

**Identification and Significance of the Problem or Opportunity**

This proposal addresses the need for a single component, zero volatile organic compounds (VOCs), epoxy primer (MIL-P-23377G) and a single component, zero (VOCs), polyurethane coating (MIL-PRF-85285C) for the exterior surfaces of aircraft.

The most logical approach to an environmentally friendly primer is to formulate a radiation-curable paint containing anticorrosion pigments. Rad-cure technology is well developed and the probability of developing a UV-curable primer coating is quite high in view of the widespread use of rad-curable systems. The challenge is to achieve the same performance of the two-component solvent-based epoxy primers containing non-chrome pigments.

The immediate goal which this proposal seeks is an environmentally friendly binder and pigment system that possesses acceptable adhesion, mechanical, chemical, anti-corrosive and rheological properties. A cross-linkable system that is capable of rapid curing at room temperature is also desirable. It is also necessary to incorporate an anti-corrosion pigment system that is compatible with the binder. Achieving this goal will facilitate formulation of the finished paint with application and film performance properties that satisfy or exceed the performance requirements of standard exterior primer specifications used by the U.S. Air Force.

The technical approach, which we will pursue in Phase I of the program, is to formulate UV and Visible-curing systems comprised of non-volatile acrylates and oligomers with epoxy groups that can react rapidly in the presence of the anticorrosion pigment upon exposure to UV or visible light. Several anticorrosion pigments will be screened during Phase I. One class of pigments will consist of nanoparticles of electroactive polymers: polyaniline, poly (ethoxy aniline); and poly (diphenyl amine).

This proposal outlines a research and development program to develop a primer and topcoat. The proposed primer will contain bisphenol A epoxy acrylates dissolved in reactive diluents and blended with the candidate pigments. The topcoat will be comprised of urethane oligomers dissolved in reactive diluents, both monofunctional and multifunctional to achieve high crosslink density.

**Phase I Technical Objectives**

The overall objective of Phase I is to demonstrate feasibility of the concept of a zero VOC and radiation curable system for corrosion resistant pigments suitable for application in the field by brush and conventional air-atomized spray. Specific technical objectives of Phase I are to:

1. Formulate UV-curable acrylic epoxy binders to demonstrate compliance with MIL-P-23377G.
2. Evaluate the adhesive, chemical, mechanical, anti-corrosion and rheological properties of the primers to demonstrate compliance with MIL-P-23377G.
3. Formulate UV-curable acrylic urethane topcoat to demonstrate compliance with MIL-PRF-85285C.
4. Determine corrosion resistance of optimized systems
5. Conduct an environmental and occupational safety analysis
6. Prepare the final report.

In pursuit of the primary goal of demonstrating feasibility of the concept, Phase I will

answer the following questions:

- A. Does the fully cured primer adhere to aluminum 2004 T3?
- B. What is the minimum concentration of each pigment necessary for acceptable corrosion resistance?
- C. Are the pigments compatible with the cross-linked acrylic epoxy?
- D. Does the binder/pigment pose a threat to the environment?
- E. Is the dispersion of the primer environmentally friendly?
- G. What is the optimum concentration of multifunctional monomer necessary for achieving adequate cross-linking?

**Phase I Work Plan**

Phase I Work Plan Outline

1) Scope

The work during Phase I involves: (1) the formulation of UV-curable acrylic epoxy primers, while demonstrating compatibility of these binders and anticorrosion pigments; and (2) the development of UV-curable acrylic urethane polymers to serve as topcoats. The ultimate aim is to demonstrate compliance with MIL-P-23377G and MIL-PRF-85285C.

2) Task Outline

The work during Phase I is organized along four main tasks as delineated above in the Technical Objectives. These tasks are: Formulation of UV-curable acrylic epoxy binders to demonstrate the appropriate mechanical, chemical and rheological properties; evaluation of the adhesive, chemical, mechanical, anti-corrosion and rheological properties of the primers; formulation of UV-curable acrylic urethane oligomers to demonstrate compliance with the appropriate specifications; determination of corrosion resistance of optimized systems; and reporting.

3) Milestone Schedule

The relevant milestones are answers to the questions posed in the Technical Objective section of the proposal. It is not possible to give precise dates at the present time because of the iterative nature of the applied research plan. Table 1, however, is a tentative schedule for reaching significant milestones during Phase I.

Table 1 Milestone Schedule

Milestone	Months following SOW
Satisfactory adhesion of fully cured primer to AL 2004 T3?	1
Identification of the minimum concentration of each pigment necessary for acceptable corrosion resistance	1
Compatibility between the inhibitors and the epoxy acrylic ester	2
Successful demonstration of acceptable corrosion resistance and other properties.	3
Indication that the formulation is environmentally and occupational	1

acceptable	
Best estimate of feasibility of concept	6

#### 4) Deliverables

- a. Kickoff meeting within 30 days of contract start.
- b. Monthly progress reports.
- c. Technical review within 6 months.
- d. Final report with SF 298
- e. Prototypes of aluminum panels with primer and with primer + topcoat before and after salt spray exposure.

