ZDOC/95FINAL

VOLUME I

ZERO DISCHARGE ORGANIC COATINGS

Powder Paint - UV Curable Paint - E-Coat

Final Technical Report
June 1993 - June 1995

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The Zero Discharge Organic Coatings (ZDOC) project developed powder paint, Ultraviolet (UV) curable paint, and electrocoating (E-coat) paint for military Applications. These technologies offer potential for high performance coatings with little or no volatile organic compound (VOC) emissions or hazardous waste generation. The ZDOC project focused on formulating non-toxic corrosion inhibitors into these coating technologies, and the applications development of powder coatings. Non-toxic replacements for traditional lead and chromate inhibitors were selected based on a previous NAWCADWAR investigation. Once incorporated, the performance of the coatings with and without inhibitors was compared. Also, the protective mechanisms of these inhibitors were studied. The applications development for powder coatings analyzed technologies to allow powder coating of non-conductive substrates and evaluated the use of IR energy to cure powder coatings.

Inhibitors were successfully incorporated into electrocoatings and powder coatings, however corrosion performance results varied with coating formulation. The use of inhibitors in UV curable coatings proved to be very difficult, but some positive results with specific UV curable coating formulations were identified. The development of application methods resulted in techniques that provided: a conductive layer for powder coating non-conductive substrates and the ability to cure powders in under two minutes dependent upon coating formulation.

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Abstract

The Zero Discharge Organic Coatings (ZDOC) R&D project has substantially advanced coatings technology through the development of high performance zero-discharge coating systems. Development efforts were performed on three coating technologies, powder paint, ultraviolet (UV) curable paint, and electro-coating (E-coat) paint. These three paint technologies offer the potential of high performance coatings with no volatile organic compound (VOC) emissions or hazardous waste generation. These three technologies and their associated application processes are applicable to a wide variety of military equipment and structures, thereby eliminating volatile organic compound (VOC's) and toxic heavy metals from coatings and painting operations.

The ZDOC project was focused on two main research and development issues, the evaluation of non-toxic corrosion inhibitors and their impact on coating technologies, and the applications development of powder coatings. Non-toxic replacements for traditional lead and chromate inhibitors were selected based on previous investigations at the NAWCADWAR. The mechanisms of corrosion inhibitors were studied and the ability to incorporate these inhibitors into the various coating materials was evaluated. Once incorporated, the performance of the coatings with and without inhibitors was compared. The applications development for powder coatings analyzed technologies to allow powder coating of non-conductive substrates and evaluated the use of IR energy to cure powder coatings.

Two techniques were developed to study corrosion inhibitors and the mechanisms of two corrosion inhibitors were determined. It appears that in order for the inhibitor to be effective, it must be able to migrate to the coating/metal interface even if it is contained in a barrier coating such as powder coatings or electrocoatings. Inhibitors were successfully incorporated into electrocoatings but the corrosion performance of the coating did not improve. Inhibitors were also incorporated into powder coatings and some improvements in coating performance were identified. The use of inhibitors in UV curable coatings proved to be very difficult. The impact on the physical properties of the coating as well as the impact of the inhibitors on the UV light presented technical challenges. Some positive results with specific UV curable coating formulations were identified.

The development of methods to allow powder coating of non-conductive substrates resulted in a technique that provided a conductive layer to the substrate to facilitate the application of the powder. This conductive film did not affect the performance of the coating and the conductivity was eliminated when the powder coating was cured. The evaluation of IR curing of powder coatings resulted in the ability to cure powders in under two minutes dependent upon the formulation of the coating. However, the shape of the part directly affected the ability to obtain uniform heating on the surface of the substrate.

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List of Acronyms and Abbreviations

CRADA	Cooperative Research and Development Agreement
E-Coat	Electrocoat
HAC	Hughes Aircraft Company
HMSC	Hughes Missile Systems Company
IR	Infrared
NAWCADWAR	Naval Air Warfare Center - Aircraft Division - Warminster, Pa
UofA	University of Arizona
UV	Ultraviolet
ZDOC	Zero Discharge Organic Coatings
TPE	Total Performance Evaluation
EIS	Electrochemical Impedance Spectroscopy

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1.0 TASK OBJECTIVES

Organic coatings, which provide the primary defense against environmental degradation of military equipment, have been identified as a major source of hazardous material emissions and waste in the Department of Defense (DOD) [1]. The current approach to solving this problem is through the incremental reduction of the coatings' toxic components. In contrast, the Zero Discharge Organic Coatings (ZDOC) R&D project was focused at advancing coatings technology through the development of high performance "zero-discharge" coating systems. Development efforts were performed on three coating technologies: powder paint, ultraviolet (UV) curable coatings and electrodeposition coatings. These three paint technologies offered the potential of high performance coatings with little or no volatile organic compound (VOC) emissions or hazardous waste generation. These three technologies and their associated application processes are applicable to a wide variety of military equipment and structures, thereby eliminating volatile organic compound (VOC's) and toxic heavy metals from coatings and painting operations.

To accomplish this task, several steps needed to be performed. The first was to research essential mechanisms such as polymer curing, adhesion, and corrosion inhibition. This information would aid in the development of the successful high performance coatings. The second step was the development of non-toxic corrosion inhibiting materials compatible with each of the three selected coatings technologies (powder coatings, UV curable coatings and electrocoatings), each addressing a segment of DOD painting operations. In addition to the material development, improved application and curing technologies were investigated to enable these coatings to be effectively applied to a wider range of military hardware.

The ZDOC team of Hughes Aircraft Company (HAC), Lehigh University, Hughes Missile Systems Company (HMSC), University of Arizona (UofA), and the Naval Air Warfare Center Aircraft Division Warminster (NAWCADWAR) was assembled to offer a blend of experience, expertise, and capabilities in all aspects of organic coatings technology. The ZDOC project involved research and development in several related coating development and application areas including advanced powder, UV curable and electrocoat paint development. Table 1 summarizes the major tasks and team members involved in the ZDOC project.

The specific task objectives for each of the coatings technology were based on the overall project objectives of developing or supporting the development of high performance, non-toxic, non-VOC containing coatings.

