of an epoxy resin. In either case, the surfactant-like properties of the curing agent promote facile dispersion of the epoxy resin when the components are mixed (12,13).

Several other commercial waterborne resins are available for curing epoxy resins. General Mills Chemicals, Inc. produces a two component, ambient cure waterborne system in which the cross-linker

is an aqueous amidoamine resin (Genamid 5701-H65). The combination is called Waterpoxy II. Ciba-Geigy offers a polyamido/amine developmental hardener (XU207) for use with conventional liquid epoxies.

Although the poor exterior durability of epoxy based coatings would suggest consideration of these systems for the primer only, Shell Development Company is developing a modified epoxy resin reported to be "weatherable" (DRH-151.2). These "weatherable" epoxies are used in combination with XD-7080 (Dow Chemical Co.). If adequate weatherability is achieved, such systems could be considered for topcoats. Flexibility of the epoxy/amine systems may not be adequate for aircraft topcoats, however.

The descriptions of resins and cross-linkers, given above, are included for the purpose of illustrating approaches to development of two-package, reactive waterborne polymer systems for high performance coatings. Inclusion of specific systems shall not be interpreted as an endorsement or recommendation. In a similar way, omission of other specific systems, of this general type, shall not be interpreted as representing an unfavorable evaluation.

##### 5. ENVIRONMENTAL IMPACT OF WATERBORNE VERSUS HIGH SOLIDS SYSTEMS

Since most waterborne coatings contain organic cosolvents and frequently other volatile organic compounds such as amine solubilizers in some cases and acidic solubilizers in other cases, it is not necessarily

true that waterborne coatings will cause less air pollution than high solids coatings. Any valid comparison of pollution abatement potential of these two approaches must take into account the emission levels expressed on the basis of equal area coverage and equal dry film thickness.

Furthermore, the level of reactivity in the environment and the toxicity (if any) of products formed on atmospheric exposure is different for different volatile compounds. For example, preliminary results suggest that certain amines form nitrosamines on exposure to the atmosphere (19). Some nitrosamines are carcinogenic. The potential hazard from this source has not been adequately established. Unfortunately detailed information on environmental reactions of many specific volatile compounds in coatings is not available.

The Environmental Protection Agency (EPA) has reiterated the need for reduction of emissions rather than substitution of low reactivity compounds for high reactivity compounds (20). In spite of this statement, twelve volatile organic compounds have been identified as having "low photochemical reactivity". Included in this list are some solvents that would be useful in coatings such as methyl ethyl ketone, acetone, isopropanol and tertiary alkyl alcohols. An earlier list of four volatile compounds identified as having "negligible photochemical reactivity" did not contain any solvents used in coatings. Alcohol ethers, such as

2-butoxyethanol (Union Carbide's product Butyl Cellosolve) and n-propoxy-2-propanol (Union Carbide's product Propasol P), are used frequently in waterborne systems but do not appear on either list (20). On the basis of solvents listed by the EPA, high solids coatings containing methyl ethyl ketone, for example, may have a less harmful effect on the environment than waterborne systems containing equal levels, or possibly even lower levels, of alcohol ethers. The unique "coupling solvent" properties of alcohol ethers (21) are important in waterborne systems and substitution of other solvents would be difficult.

## SECTION V

### SUMMARY

Practical considerations demand that Air Force coating procedures continue to consist of spray application (preferably airless electrostatic spray), ambient temperature cure, and strip and recoat on a three to five year cycle. With these procedures stipulated, it is clear that waterborne coatings prepared from currently available waterborne polymer systems do not meet requirements for use as aircraft primers and topcoats. However, the paint industry is actively involved in research directed at improvement of properties of waterborne coatings.

When coating procedures are limited to spray application and ambient temperature cure, there are only three types of waterborne coatings to consider for further research and development. In order of decreasing potential for replacement of current aircraft coatings, these types are: 1) two-package, reactive coatings, 2) one-package coatings that cure by air oxidation of fatty acid chains, and 3) one-package latex coatings. Latex coatings, type 3, are ranked below type 1 primarily because it is anticipated that adequate resistance to organic liquids, used in aircraft, will be difficult to achieve. Type 2 coatings are ranked below type 1 primarily because achieving flexibility and toughness and retention of these properties is judged to be difficult. A major concern for type 1 coatings is exposure of application personnel

to potentially toxic substances. Use of an independent source of breathing air and specially designed clothing which prevents skin exposure is recommended when type 1 coatings are applied. These precautions should also be considered for the current solvent borne urethane, primarily to reduce hazards from the isocyanate component.

Examples of two-package reactive waterborne polymer systems that are suitable as a starting point for development of waterborne coatings are known. One type consists of aqueous urethane dispersions cross-linked by polyfunctional aziridine cross-linkers. A second type is based on amine or amidoamine cross-linkers for epoxy resins. The amine or amidoamine component contains ionic groups which make the curing agent water soluble and also introduce surfactant-like properties so that epoxy resins are readily dispersed when the components are mixed.

When comparing the environmental advantages of waterborne systems and high solids systems, it is necessary to consider the amount of volatile organic compounds emitted on an equal area coverage and equal film thickness basis, and also, to the extent possible, specific reactions in the atmosphere on a compound by compound basis.

APPENDIX  
OUTLINE AND QUESTIONS USED IN  
TECHNICAL DISCUSSIONS

During the initial contact with a company it will be made clear that technical personnel who are responsible for development of waterborne coatings as well as market managers and technical directors should be present during discussions. A minimum time of two hours will be requested.