The work plan during Phase I is divided into four main tasks which will be carried out in iterative fashion: They are:

Task 1. Formulation of UV-Curable Bisphenol A Acrylic Ester Binder

Task 2. Evaluation of Primers as per specification

Task 3. Formulation of UV-Curable Polyurethane Topcoat

Task 4. Determination of Corrosion Resistance of Optimized Topcoats as per specification and above primer

Task 5. Environmental and Occupational Safety Analysis

Task 6. Preparation of Final Report.

### TASK 1. FORMULATION OF UV-CURABLE BISPHENOL A ACRYLIC ESTER BINDER

#### 1.1 Identification and Selection of Base Polymer

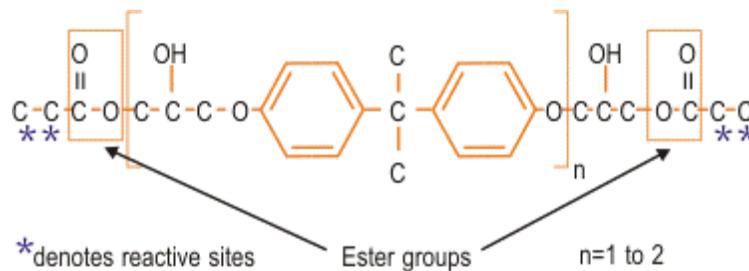


Figure 1. Idealized chemical structure of a bis-phenol A epoxy based acrylic ester resin.

Epoxy acrylic ester resins are available from many commercial sources and are typically diluted with reactive diluents. With a view towards commercialization, we will request samples from all major suppliers, but we start work with CN120 from the Sartomer Company.

#### 1.2 Curing of Neat Epoxy Acrylic Ester

##### 1.2.1 Reactive diluent

Because the viscosity of the epoxy based acrylic ester resin is too high, it is necessary to use a reactive diluent, such as glycidyl acrylate or glycidyl methacrylate with both acrylic and

epoxy linkages, to reduce the viscosity to enable addition of anticorrosion pigments and ease of application to Al 2024-T3. But in addition to these monomers, we will also investigate blends of CN120 with 3 nonvolatile monomers sold by Sartomer. They are available in blends with CN120: CN120A75 (25% tripropylene glycol diacrylate); CN120C60 (40% trimethylol propane triacrylate); and CN120B60 (20% hexandiol diacrylate).

### 1.2.2 Multifunctional monomer

Even though the reaction of the diluent with the ester leads to cross-linking, it is also necessary to form a more highly cross-linked network for reasons which will be discussed later. The type and concentration of multifunctional monomer are important variables, and have decided to evaluate pentaerythritol tetraacrylate and trimethylol propane triacrylate, which provide high crosslink density in UV cured formulations and enhanced protection because permeability decreases with increased cross-link density.

### 1.2.3 Additives

It is customary to use surfactants to improve the wettability and leveling, antioxidants (e.g. 0.2% butylated hydroxytoluene) to extend the shelf-life of the coating before curing, as well as the durability of the coating after curing.

### 1.2.4 Photoinitiator

The function of the initiator is to catalytically convert the liquid primer into a solid by initiating chemical copolymerization of the epoxy acrylic ester, the reactive diluent monomer, and tetrafunctional monomer. The proposer has samples in its laboratory of all photoinitiators and synergists supplied by Sartomer Company

Since the technology underlying radiation curing is mature, there is a large number of free radical initiators for ultraviolet curing. Accordingly, we will investigate the following: a mixture of benzoin normal butyl ethers; oligo(2-hydroxy-2-methyl-1-4 (1-methylvinyl)phenyl)propanone; 2-hydroxy-2-methyl-1-phenyl-1-propanone (monomeric); oligo(2-hydroxy-2-methyl-1,4(1-methylvinyl)phenyl) propanone; 2-hydroxy-2-methyl-1-phenyl-1-propanone (polymeric); trimethylbenzophenone; and methylbenzophenone, samples of all are already in the proposer's laboratory.

As mentioned above, there is a need for a synergist in the formulation to promote faster cure and overcome inhibition by oxygen. Therefore, we will investigate the reactive amine coinitiators as photoinitiator synergists.

This task is essentially a preliminary screening program, during which we will prepare numerous formulations and cure them with UV initiation in our laboratory to a tack free state. A starting formulation is as follows: Bisphenol A acrylic ester, CN120 (45%), Glycidyl acrylate (38%), Pentaerythritol tetraacrylate (10%), Photoinitiator (4%), Synergist (1%), and Surfactant (2%).