Table 1. Zero Discharge Organic Coatings Project Team Assignments

Task	Organizations
Material Development Tasks	
Corrosion Inhibitor Materials	**NAWCADWAR**, Lehigh
Powder Paint	**HMSC**, NAWCADWAR, Lehigh, HAC
UV Cure Paint	**HAC**, NAWCADWAR, Lehigh
Electrocoat Paint	**NAWCADWAR**, Lehigh
Applications Development Tasks	
Powder Paint - IR Cure	**HMSC**, UofA
Powder Painting Non-conductive materials	**HMSC**, UofA
UV-Cure Applications Techniques	**HAC**
Project Management	**HMSC**

Note: Primary team organization for each task is listed in **BOLD**.

1.1 Electrocoatings Material Development. The tasks for the electrocoatings material development were designed to develop process methods of electrocoating and electrocoating materials containing non-toxic corrosion inhibitors to meet the stringent requirements of DOD coatings. Methods to formulate and apply electrocoatings containing non-toxic corrosion inhibitors were developed to accomplish this task. Electrochemical Impedance Spectroscopy was applied for evaluating and modeling cathodic electrocoats.

1.2 UV Cure Coatings Material Development. Like the powder coatings development, the UV cure coatings material development tasks were designed to develop improved materials to meet the stringent requirements of DOD coatings. The development of these high performance UV curable coatings would be accomplished through the research and selection of non-toxic inhibitors for incorporation into the UV curable coatings. These coatings would provide a non-VOC containing coating with increased corrosion inhibition over typical paint coatings.

1.3 Powder Coatings Development. The powder coating material development tasks were designed to develop improved powder coating materials to meet the stringent requirements of DOD coatings. The development of these high performance powder coatings would be accomplished through the research and selection of non-toxic inhibitors for incorporation into the powder coatings. These coatings would provide a non-VOC coating with increased corrosion inhibition over typical powder coatings.

1.4 Powder Paint Applications Development. The powder paint technology application effort was designed to increase the quantity of potential DOD related powder painting uses by developing application technologies compatible with a wide range of parts that are not currently suitable for powder painting. The two application technologies evaluated were IR curing of powder coatings and powder coating of non-conductive substrates. The use of IR curing would potentially allow parts with critical temperature restrictions to be powder coated by only heating the surface of the part for a short period of time and would provide for a short cure cycle for production operations. The applications development for non-conductive substrates would allow the use of powder coatings on non-metallic parts. Both applications development tasks were designed to test the application methods for their ability to meet these objectives.

1.5 Inhibitor Characterization and Analysis. Lehigh University's objective was to develop strategies for the replacement of toxic corrosion inhibitors with non toxic inhibitors along with a demonstration program to incorporate these new inhibitors in electrocoat, powder and UV resin systems. Individually or collectively, these three types of coating systems could provide the high performance required for military systems while being environmentally acceptable. Civilian applications would also benefit from this study.

The first step in accomplishing this task was to research essential mechanisms such as polymer curing, adhesion, and corrosion inhibition. The second step was the development of non-toxic materials for each of the three selected coatings technologies. The methods used in applying these coatings was critical, since the results obtained were dependent on the substrate and the type of conversion coating employed. The final test would be to demonstrate their performance and environmental compatibility.

Lehigh University was chosen for this phase of the program because of their long history in the study of corrosion, under the guidance of Henry Leidheiser, Jr. and Richard D. Granata. Although many technical papers have been published in this field over the past 14 years, the number of research programs that have been carried out to improve the understanding of the mechanism of corrosion inhibitors in coatings have been limited.

In 1981 Leidheiser [2] proposed several specific areas of research to study inhibitors in coatings. He suggested the following research programs:

1. Cathodic Polarization Behavior of Metals Exposed to Inhibitors
2. Accelerated Corrosion Tests For Inhibitors in Formulated Coatings
3. Cyclic Dissolution and Precipitation of Inhibitive Pigments in Coatings (The mechanism of solution and re-precipitation of inhibitors at the metal coating interface and their resultant behavior)
4. Nature of Inhibitor Components Included in Film on Metal Surface
5. Character of Interfacial Oxide at Metal/Organic Coating Interface as a Function of Time of Exposure to an Inhibitor

All of these areas in one way or another are involved in the study of mechanisms; however, because of the constraints of time and manpower, it was decided to focus our main efforts on two of these proposals. The issues were reduced to a study of barrier versus inhibitor properties and inhibitor solution properties. The goal of this task was to study various types of inhibitors, and by understanding the mechanism of how they worked, to be able to predict their ability to perform in the field as effective corrosion inhibitors by their behavior under accelerated laboratory conditions. If this task were accomplished, then a priori predictions of behavior should be possible.

2.0 TECHNICAL PROBLEMS

Organic coatings perform a number of critical functions on military aircraft, equipment and structures including: corrosion and wear prevention, camouflage, and infrared/radar suppression. Optimum coating performance is essential to the operational readiness, mission performance, and service life-time of this equipment. Complicating this performance issue is the fact that coatings for a variety of military equipment and structures have vastly different application and performance requirements. Recently, federal, state and local environmental agencies have placed severe restrictions on the emission of hazardous materials. Since most high performance organic coatings contain both volatile organic compounds (VOC's) and toxic corrosion inhibitors, these regulations limit the types, quantities, and effectiveness of current coatings applied to military equipment. Therefore, versatile high performance protective coatings which are environmentally compatible must be developed for critical military equipment.

The traditional approach to addressing this issue has been small incremental reductions in the concentration of toxic constituents in coating compositions. These reductions have come hand-in-hand with the associated environmental regulations. The compliant paints entering service have reduced the level of VOC's emitted; however, these paints demand careful attention to cleanliness and application technique to achieve good results. As allowable VOC limits are reduced even the existing "compliant paints," on which the aerospace industry currently depends, will eventually be banned from production use.