It is anticipated that the sessions will consist of

- (a) A Briefing -- Will include a summary of the work statement (on a transparency) and a description of the most demanding aircraft coating requirements along with the advantages of air force coating procedures (on a transparency).
- (b) A Question and Answer Period -- Eight questions have been prepared and will be asked during each session. Any of those attending will be asked to feel free to answer and an attempt will be made to keep the atmosphere as informal as possible. Notes will be taken on the responses.
- (c) A General Discussion -- The discussion will be initiated by a general question; "Do you feel that waterborne ambient cure systems can be developed that will match properties of the current solvent borne systems?" Preliminary literature search results will be presented (on a transparency), and the participants will be encouraged to suggest alternatives.

## QUESTION LIST

### Topcoat

1. If the AFML/MBE requested proposals for a research contract directed at development of a waterborne aircraft topcoat to replace the current two-package aliphatic urethane, would your company submit a proposal?
2. (a) Do you currently have available or under development an ambient cure waterborne coating that you think could match the performance of the current topcoat?  
(b) Can you describe the system? If so, do.
3. In your opinion which type of waterborne system (soluble, dispersion, or emulsion as well as polymer type) has the best chance of topcoat replacement without sacrifice of performance properties?
4. (a) Have you had any experience with urethane dispersions containing pre-reacted isocyanate/alcohol groups? If so, describe your experience.  
(b) Do you feel that polyfunctional aziridine cross-linkers can be used under carefully controlled conditions which minimize the health hazards?

### Primer

5. Would you prefer to submit a proposal for development of a primer/topcoat system or for the topcoat only?
6. (a) Do you currently have available or under development a waterborne system that you think could match the properties of the current epoxy-polyamide solvent borne two-package system?  
(b) Can you describe the system? If so, do.
7. In your opinion which type of waterborne system is most promising as a replacement for the current primer?
8. Have you had experience with two-package waterborne systems in which the cross-linker is water soluble and is surface active so that it can be used to emulsify epoxy resins prior to application? If so, describe your experience.

## REFERENCES

1. Military Specification; Primer Coating; Epoxy-Polyamide, Chemical and Solvent Resistant; MIL-P-23377C, Amendment 2, 31 May 1974.
2. Military Specification; Coating, Urethane, Aliphatic Isocyanate, For Aerospace Application; MIL-C-83286B (USAF), 5 October 1973.
3. A.P.Altshuller and J.J.Bufalini, "Photochemical Aspects of Air Pollution: A Review," Environ.Sci.Technol., 5, 39 (1971).
4. H.Niki, E.E.Daby, and B.Weinstock in Photochemical Smog and Ozone Reactions, R.F.Gould,Ed., American Chemical Society, Washington, D.C., 1972, pp 16-57.
5. J.W.Vanderhoff, "Water-Base Coatings", Technical Report AFML-TR-74-208, Part I, Nov.1974; Part II, Aug. 1976.
6. P.W.Dillon, "Application of Critical Relative Humidity to Water-Borne Coatings", J.Coatings Technol., 49, No. 634, 38 (1977).
7. G.C.Wildman and B.G.Bufkin, "Water-Borne's Position in the Spectrum of Industrial Coatings", Am.Paint J., 59 (57) 18 (1975).
8. W.H.Brendly, Jr. and E.C.Karl, "Water-Borne Acrylic Polymers for Industrial Coatings", Paint and Varn.Prod., 63 (3), 23 (1973).
9. J.A.Mock, "Water-Borne Coatings", Materials Eng., 82 (2), 55 (1975).
10. L.W.Hill and L.B.Brandenburger, "Viscosity Variation and Solvent Balance in Water-Soluble Coatings", Prog.Org.Coatings, 3, 361 (1975).
11. J.A.Cala and M.Lapkin, "Film-Forming High Performance Polyurethane Latices", Am.Chem.Soc.Div.Org.Coat.Plast.Chem.Pap., 36, No.2, 431 (1976).
12. R.G.Young, "Novel Ambient-Cured, Water-Borne, Acrylic-Epoxy Coatings", Am.Chem.Soc.Div.Org.Coat.Plast.Chem.Pap., 36 No.2, 419 (1976).

13. R.G.Young, "Novel Ambient-Cured, Water-Borne, Acrylic-Epoxy Coatings," J.Paint Technol., 49, No.632, 76 (1977).
14. M.Lapkin, personal communication.
15. M.J.Moscynski, Test Evaluation Report, 14 January 1977.
16. D.J.Brusick, Report to Polyvinyl Chemical Industries submitted by Litton Bionetics, Inc., July 1977.
17. P.H.Martin, et.al., "Water Thinnable Coating Compositions from Aminoethylated Interpolymers," U.S.Patent 3,719,629.
18. R.T.McFadden, "Vinyl Interpolymer Compositions Containing Pendant Amine Groups," U.S.Patent 3,634,372.
19. J.N.Pitts, Jr., personal communication to Z.W.Wicks, Jr.
20. E.F.Tuerk, "Recommended Policy on Control of Volatile Organic Compounds," Federal Register, 42, (131) 35314 (1977).
21. K.L.Hoy, "New Values of the Solubility Parameters from Vapor Pressure Data," J.Paint Technol., 42, No.541, 76 (1970).