The UV cured coatings on aluminum alloy 2024 T3 panels will be screened for adhesion and hardness and degree of conversion. Those coatings showing satisfactory properties will be selected for further work in the next task. Adjustments in concentration of each ingredient will be made to give the proper viscosity for application by brush or spraying.

## 1.3 Selection of Pigments

The objectives of this crucial subtask are to identify and select suitable pigments that will do the

following:

- will not interfere with the curing system;
- will be compatible with the binder;
- will provide corrosion resistance to the metal by performing the four functions. These functions are the same as those offered by hexavalent chromium.

The four functions that chromate performs are:

1. Rapid exit from a carrier matrix;
2. Adsorption of the chromate anion on the bare metal or metal oxide. This alters space charge distributions at the interface, lowering the isoelectric point of the protective anodic metal oxide layer naturally forming on active metals. This repels chloride attack, and or shifts the corrosion potential of that metal and or its pitting potential in the noble direction.
3. Instead of oxygen reduction at cathode sites, reduction of Cr (VI) anion occurs to form an acid insoluble (persisting), Cr (III) oxide layer at cathodic sites. This fills oxide voids over cathodic sites and blocks further corrosion reaction.
4. Buffering the pH or neutralizing increasing acidity at the metal/electrolyte interface which comes from metal oxidation in the absence of air. Increasing acidity accelerates corrosion exponentially (1, 2)

Chromate salts have other advantages: they promote adhesion at the metal resin interface; they work well on a wide variety of metal and alloy substrates because they passivate both anodically and cathodically; they are relatively neutral in pH; and they are strong oxidants only in acid conditions, and thus they do not react with their resin matrix (1, 2)..

### 1.3.1 Curing of Pigmented System

Two relevant patents (1, 2) describe many non-chrome compounds which are capable of performing some of the functions listed above. Because these form the basis and rationale for the selection of pigments that will be considered in this task, they are listed here in Table 2.

Table 2. Non-chrome corrosion inhibitors

Sodium tetraborate	Calcium dihydrogen phosphate	Zinc cyanamide
Boric acid	Dipotassium monohydrogen phosphate	Zinc adipate
Magnesium	Ammonium dihydrogen phosphate	Zinc acetate
Sodium titanium oxide	Sodium pyrophosphate	Zinc poly(methacrylate)
	Calcium phosphosilicate	
Ceric oxide	Strontium phosphosilicate	
	Zinc phosphosilicate	
Zinc molybdate phosphate	Zinc phosphate	

The inventors have emphasized that a combination of several of these is necessary to achieve a synergistic effect that results in the performance of all functions. Based on the historical evidence, a list of the inhibitors that will be considered in Phase I is shown in Table 3.

Table 3. List of inhibitors that will be screened in Phase I.

Poly(aniline) Emeraldine base	Bis (2-methacryloxy ethyl) phosphate)	Copper (II) dimethacrylate
Poly(o-ethoxy aniline) Emeraldine base	3-Methacryloxypropyl trimethoxy silane	Magnesium acrylate
Poly(diphenyl amine) Emeraldine base	Boron vinyl dimethyl siloxide	Zinc dimethacrylate
	Zinc cyanamide	Aluminum triacrylate
	Zirconium (bis-2,2-(allyloxymethyl)-butoxide tris(dioctyl phosphate)	Zirconium methacrylate

All compounds listed in Table 3 are commercially available. Each will be added to the optimized binder composition during the formulation and cured with UV radiation in our laboratory. Extent of cure, adhesion to Al 2024-T3, flexibility, and other relevant parameters will be evaluated in this preliminary screening program.

It is noteworthy that zinc, cobalt, nickel and lead cyanamides have been used to passivate silver and other metals(3-5). This suggests that minute or catalytic amounts of **hydrogen cyanamide**, boric, phosphoric, fluorotitanic, dihydrohexafluorotitanic, dihydro hexafluoro zirconic, or molybdcic acid can be added to the emeraldine bases of the conducting polymer candidates and rapidly screened.

We will apply each coating will be applied by brush, and later spray, to the alloy prior to exposure to the UV lamp. And during formulation we will be constantly looking at the appearance of the dry films. We can assume that during application and curing many kinds of defects or imperfection will develop in the films. The concerns here are with the following: (a) leveling; (b) sagging; (c) crawling, cratering and related defects; (d) floating and flooding; (e) wrinkling; and (g) foaming. To the extent possible in this task, we will attempt to address each of these as they arise during application and curing of the films.

Because of the large body of work on the application of conducting polymers with success in the corrosion protection of Al 2024-T3, it seems logical to evaluate them in a UV-curable primer. Starting with the emeraldine bases in one series, we will continue our investigation by adding varying amounts of various acids directly to each emeraldine base to produce a mixture of base and salt in efforts to achieve performance of all functions. Of particular interest is the use of counterions that will produce some water solubility, which is necessary for more protection.