This development project provides a significant advancement in coating technology with the development of zero-discharge coating materials and improved application processes. While existing coating systems rely heavily on organic solvent systems for their application and performance properties, these coatings contain little or no organic solvent. However, they do not inherently provide the high level of durability, chemical and corrosion resistance required for many military applications. Traditional coatings provide corrosion protection through the use of toxic inhibitors (chromates and lead). Recent investigations have illustrated that non-toxic inhibitors can offer superior corrosion inhibition if formulated properly into appropriate polymer matrix systems. This performance has been demonstrated in one-coat, self-priming topcoats which are replacing traditional multi-coat systems [3-7]. Therefore, the potential for combining this technology with powder, UV cure, and electrocoatings to develop zero-discharge coatings for a wide variety of military applications is technologically feasible. This development will offer a huge advancement in environmentally compatible, high performance coating systems. Technical issues associated with the use of powder coatings, UV curable paint coatings, and electrocoatings have been addressed.

2.1 Electrocoatings Material Development

2.1.1 Electrocoatings Material Development. The objective of this research project was the development of a high performance, zero discharge organic coating (ZDOC) based on an electrocoat process. Current electrocoats emit a low level of VOC's [8, 9] (typically 50 to 100 g/l) that is well below the current environmental regulations. However, the only substances available for corrosion inhibition in current electrocoat processes contain toxic, heavy metal compounds [10]. The primary goal of the proposed research project was to incorporate non-toxic compounds for corrosion inhibition into the electrocoat systems. A secondary goal was to further reduce or completely eliminate the already low level release of VOC's. The new coating was evaluated based upon the pertinent military specifications. Pierce investigated the cathodic electrocoat chemical process in detail in 1981 [11].

The advantages provided by the use of a non-toxic inhibited electrocoat process include:

1. Significant reduction in the amount of VOC emission to meet increasingly restrictive limits.
2. Significant reduction or complete elimination of the content of toxic metal compounds currently used for corrosion inhibition.
3. Increased level of barrier protection over present primers [9, 10]. If this barrier protection is coupled with an aggressive inhibition mechanism the developed coating will provide superior protection from corrosion.
4. Production of a uniform thickness coating regardless of the part geometry [12]. The electrocoat system is a self-limiting process. As film thickness increases the electrical resistance increases driving the process to proceed on less accessible areas of the part being coated. This property will provide improved coverage in recessed areas that prove difficult for spray application.
5. Improved application process of the electrocoat system will save time and reduce material waste and unnecessary VOC emissions due to overspraying [10].
6. Provide coatings that are free of toxic compounds which provide superior material composition for initial application and subsequent maintenance and paint removal. They reduce exposure to hazardous materials for both manufacturing and maintenance workers.

Organic coatings cover and protect the surface of the metal substrate. They provide protection by excluding water and ions from the substrate and by preventing conduction between the cathode and the anode [13]. However, no coating by itself can completely stop these processes. Additional protection is required when an ionic, conductive, aqueous phase is present at the metal surface and especially at film defects that expose the metal.

This additional protection is provided by the use of active chemical compounds that inhibit either the anodic or the cathodic reaction [13]. These chemical compounds produce a thin unreactive surface on the metal substrate which stops or greatly reduces the corrosion rate. Ideally this unreactive surface is capable of self repair whenever a defect occurs and the conditions are favorable for the corrosion reaction. These inhibitive compounds have usually been in the form of inorganic pigments that are dispersed throughout the organic coating system. However, there are some organic compounds which may be added to the coating and act as an inhibitor.

Compounds of lead and of chromium have been used extensively as inhibitive pigments [14]. These compounds proved to be very effective inhibitors capable of usage in a wide range of circumstances. They are capable of formulation into a large number of coating systems yielding a wide pigment volume concentration (PVC) range of optimum performance [13]. The resulting coatings are useful in many applications subject to different conditions. Recently, these compounds have become increasingly subject to environmental regulations that eliminate or restrict their use.

A large number of alternative compounds have been proposed to replace the lead and chromate inhibitors [13, 14]. None of these will ever fully replace the lead and chromate versatility. Each coating system will require a fine tuned inhibitive pigment package specific to that particular system chemistry and planned application. This requires a total system design methodology so that all components of the final coating system work together.

In many situations a single inhibitor may not be capable of providing adequate protection. A combination inhibitor package may be required that utilizes several different inhibition mechanisms. An oxidizing inhibitor forms a protective oxide film that retards either the anodic or the cathodic reactions. A sacrificial pigment is a compound that preferentially reacts at the surface instead of the substrate metal. A barrier pigment lengthens the actual pathway that the ions must travel and so retards the reaction rate [13].

The addition of a pigment or a pigment package into an electrocoat system is a complex process. Besides the usual considerations of pigment effectiveness in the particular coating system there is the additional complication of compatibility within the electrocoat bath itself. To be compatible with the electrocoat bath process the pigment should have the following properties [10, 15, 16]:

1. Low water solubility in the electrocoat bath
2. Freedom from water soluble salts that could enter the bath
3. Proper specific conductivity that allows good mobility
4. Chemical stability over the pH range of the bath and film
5. Good dispersibility and wetting
6. Be subject to minimum settling
7. Chemical stability to heat stoving
8. Small particle size and narrow distribution

The following pigments have been used, mostly in anodic systems, as corrosion inhibitors [10, 15, 16]:

1. Basic lead silicochromate
2. White lead silicate
3. Lead phthalocyanine
4. Barium chromate
5. Barium metaborate
6. Zinc flake
7. Strontium chromate
8. Zinc chromate

The strontium chromate and zinc chromate inhibitors are not very good for electrocoats.

2.1.2 Electrochemical Impedance Spectroscopy Analysis. The impedance of electrochemical systems has been investigated for over a century. At first, obtaining valid impedance data as a function of frequency was a very difficult experimental task. The application of modern electronic circuitry to the problem and the commercial availability of automatic computer controlled instruments has now made the acquisition of data relatively simple.

Many technologically interesting systems can now be studied, including painted metal surfaces in contact with aqueous electrolytic solutions. Work in the painted metal area started appearing in the 1970's. The field was reviewed by Scully in 1986 [17].

It has taken some time for data analysis methods to catch up with the new data acquisition methods. Many workers in the coating field have tried to use EIS to solve applied problems equipped only with qualitative or heuristic analysis methods. Graphical methods, as discussed by Walter, are a better approach, but these can be time consuming and inaccurate [18]. The graphical methods work best for systems which give very simple, ideal impedance spectra. The best general approach for data analysis is complex, non-linear, curve fitting. Fortunately, several computer programs to do this are now available.