## Task 2. Evaluation of Primers

The objective of this crucial task is to study the kinetics and mechanism of the corrosion of Al 2024 T-3, coated with the radiation cured primers, and to develop evidence necessary to demonstrate the feasibility of the concept. Accordingly, we will conduct the following tests:

## 2.1 Adhesion

Adhesion will be tested using a cross hatch test in our laboratory on 2 mil dry films. Using a device with 11 sharp blades, a scratch pattern is made across the sample followed by a second set cut perpendicular to the first. A strip of pressure sensitive adhesive tape is then pressed over the pattern of squares and rapidly pulled away. The number of squares of coating left on the substrate is taken as the degree of adhesion.

## 2.2 Viscosity

For the finished paint formulations, we will determine the following formulation constants: pigment volume content (%); volume solids (%); pH; Stormer Viscosity (Kreb Units); ICI viscosity (poise); VOC (gm/liter).

## 2.3 Sprayability

These will be determined in our laboratory following FED-STD-141, method 4331. During the application of the coatings on horizontal and vertical surfaces, we will look for any evidence of running, adherence to angled surfaces, quality of finish, blistering, cracking and other defects after complete drying. We will also look for evidence of separation from the surface and curling at corners or along edges. Ease of application is an important parameter in our screening program.

## 2.4 Knife Test

This test is limited to the brittleness and quality to ribbon when a film is cut with a standard knife with a very sharp blade. In this test, a film is applied and cured at room temperature. It is then tested for brittleness, toughness and tendency to ribbon from the test panel with the knife while the blade is held at an angle of approximately 30 degrees to the panel.

## 2.5 Corrosion Resistance

### 2.5.1 Open Circuit Potential Measurement

Any conducting metal in an electrolyte solution always forms an electrochemical interface between the metal surface and solution surface facing the metal. This interface is associated with an electrochemical potential difference called Open Circuit Potential (OCP) or Free Corrosion Potential which is always in state of dynamic equilibrium. OCP is an indicator of the thermodynamic stability of the metal in that test environment. The higher (positive) the OCP is the more stable. The surrounding environment has an important effect on the OCP of metal. OCP changes with the applied inhibitor in primer, pH and temperature. Monitoring the OCP change over time, we will learn the stability information of the inhibitor.

### 2.5.2 Electrochemical Impedance Spectroscopy (EIS)

EIS is one of the most important electrochemical techniques used for the evaluation of performance of organic coatings. In EIS, an AC voltage signal is applied over an electrochemical cell and the response of the current is measured. By measuring the change in complex impedance of polymeric coated metals, it is possible to characterize the coating degradation processes under

different exposure conditions. EIS testing will be carried out by Policell Technologies in Newark, NJ.

EIS can generate quantitative data that relates to the quality of a coating on a metal substrate. Its theory relies on analogies between the electrochemical cell and networks of resistors and capacitors that are thought to behave like the cell. EIS is useful here, because using EIS to characterize a coated metal substrate simultaneously measures two phenomena: a. the deterioration of the organic coating (top coating and primer) and b. the increase in corrosion rate of the underlying substrate due to the deterioration of the coating and subsequent attack by the electrolyte.

In EIS, an AC voltage of varying frequency is applied to the sample. It is useful to think of the frequency as a camera shutter that can be very fast (high frequency) for fast reactions and very slow (low frequency) for slow reactions. This is the technical feature that allows EIS to gather so much information on an electrochemical reaction in one experiment. EIS can quantitatively measure both resistances and capacitances in the electrochemical cell. A resistance corresponds to electron transfer reactions such as corrosion. The capacitance of a metal electrode in contact with an electrolyte is important information for any electrochemical system. For organic coatings, the capacitance measurement is particularly revealing. As the organic coating deteriorates with time during exposure to an electrolyte, EIS can track changes in the capacitance of the coating. The capacitance will change as the coating swells or absorbs water, for example. In addition, we can measure changes in the porosity of the coating. EIS also simultaneously monitors the rate of corrosion of the metallic substrate which generally increases as the protective coating fails, allowing the electrolyte to contact the substrate. To quantify these physical and chemical processes with EIS, we need an appropriate equivalent circuit. We need to think of the coated sample as a collection of electrical elements. Each element of the equivalent circuit should model a specific function of the sample. The equivalent circuit that is most commonly used to describe an organic coating on a metallic substrate is shown in Figure 1.