2.2 UV Cure Coatings Material Development. The UV curable coating development required the formulation of 100% solids coatings that contained non-chromated corrosion inhibitors. Prior to addition of the corrosion-inhibiting powders, the UV curable coatings are viscous and can be difficult to apply by spray application. The incorporation of any solid component into the resin systems would magnify this problem. In addition, mixing the corrosion inhibiting pigments into certain resin components was difficult, and in some instances required modifications of the resin systems or solvent addition. Solvent addition is highly undesirable when the goal is to produce a non-VOC coating.

The performance properties of the cured coatings were significantly reduced by the addition of the corrosion inhibitors evaluated in this program. Most notable was the very poor flexibility of the coatings into which the inhibitors had been incorporated.

The ultraviolet light transmission properties of the corrosion inhibiting powders were found to adversely affect the cure properties of the UV curable coatings. When the pigments absorb or reflect light in the wavelength region in which the photoinitiators react, the UV light energy never reaches the coating/substrate interface and the film cure is incomplete. Inadequate curing results in several poor performance characteristics of the coated product. It is desirable for the pigment or pigment mix to transmit ultraviolet light in the same wavelength region required to activate the photoinitiator.

2.3 Powder Coatings Development. The powder coating development required the formulation of powder coatings containing non-toxic corrosion inhibitors. Since these inhibitors are not typically incorporated into powder coatings, the effects of the inhibitors on the application of the powder coating, and on the properties of the coating when cured, required evaluation. The performance of these inhibited coatings when evaluated to military requirements was determined.

The inherent hiding power of the NAWCADWAR inhibitive pigment systems is low. This characteristic allows the inhibitive pigment systems to have only a minor influence on the color of a coating. Color production thus must originate from other sources such as primary pigments. Primary pigments have high refractive indices and can impart barrier properties; however, they are not known to participate in active corrosion inhibition. Due to the coalescent mechanism of powder coating film formation, rheology and thus the concentration of resin and pigment solid particles influences the critical film performance of a powder coating. Solids content and rheology thus dictates the practical formulation range of powder coatings which is significantly less than the range achievable in traditional solvent-borne and water-borne liquid coatings.

Gloss control is an inherent problem with powder coatings. Unlike liquid coatings, the gloss of powder coatings can not be reduced by simply adding flattening agents or fillers to the formulation. Instead, micro-imperfections must be imparted to the formulation in order to alter the surface characteristics. This is typically accomplished by using multiple cure rate catalysts which can over cross-link the polymer matrix and produce brittleness [19]. Little to no work has been performed in the industry with respect to the research and development of active corrosion inhibitive powder coatings. Thus historical data is not available to aid in the present effort.

2.4 Powder Coatings Applications Development. The powder coatings application development evaluated the ability of IR curing to properly cure powder coatings and the performance of coatings cured with IR energy. Various factors such as the chemistry of the powder coating, the substrate material, and the shape of the substrate can affect the ability to properly cure powder coatings with IR energy. The type of IR energy used is also a critical factor. Various wavelengths of the IR spectrum can be used and the proper wavelength for curing powder coatings was determined.

Development of powder coating non-conductive substrates addressed the ability to modify the surface conductivity to allow electrostatic powder coating. The affects of the surface enhancing agents on the coating characteristics is important to insure that the coatings meet military specifications.

2.5 Inhibitor Characterization and Analysis. The inhibitor characterization efforts required the development of test methods for analyzing inhibited coatings. These tests determined the effects of various inhibitors on corrosion protection as well as the mechanism of corrosion protection. The test methods themselves required modification as the evaluation proceeded to account for the inability to target the desired properties.

2.6 Inorganic Surface Pretreatments for Coating Evaluation. During the course of this program, it came to our attention that the team had experienced salt spray exposure failures in resin systems that would normally have been expected to pass. This raised the question of the quality of the chromium conversion coating (CCC) being used in the study. A search of the literature [20] and discussions with conversion coating job shops in the field confirmed that there was no simple quality control technique that could be used to determine whether or not a conversion coating on an aluminum panel would pass military specifications C-5541D and MIL-C-81706A. A limited effort was made to evaluate a series of techniques developed at Lehigh and Naval Air Warfare Center that would enable the user to evaluate the integrity of the CCC aluminum panel.

3.0 GENERAL METHODOLOGY

3.1 General Formulation Development Methodology

3.1.1 Formulating with Non-Toxic Corrosion Inhibitors. Military equipment is required to operate in extremely corrosive environments. Traditionally, corrosion inhibition has been provided by coatings with high concentrations of chromate and/or lead pigments. These inhibitors provide excellent protection in a wide range of conditions (e.g. pH, substrate type, temperature, and coating composition). Their primary disadvantage is that they are toxic and their use in the future will be prohibited. Therefore, non-toxic alternatives which provide equivalent or superior performance properties in the desired application(s) needed to be identified.

Recent efforts to develop high performance primers and topcoats have uncovered several promising non-toxic corrosion inhibitors for organic coatings [6,7]. Generically, these compounds include phosphates, molybdates, silicates, borates, and organo-metallic salts. Unfortunately, none of these compounds individually perform in the wide range of scenarios covered by lead and chromate inhibitors. Some of these deficiencies have been overcome by combining non-toxic inhibitors to form filler systems for coatings. These combinations exhibit synergistic effects and enhanced performance properties, including superior corrosion inhibition. Previous research at the Naval Air Warfare Center Aircraft Division Warminster was performed to explain the mechanisms causing these effects. This information would be used in future development efforts. This work was extended in this program by the Lehigh University efforts.

In developing zero-discharge organic coatings, the most promising non-toxic corrosion inhibitors were identified for formulation into powder coatings, UV curable coatings, and electrocoat systems, respectively. Existing polymeric binders for these applications were evaluated and selected based on their performance and compatibility with these non-toxic fillers. In order to take advantage of any possible synergistic effects which may occur in these zero-discharge coatings, statistical formulation and experimentation methodology was used to combine corrosion inhibiting pigments into polymeric binder systems. This approach has been extremely successful in the development of advanced coating systems. A discussion of this methodology is presented in the following section.

3.1.2 Statistical Design and Analysis. Coating formulations are complex mixtures, often containing up to 20 individual compounds. Each of these compounds performs a separate function; for example, the polymer binds the constituents into a coherent and adherent film after the coating is cured; pigments may provide color, corrosion inhibition, or durability to the coating; and additives may be included for cure kinetics, rheology, and UV stability. In addition to their individual contributions, various compounds within a coating composition may interact with each other [21], thereby causing unexpected effects. The traditional approach to uncovering these effects and developing multi-component materials is a time consuming and costly trial and error formulation process. In contrast, an alternative method has been devised to efficiently obtain optimum coating compositions while making, characterizing, and analyzing a minimal number of formulations [22].

Theoretical predictions of optimal compositions are integrated with statistical formulation design. By combining pigmentation surface properties with particle size and distribution characteristics, critical pigment volume concentrations (CPVC's) of individual pigments and complex pigment mixtures in polymer binders can be predicted. These concentrations are then used as composition constraint boundaries in a statistical mixture design such as simplex or extreme vertices. In this manner, it is possible to "screen" all combinations of coating constituents (i.e., polymers, fillers, and additives) for beneficial effects without performing an excessive number of experiments [22].

The formulation of the ZDOC's utilized high performance corrosion inhibitor pigment systems which have been determined and validated in conventional liquid coating systems using the above formulation design methodology. After the ZDOC's were made and tested, a total performance evaluation (TPE) was performed which assigned an overall quantitative coating performance value based on the cumulative effects of all properties [23]. This was done to minimize property trade-off and select the optimum coating composition for a particular application [23]. Also, appropriate statistical analysis methods (i.e., t-test, ANOVA, linear regression, etc.) were used in order to obtain statistically determined trends, effects, and/or models which accurately described property responses to compositional changes.

The approach described above was followed in order to facilitate the development of powder, UV cure, and electrocoat coatings within program development time, while assuring optimum properties and performance. Specific considerations for the development of each of these materials are discussed below.

3.1.3 Coating Performance Analysis. Correlation's between natural and accelerated evaluations are difficult due to the complexity of corrosion processes. One industry which has devoted a great effort in this area and shares some problems encountered in military applications is the automotive industry [24]. Detailed studies of steel protection systems' performance under natural and accelerated testing have been performed. A great many methodological "lessons learned" can be derived from following the progress of the automotive studies. In particular, reliance upon any one accelerated test method is not appropriate. Indeed, the process of determining the most appropriate method or methods is evolutionary. As each component of the environment is identified, it must be evaluated for significance to and synergism with the other components. One approach to resolving the difficulties has been summarized as a uniform strategy of service life prediction [25].

The approach for this study consisted of establishing the identity of the most probable fundamental processes (blistering, adhesion and undercutting), observing their behavior under field conditions and correlating the behavior with appropriate accelerated tests. The real-time in-service electrochemical impedance spectroscopic monitoring provided a serviceable means of correlation to materials service life (inhibitor performance). Positron annihilation measurements were used to help characterize microvoid properties of protective coatings as they relate to elimination of volatile formulation components and determination of polymer matrix void structure necessary for inhibitor function [26]. Along with this approach, a total performance evaluation model was utilized which determined the cumulative effect of coating properties on overall performance, thus enabling the selection of the most promising coating for an intended application.

3.2 Electrocoat Material Development

3.2.1 System Development with Non-Toxic Corrosion Inhibitors. In the past, the development of corrosion inhibitors for electrocoat systems has not been strongly or successfully pursued. This situation is probably due to the complexity of the electrocoat systems. Inhibitor additives are not easily developed for electrocoat applications. Also, the net improvement to those most likely to benefit (automotive industry) would be minimal since impact damage is better accommodated by galvanic protection for vehicle applications. Development of inhibitor additives for electrocoat systems requires implementation of appropriate inhibitor solubilities and electrophoretic charge properties which are compatible with electrocoat system chemistry. Inhibitor materials must be carefully selected based upon electrocoat requirements as well as anticorrosive properties. The surface properties of desirable inhibitor pigments can be modified to provide appropriate surface charges for the electrocoat process. Small amounts of soluble inhibitor materials can also be considered for additive use such as quaternary ammonium compounds. Close coordination of inhibitor properties with electrocoat system requirements is essential in the development of non-toxic corrosion inhibitors. The proximity and established professional ties between Lehigh University and Naval Air Warfare Center was particularly valuable in performing the work necessary to meet the challenges described above.

3.2.2 Electrocoat Demonstration. Full-scale, single-piece electrocoat processing has previously been successfully performed on components as large as farming equipment and automotive chassis [27]. While being technically possible, a single, full-scale test on an aircraft structure or truck body would be difficult, expensive and not cost-effective within the contract time-period. Therefore, demonstration of non-toxic inhibitor formulations were based on benchtop systems capable of coating a sufficient number of test panels and small components to permit accelerated and in-service evaluations. Several commercially available cathodic electrocoat systems were modified to accommodate non-toxic inhibitor materials. Cooperation of electrocoat material suppliers and inhibitor suppliers was solicited in formulation of demonstration systems.

3.3 UV Cure Coatings Material Development

3.3.1 Current Technology. Over the last five years, extensive development of UV materials has been conducted for various applications which has led to the development of inexpensive UV curing equipment. This has greatly increased the potential for utilizing UV materials in military surface coatings applications. Further development of this technology by the incorporation of corrosion inhibiting pigments into the UV curable coatings would offer the potential for implementing these zero discharge coatings in DOD applications.

Many UV material types have been developed including epoxies, urethanes, and acrylics. Some of these systems have dual curing mechanisms (UV light - air moisture) to insure full cure and overcome the effects of shadowing and cure depth. These hybrid materials were considered the basis in developing a UV coating that meets military specifications. The integration of the non-toxic corrosion inhibitors into the UV polymer system was then considered the major focus in defining the UV system.