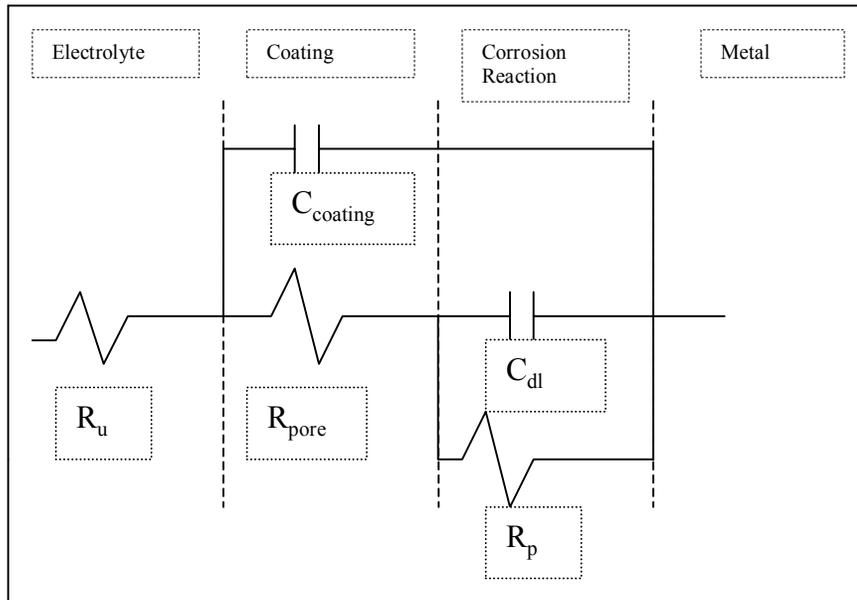


Figure 1 Equivalent circuit of an organic coating on a metal substrate

In the figure,  $R_u$  is uncompensated resistance---the resistance of the electrolyte between the working electrode and reference electrode.  $C_{\text{coating}}$  is coating capacitance---the capacitance of the organic coating is an important parameter to measure during coating failure. Most coatings are relatively thick; the coating capacitance tends to be rather low, in the range of 1 nF/cm<sup>2</sup>. The physical and chemical properties of the coating that affect the capacitance are

$$C_{\text{coating}} = (\epsilon)(\epsilon_0)(A)/t \quad (1)$$

Where  $\epsilon$  is the dielectric constant of the coating,  $\epsilon_0$  is  $8.85 \times 10^{-14}$  Farads/cm,  $A$  is the area (cm<sup>2</sup>), and  $t$  is the thickness (cm).

The capacitance is related to the magnitude of the impedance ( $|Z|$ ) by

$$|Z| = 1/(2\pi f C_{\text{coating}}) \quad (2)$$

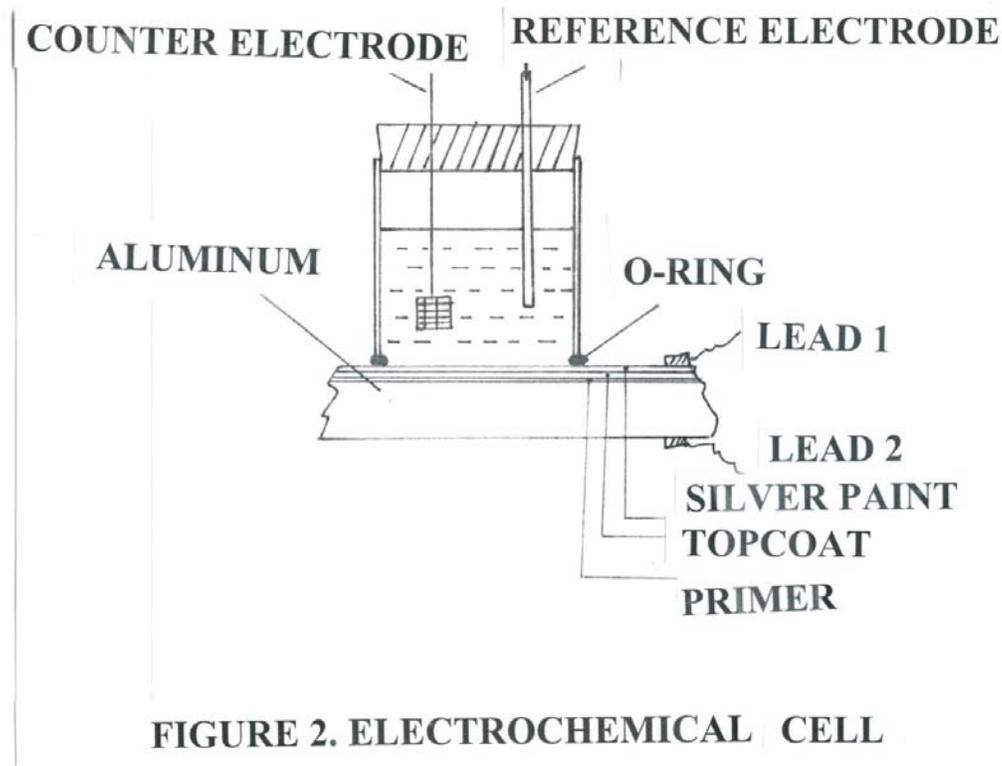
where  $f$  is frequency of the applied AC voltage.