The pigments utilized to obtain the color finish of the coating was also an important parameter. Pigments are known for absorbing UV energy and as such become critical to obtaining proper polymerization in the coatings. To overcome this phenomenon, novel resin chemistries were required to insure the proper cure depths. Application technology development was required since 100% solid materials are difficult to apply and at present have applications limitations. These limitations include flow, surface finish, and film uniformity.

3.3.2 System Development. The development of photocurable coatings for use as interior and exterior coatings on weapons systems was begun by evaluating state-of-the-art materials and modifying them to produce more durable and lower VOC containing systems. These UV curable coatings were evaluated as primers, topcoats, or self-priming topcoats depending on pigmentation composition. Although emphasis was placed on existing materials in other industries, where suitable properties were not be found, in-house formulation was performed. Potential resin systems and non-toxic inhibitor pigments were investigated based on their potential for meeting military equipment requirements.

3.3.2.1 Survey of Existing Technology. Existing technology in pigmented UV curable materials used in commercial applications was surveyed for applicability for this project. Modifications and improvements based on performance requirements were investigated. Table 2 shows the results of the commercial UV curable coatings survey.

3.3.2.2 Selection of Available Resin and Photoinitiator Systems. Resins with sufficient durability were selected from available polymers. Aside from performance properties, sprayable viscosity range must be achievable with selected prepolymers. Addition of low molecular weight resins can lower viscosity, but this generally creates less flexible coatings. Since addition of pigment will further increase the viscosity, the addition of some amount of solvent, or heating of the coating during application was necessary to produce a sprayable coating with acceptable appearance for some of the systems.

3.3.2.3 Selection of Compatible Pigments. Use of UV coatings as alternatives to conventional topcoats require color conformance to FED-STD-595 requirements. Pigments which are UV-transparent to some degree were evaluated for incorporation into selected resin systems. Most inorganic pigments used in conventional paints will block the UV radiation from reaching the substrate/coating interface, therefore organic pigments were also evaluated in these systems.

3.3.2.4 Selection of Non-toxic Corrosion Inhibitors. Non-toxic inhibitors based on NAWCADWAR studies were incorporated into selected resin systems. Standard coatings tests were then performed on these systems to characterize their performance properties, particularly corrosion resistance.

3.3.3 System Performance Analysis

3.3.3.1 MIL-SPEC Performance Properties. Performance evaluation of UV coating formulations which met all screening criteria during development stage were based on requirements in standard coating specifications for military equipment including: MIL-P-23377, MIL-P-53030, MIL-C-22750, MIL-C-85285 and MIL-C-83286. Table 3 illustrates the Mil Spec coating requirements for UV coatings. A variety of substrates and surface treatments, listed in Table 4, were tested for compatibility with this technology, primarily aluminum and steel substrates. Performance testing included the following:

Interior requirements: lube oil and hydraulic oil resistance; gloss; adhesion (dry & wet); heat resistance; flexibility; solvent resistance; impact resistance; and strippability.

Exterior requirements included the above along with the following: impact resistance after weathering and fluid exposure; weatherability; Skydrol, hydrocarbon, and water resistance; low temperature flexibility; humidity resistance; and corrosion resistance.

3.3.3.2 Application Properties. The pigmented UV coatings were formulated to be applied by conventional spray or high volume low pressure (HVLP) spray methods. Formulation of the coatings emphasized that they be equal to existing paints in ease of application.

3.4 Powder Coatings Development

3.4.1 Powder Coatings Development and Testing

3.4.1.1 Formulating Powder Paints with Non-toxic Corrosion Inhibitors. The objective of this effort was to develop powder coatings for military equipment, which have a zero discharge of volatile organic compounds (VOC's) and a non-toxic pigment composition. In addition, these coatings would display the high performance properties of current coating systems which provide corrosion inhibition, wear protection, color conformance, etc..

Table 2. Survey of Commercial UV Curable Coatings

COMPANY	CONTACT	COATING DESCRIPTION	COMMENTS
Miles Coatings Pittsburgh, Penn.	David McClurg (412) 777-4963 Fax (x 2132) Leon Boretzky (412) 777-2725 Fax (x2132)	Have numerous candidates and full facilities.	Group support Military applications do not have experience with UV curables. However, the Wood Products Division has extensive experience. Met Mike Dvorchak at RADTECH who indicated he will provide input to D. McClurg for our program. Telecon with McClurg indicated interest in supplying a water based material. Not interested in supplying a solvent based or 100% solids type. Can we expand our evaluation to include Zero **Organic** Discharge Organic Coatings?
DSM Desotech **Chicago**	Myron Bezdicek (708) 468-7721 Fax (708) 695-1748		After extended discussions over two months, including at Radtech, Desotech has decided not to obligate resources in this area, which is not a focus of the company. DELETE
Aptek, Inc.	Joe Vaccaro (805) 257-1677 Fax (805) 257-8939	Aptek manufactures dual cure UV curable confomal coatings, very tough, with very tenacious adhesion to metal and other substrates. They will be submitting a pigmented candidate for evaluation.	Submitted a green pigmented coating which was much too soft for any testing. Not interested in pursuing this program. DELETE
3M Corp. Research Labs 3M Center Bldg. 201-2N-19 St. Paul, MN 55144	Kevin Kinzer (612) 733-6575 (612) 737-2590 (fax)	Currently working on a DOE contract to develop a pigmented dual cure topcoat formulated to meet requirements of MIL-C-83286 or Mil-C-85285. This work should be a very good basis for supplying materials for this contract. However, 3M's goal was not a ZDOC coating.	Work on an associated gov't contract makes 3M a strong candidate to provide a suitable coating.
Sokol Enterprises Valley View, OH	Andrew Sokol (216) 777-1286 (216) 328-1023 (fax)	Interesting chemical resistant, flexible corrosion resistant pigmented coating targeted for the automotive industry. 4 candidates received. Latest one received for testing (6/3).	Funding Sokol ~$9K/month for his development work.

Table 2. Survey of Commercial UV Curable Coatings- Continued

COMPANY	CONTACT	COATING DESCRIPTION	COMMENTS
UVEXS, Inc. 1025 Terra Bella Ave. Mountain View, CA 94043	Brent Puder 408-737-7100 X18	Acrylated urethane chemistry, primarily for conformal coating, but they also manufacture pigmented inks for the electronics industry.	They were sent chemfilmed panels to coat, but did not return them for test.
Caschem, Inc. 40 Ave. A Bayonne, NJ 07002 **DELETE**	Don Lamotta (201) 858-7924	Dual cure UV curable conformal coating where secondary cure is fairly quick (<24 hours). They have modified this product to meet requirements of this project.	They have added a corrosion resistant additive to a clear coating.
Naval Surface Warfare Center Annapolis, MD **CONTRACT AWARDED**	Barbara Howell (410) 267-2853	Solventless UV curable coating for use in submarine interior applications. Developed at NSWC. Pigmented.	She has worked somewhat w/NAWC on pigmentation of this product.
Sartomer 502 Thomas Jones Way Exton PA 19341 Radtech	Craig Glotfelter (610)363-4189 (610)594-0252 FAX	UV ingredient manufacturer. Dual cure with cationic free radical system to get the best overall physical properties. Bulk of cationics are vinyl ether and epoxy. Sartomer supplies free radical constituents.	UV ingredient manufacturer introduced at Radtech.
PD George, Co. 5200 N. Second St PO BAX 66576 St. Louis, MO 63166 Radtech	Dr. Roger L McCartney (314)621-5700 (314)436-1030 FAX	Interested in supplying/formulating innovative UV curable materials.	Will look at best material for conformal coating. Will take a look at cure and send us something
Allied Signal Radtech	Eugene Sitzmann (708)391-3707	Supplies oligimers to formulators of cationic systems. Find a Union Carbide person for him to talk to. UC (or someone else) will be the provider of the finished formulation.	
University of Akron Radtech	Dr. Darrell H. Reneker (216)972-5110 (216)972-5290 FAX		
Hardman 600 Cortlandt St. Belleville, NJ 07109 Radtech	Scott Gregory (201)751-3000 (201)751-8407 FAX Don Bodewig (714)256-9190	Modifying an electronic conformal coating for our needs. UV plus 50 to 60 C for 10 mins.	
Akzo (Union Carbide pplier) adtech	Robert (Bob) Zilke (502)367-6111		

Table 2. Survey of Commercial UV Curable Coatings- Continued

COMPANY	CONTACT	COATING DESCRIPTION	COMMENTS
UCB Radcure 2000 Lake Park Dr. Smyrna Georgia 30080 Radtech	William F. Mahon , (MAN) (404)801-3287 (404)801-3234 FAX	Very optimistic in conversation at Radtech.	They formulate for certain specialty applications. They supply acrylic ingredients.
Sun Chemical General Printing Ink Division 135 West Lake St. Northlake IL 60164 Radtech **DELETE**	Howard R. Ragin (708)562-0550 (708)562-0580 FAX	Company declined to become involved in products outside of their printing ink product line.	DELETE
Red Spot Paint & Varnish PO Box 418 1016 E. Columbia Evansville, Indiana 47711 Radtech	Randall T. Lake (812)428-9123 (812)428-9160 FAX	Clear coatings only.	DELETE
Craig Adhesives Radtech	John Buck (201)344-1483 (210)344-4767 FAX		DELETE, NO RESPONSE
Microlight Technologies MLT 6009 East Sanford Circle Mesa, AZ 85215 (Steve Delong contact)	Michael Lucey Cynthia Giacchetti 602-807-5200 FAX 602-807-5225	Working with Barbara Howell also. Working with the the government on air force and submarine applications. Secondary cure will probably be an oven cycle.	Steve DeLong says they may be interested in supplying material.
Borden, Inc.	Rohn Johnson (513) 782-6389	Properties of this potential submittal are unknown	Discussed his participation in project at Radtech. He is not very optimistic about being able to supply a candidate. DELETE

Last revised: June 23, 1995

Table 3. MIL-SPEC Coating Requirements for UV Coatings

PROPERTY & TEST METHOD	MIL-C-22750E REQMT (Interior Ctg System)	MIL-C-83286B REQMT (Exterior Coating System)	MIL-C-85285B REQMT (Exterior Coating System)	TT-C-2756 REQMT (Unicoat)
Weather resistance (6000W weatherometer with cycles of 102 mins light w/o water, and 18 mins of water spray+light) ASTM G26, TY BH	N/R	After 500 hrs exposure in a weatherometer, specimens shall show no more than 10% loss of gloss, and no cracking or loss of adhesion. Impact flexibility shall be unchanged.	After 500 hrs exposure in weatherometer, color change shall be <1 (Delta E value per ASTM D2244). 60° Gloss: Gloss colors - 80 minimum Semi-gloss - 15 minimum Camouflage - 3 minimum	After 500 hrs exposure in weatherometer, color change shall be <1 (Delta E value per ASTM D2244). 60° Gloss: Gloss colors - 90 minimum Semi-gloss - 10 minimum Camouflage - 3 max.
Impact flexibility • Initial - Gloss Camouflage • After 1 yr weathering • After 500 hrs in weatherometer • After 4 hrs @ 300°F • After 24 hrs in 250°F lube oil	N/R	Gloss colors - 60% elongation Camo. colors - 20% elongation • no change • no change • no change • no change	Gloss colors - 40% elongation Camo colors - 40% elongation • N/R • N/R • N/R • N/R	Gloss colors - 40% elongation Camo colors - 20% elongation • N/R • N/R • N/R • N/R
Outdoor weathering (Exposure in Key West, Florida for 1 year at 45° angle to horizon)	N/R	No cracking, or loss of adhesion. 10% gloss loss allowed. allowed. Slight color change allowed.	Color change shall be <1 (Delta E value per ASTM D2244) 60° Gloss after exposure: Gloss colors - 80 minimum Semi-gloss - 15 minimum Camouflage - 3 minimum	Color change shall be <1 (Delta E value per ASTM D2244). 60° Gloss: Gloss colors - 90 minimum Semi-gloss - 10 minimum Camouflage - 3 max.
Fluid resistance • Lubricating oil @ 250°F, 24 hrs. • Hydraulic fluid @ 150°F, 24 hrs.	No blistering, softening or dark staining with either fluid	See below	No blistering, softening or dark staining with either fluid.	No blistering, softening or dark staining with either fluid.
Fluid resistance • Lubricating oil @ 250°F, 24 hrs. • Hydraulic fluid @ r.t, 7 days • D.I. water @ 100°F, 4 days • Hydrocarbon fluid @ r.t., 7 days • Skydrol 500B fluid @ r.t., 7 days	See above	Less than one pencil hardness decrease after exposure except for Skydrol, which may decrease two pencil hardness. No corrosion or loss of adhesion.	See above	See above
Salt fog (topcoat only) • 5% soln per ASTM B117 • SO2 salt fog per ASTM G-85	N/R	• 300 hrs • N/R	N/R	• 2000 hrs (ASTM B-117) • 500 hrs (ASTM G-85)
Corrosion resist. (w/primer) • 5% salt fog • Filliform corrosion • Graphite / aluminum panels	• 1000 hours (no defects) • 1000 hours (<1/8" threads) • 500 hours (no defects)	• 1000 hours (no defects) • 1000 hours (<1/8" threads) • 500 hours (no defects)	• 1000 hours (no defects) • 1000 hours (<1/8" threads) • 500 hours (no defects)	N/R