$R_{\text{pore}}$  is pore resistance---the resistance of the coating changes during exposure due to the penetration of electrolyte into the micropores of the coating. Upon immersion, the pore resistance can be very high ( $>10^{10}$  ohm) and usually decreases with time of exposure to the electrolyte.

$R_p$  is polarization resistance---the corrosion rate of the metal substrate beneath the coating is described by the polarization resistance. For a metal in the absence of a coating, the corrosion rate can be determined from the polarization resistance. The polarization resistance is inversely proportional to the corrosion rate. A typical polarization resistance for a bare metal is 5000 ohm-cm<sup>2</sup>.

$C_{dl}$  is double layer capacitance---the coating is not the only structural feature of the sample that gives rise to capacitance. There is a charge on the metal electrode and a charge in the electrolyte that are separated by the metal-electrolyte interface. Since this interface is commonly known as the double layer in electrochemical theory, the capacitance is called the double layer capacitance. This capacitance is in the range of 10-40  $\mu\text{F}/\text{cm}^2$ . So  $C_{dl}$  can sometimes be related to delamination of the coating.

EIS will be performed in a customized electrochemical cell shown in Figure 2 by Policell Technologies in Newark, NJ.



**FIGURE 2. ELECTROCHEMICAL CELL**

### 2.5.3 Potential Sweep Method

The complete electrochemical behavior of a system can be obtained through a series of steps to different potentials with recording of the current-time curves. More information can be gained in a single experiment by sweeping the potential with time and recording the i-E curve directly. The technical name for the method is Linear Sweep Voltammetry. A typical i-E curve is shown in Figure 3:

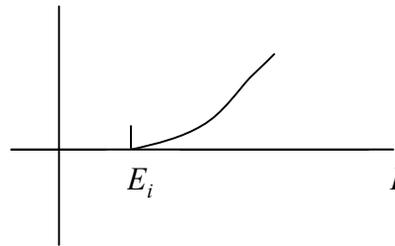


Figure 3. i-E curve

In Figure 3,  $E_i$  is initial potential, oxidation or reduction depending on the sweep direction. Based on our experience, we plan to focus on the initial oxidation potential where corrosion starts.

### 2.6 Salt Spray Resistance

We will send 10 samples of Al 2024 T3 panels coated with optimized primers to Matco Associates, Inc. in Pittsburgh, PA for salt spray testing according ASTM Method B-117. After 500 hours, the panels will be removed and subjected to EIS tests.

### 2.6 Accelerated Aging

Accelerated aging using the Xenon Arc with a repetitive cycle, which includes exposure to UV light with controlled irradiance of  $0.35 \text{ W/cm}^2$  for 102 minutes at a black panel temperature of  $50^\circ\text{C}$ , followed by 18 minutes of water spray. This artificial aging test will be performed by the Akron Rubber Development Laboratory on a single batch of 10 (4 inches x 6 inches) Al 2024-T3 panels. After 500 hours, some of the panels will be subjected to EIS analysis.

### 2.7 Filiform Corrosion

This a simple test which will be performed in our laboratory, It involves exposure of coated panels to HCl gas in a chamber where the relative humidity is between 85 and 95% and inspecting for visual evidence of corrosion,

## TASK 3. FORMULATION OF ACRYLIC URETHANE TOPCOAT

A list of the ingredients currently used in MIL-PRF-85285C aliphatic polyurethanes is given in Table 4 and it suggests that a polymer chemist knowledgeable in formulating UV-curable systems can readily replace this topcoat with a solventless one.

Table 4. Composition of MIL-PRF-85285C from Material Safety Data Sheet

Ingredient	Concentration, w/w Percent
Silica, Amorphous	20%
Microcrystalline Silica	13%
Methyl ethyl ketone	12%
Barium sulfate	11%

Methyl normal amyl ketone	5%
N-Butyl acetate	4%
Propylene glycol monomethyl ether	4%
Methyl isobutyl ketone	3%
Oxazolidine	2%
Xylene	1%
2,4-Pentanedione	1%
TOTAL	76%

The remainder is a two component aliphatic polyurethane, which can be replaced with a one component system. Hence, a combination of an aliphatic urethane oligomer, photoinitiator, and environmentally acceptable extender pigments to replace the hazardous microcrystalline silica and barium sulfate and amorphous silica will be formulated during this Task. Urethane oligomers are low molecular weight polyurethanes with acrylic end groups. The proposer has samples of all supplied by the Sartomer Company, along with promotional brochures, which describe the properties of coatings formulated by Sartomer scientists.

We will screen the following: CN9178 (difunctional aliphatic urethane acrylate); CN2920 (aliphatic urethane acrylate oligomer); CN959 (difunctional aliphatic urethane acrylate oligomer with acrylate diluent); CN929 (trifunctional urethane acrylate oligomer); and CN9010 (aliphatic urethane acrylate oligomer).

#### TASK 4. EVALUATION OF TOPCOAT

The topcoat will be evaluated as a coating above the optimized and extensively tested primer. The crucial test is the accelerated aging test which assesses the independent and combined effects of UV exposure, moisture, and temperature on the barrier properties of the coating system. Other tests include corrosion resistance and salt spray.

##### 4.1 Accelerated Aging

Accelerated aging will be conducted by ARDL as described earlier.

##### 4.2 Corrosion Resistance

###### 4.2.1 Electrochemical Impedance Spectroscopy (EIS)

After 500 hours of exposure to UV and moisture at 50°C, we will subject the exposed panels to EIS testing.

##### 4.3 Salt Spray Resistance

We will send 10 samples to Matco Associates, Inc. in Pittsburgh, PA for salt spray testing. This firm, which specializes in conducting corrosion testing, is also well equipped to assist during Phase I with a comprehensive evaluation of the corrosion and environmental behavior testing required by the sponsor. We will also subject 2 panels to EIS testing before and after exposure.

This test will be performed in our laboratory as mentioned earlier,

#### TASK 5. ENVIRONMENTAL AND OCCUPATIONAL SAFETY ANALYSIS

We will prepare material and safety data sheets for the most promising candidates after we have filed patent applications on the proposed technology. Each sheet will contain sections on the following: Material Identity; Proposer's Information; Physical/Chemical Characteristics; Fire and Explosion Hazard Data; Reactivity Data; Health Hazard Data; Precautions for Safe Handling and Use; Control Measures; Label Data; Site Specific/Reporting Information; and Ingredients/Identity Information.

#### TASK 6. PREPARATION OF FINAL REPORT

At the completion of the previous tasks, we will prepare a final report describing our findings, test results and estimates of technical feasibility.

#### **Related Work**

Corrosion studies of Al 2024-T3 coated with conducting polymers have been reviewed elsewhere (6). Polyaniline, poly(o-ethoxyaniline), poly(diphenylamine), poly (2,5-bis-(N-hexyl-N-methylamino)-p-phenylene vinylene) and other poly (bis-dialkylamino-p-phenylene vinylenes) are exemplary. Electrochemical techniques used included EIS and potentiodynamic techniques, cyclic polarization, and Tafel extrapolation.

The Bode plots from EIS studies on aluminum alloy 2024 coupons with doped polyaniline indicated that this polymer can increase the charge transfer resistance three fold the value of bare corroding aluminum in 3.5% NaCl. Potentiodynamic scans show that the polymer coating significantly shifts the corrosion potential to more positive values but substantially reduce the corrosion rate of the metal relative to the uncoated specimen. Cyclic polarization studies on aluminum alloy coated with polyaniline and over coated with epoxy and having small areas of exposed bare aluminum exhibit strong suppression of pitting corrosion in the exposed area. Visual observation and spectroscopic investigations on aluminum alloys coated with doped polyaniline have been made (6).

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Proposal No. F071-110-2605

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### **Relationship with Future Research or Research and Development**

It is anticipated that Phase I will successfully demonstrate the feasibility of the concept of radiation curable primers and topcoats early in the program. Achieving this critical goal early in the program will provide a strong foundation for work with additional binder/pigment formulations and more extensive testing to ensure that these products are placed on the Qualified Products List during Phase II.

### **Commercialization Strategy**

The proposer intends to file many patent applications as a result of the project early in Phase I because this project is innovative and it attempts to offer corrosion resistance using a 100% solids, nonchrome primer and topcoat. The overall markets for the resulting technology are corrosion resistant aircraft coatings. The entire market for protective coatings is large and diverse. Specific sales information for most companies is not available.

The manufacture of the proposed coatings does not present a problem because it involves simple blending of oligomer in the diluent monomers at room temperature without the need for specialized equipment. Both oligomer and monomers are commercially available and 55-gallon drum quantities can be produced at the present location, if necessary.

We plan to secure a commitment for Phase III that is of the same order of magnitude as the Phase II funding. We expect that this will be adequate to commercialize the proposed coatings after they are placed on the Qualified Products List.

There are two drivers which support commercialization. First is the environmental and occupational concern with hexavalent chromium and organic solvents. Second, successful demonstration of the protective capabilities of the proposed coating with extensive corrosion tests by independent laboratories will ensure acceptance by the Air Force. Commercialization of the technology should therefore be successful, if the product is placed on the Qualified Products List. All materials are commercially available and manufacture of the coating involves simple blending. The coating may be applied by brush or spray and curing takes place with UV radiation.

### **Key Personnel**

Dr. Ronald W. Gumbs, a materials scientist with over thirty years of combined academic and industrial experience in the synthesis, characterization and evaluation of polymeric materials, will serve as principal investigator on the project. He was an instructor at the Summer Institute in Polymer Science and Technology at SUNY New Palz, May 21 - June 27, 1979, and has served on the advisory board of the New Jersey Institute of Technology Enterprise



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Topic No. AF071-110

Proposal No. XXXX

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  9. R.W. Gumbs, [Polythiophene and Polypyrrole Copolymers], in Handbook of Organic Conductive Molecules and Polymers: Vol. 2, Conductive Polymers: Synthesis and Electrical Properties, edited by H.S. Nalwa, John Wiley & Sons, New York, 1997, pp. 469-504.
  10. Ronald W. Gumbs, "Conducting Polymers," in Encyclopedia of Chemical Processing, edited by Sunggyu Lee, Marcel Dekker, New York, 2006, pp. 526-537.

#### Patents:

1. M.F. Carty, M.R. Dock, C.P. West, P. Esemplare and R. Gumbs, "Micro-filter for Tobacco Smoke", Fr. Pat. 1,484,033, 9 June, 1967.
2. R. W. Gumbs, "Nonlinear Optical Shield", U.S. Pat. 5,173,811, 22 December 1992.
3. P.E. Esemplare and R.W. Gumbs, "Hot Melt Adhesive Composition that Melts at Relatively Low Temperatures," U.S. Pat. 5,326,413, 5 July 1994.

### **Facilities/Equipment**

RWG Corporation has a modern research facility in East Brunswick, NJ with 1,400 square feet of laboratory space and the option to lease more space as the need arises. The firm maintains a library, machine shop and a glass-blowing capability at this location. Equipment includes all standard equipment, including two custom-built 6' fume hoods, for chemical synthesis and characterization.

This facility meets all environmental laws and regulations of federal, New Jersey, and local Governments for the following groupings: airborne emissions, waterborne effluents, external radiation levels, outdoor noise, solid and bulk waste disposal practices, and handling and storage of toxic and hazardous materials. Dr. Ira Whitman of the Whitman Companies serves as an environmental consultant to the proposer.

Additional specific major pieces of equipment owned by the proposing firm and located in its laboratory in East. Brunswick include:

1. A complete electrochemical research system based on an EG & G Princeton Applied Research (PARC) Model 273 Potentiostat/Galvanostat and Houston Instruments Model 2200GW X-Y recorder.
2. Spectra-Physics Model GCR-11-3 Nd:YAG ns pulsed laser with 2nd, 3rd harmonic generation and pulse compression, associated optics, positioners, two Scientech Model

RWG Corporation

Topic No. AF071-110

Proposal No. XXXX

36-5002 digital power meters, an Antel Optronics Model AR-S1-C custom large-area picosecond photodetector, mounted on a Newport precision optical table. A 2.5 - 7.0 ns, 200 mJ (@ 532 nm) laser pulse repeating at 1 - 15 Hz is available.

3. Instron Model 4201 Universal Testing Machine; a state-of-the-art instrument for measuring mechanical properties of polymeric materials.
4. Perkin-Elmer Model Lambda 3B automated UV-Vis. Spectrophotometer; also used in conjunction with PARC 273 for spectro-electrochemistry.
5. Perkin-Elmer Model 1615 FT-IR.
6. Tektronix oscilloscopes: Model 2210, digital storage, Model DCA 602, pico-second digital storage.
7. Optical train and laser/optic instruments incl. Newport Model C-2001-65ML 65 mW Ar ion laser with acousto-optic (Isomet) modulation, Newport Model M-877 200 ps photodetector, Oriel Model 66165 150 W Xe source, Model 77250 monochromators, associated wavelength controllers, drives, optics, 3-axis positioners. Used for spectroelectrochemical, polymer studies.
8. Denton Vacuum Model 502A high vacuum thermal evaporation system (for thin film semiconductor, metal and other depositions).
9. Resistivity/conductivity and electrical test instrumentation: Signatone Model S301-4 4-point resistivity probe interfaced to Keithley Model 617 electrometer, Keithley Model 220 current source; Keithley Model 197A digital multimeter.
10. Integrated Technologies, Inc. Model P6204 Spin Coater.
11. Power supplies for Electropolymerization: Micronta Dual Tracking and Vector-Viz WP-773A, associated bulk (1 L) synthesis cells.
12. Precision Instruments vacuum pumps and high-vacuum line system.
13. Ovens/Furnaces: Labline IV and Thermolyne F21100 tube furnace (to 1200°C).
14. Large capacity LabLine Imperial controlled-temperature system.
15. Ultraviolet light sources for polymerization initiation, related functions.
16. U.S. Stoneware Ball and Jar Mill, Model No. 753 RM/V.
17. Brookfield Viscometer
19. Dymax Model 1200 Focused Beam UV-curing system

#### **Subcontractors/Consultants**

No formal subcontracting or consulting is planned in Phase I.

#### **Prior, Current, or Pending Support of Similar Proposals or Awards**

No prior, Current, or Pending Support of Similar Proposals or Awards.