Table 3. MIL-SPEC Coating Requirements for UV Coatings - Continued

PROPERTY & TEST METHOD	MIL-C-22750E REQMT (Interior Ctg System)	MIL-C-83286B REQMT (Exterior Coating System)	MIL-C-85285B REQMT (Exterior Coating System)	TT-C-2756 REQMT (Unicoat)
Adhesion • 24 hour water immersion • Scrape test (ASTM D2197) • 7 day water immersion, 150°F	• No delamination (tape test) • Resists 3kg wt. scrape • N/R	• No delamination (tape test) N/R • N/R	• No delamination (tape test) • Resists 3kg wt. scrape • N/R	• N/R • Resists 5 kg wt. scrape • 5A rating
60° Gloss • Gloss colors • Semi-gloss colors • Camouflage **85° Gloss (Camouflage only)**	• 90 minimum • 15-30 • 5 maximum • 9 maximum	• 90 minimum N/R • 7 maximum N/R	• 90 minimum • 15-45 • 3 maximum N/R	• 90 minimum • 15-45 • 6 maximum • N/R
Heat resistance	After 1 hr at 250°F, color change shall be <2 (Delta E value per ASTM D2244)	After 4 hrs at 300°F, specimens must meet gloss and impact flexibility reqmts	After 1 hr at 250°F, color change shall be <1 (Delta E value per ASTM D2244)	After 4 hrs at 250°F, color change shall be <1 (Delta E value per ASTM D2244)
Low temperature resistance (Tested at -65°F, mandrel test)	N/R	Gloss colors - 1" mandrel Camo. colors - 2" mandrel	Gloss & semi - 1" mandrel Camo. colors - 2" mandrel	1/4" mandrel @ -60°F
Flexibility (1/4" mandrel)	No cracking, peeling or adhesion loss	N/R	N/R	N/R
Humidity (30 days, 95% r.h., 120°F)	N/R	No blistering, softening or loss of adhesion	No blistering, softening or loss of adhesion	No blistering, softening or loss of adhesion
DS2 resistance (30 min exposure)	No blistering, wrinkling or film softening.	N/R	N/R	N/R
Solvent resistance (50 rubs w/MEK)	No coating removal down to bare metal	N/R	No coating removal down to bare metal	No coating removal down to bare metal
Tape resistance (Apply 3M250 tape for 1 hr)	No permanent marring	No permanent marring	No permanent marring	No permanent marring
Strippability (MIL-R-81294, TY I, Cl 1 paint stripper)	90% stripped in 1 hour	N/R	90% stripped in 1 hour	90% stripped in 1 hour

Table 4. Test Substrates for UV Curable Coatings

SUBSTRATE	SURFACE TREATMENT	PRIMER
1010 C Steel	Zinc-Phosphate per Mil-P-16232,TY Z	None
1010 C Steel	Zinc-Phosphate per Mil-P-16232,TY Z	Wash Primer, Mil-C-8514
1010 C Steel	Zinc-Phosphate per Mil-P-16232,TY Z	Wash Primer, Mil-C-8514 and Primer per Mil-P-23377
2024 Aluminum, T0	None	None
2024 Aluminum, T0	Conversion Coat per Mil-C-5541	None
2024 Aluminum, T0	Conversion Coat per Mil-C-5541	Primer per Mil-P-23377

Powder coatings, unlike liquid coatings systems, must be cured by heat convection or some other radiant energy source (i.e., IR, UV, laser, etc.). For aerospace applications this is a serious concern since the temper of typical aluminum alloy airframe materials can be significantly altered by exposure to heat sources in excess of 300°F. Therefore, in this powder coating effort, the polymeric binder systems were limited to materials that cure at 300°F or less.

Although Hughes (Tucson) has powder coating application capabilities, none of the ZDOC team members have the expertise and/or equipment to produce powder coating raw materials and to compound those materials into a formulated industrial production-grade final product. Agreements were established with two powder coating manufacturers (Herberts Powder Coatings, Inc. and Morton International, Inc.) in order to gain this powder coating production capability.

During separate discussions with these coatings manufacturers, polymer coating chemistries were identified that met our initial general requirements. Appropriate powder polymer systems were evaluated for performance and compatibility with potential non-toxic corrosion inhibitors and primary pigments. The powder industry efforts to develop a UV resistant epoxy paint was evaluated for status and potential. Recent work on non-toxic corrosion inhibitors and color pigments was reviewed to select appropriate pigment systems for formulation into the polymer matrix. Laboratory experiments for critical performance properties (adhesion, flexibility, chemical/weather resistance, etc.) were performed on coating systems as they were developed to screen, select, optimize, and characterize these systems.

3.4.2 Advanced Powder Coating Applications and Curing Technology

3.4.2.1 Electrostatic Application on Non-Conductive Materials. Various techniques could be used to powder paint a non-conductive substrate; these include placing a metal backing onto a non-conductive substrate, coating of the substrate with a conductive primer, and adding a conductive component into the resin from which the non-conductive substrate is made.

A non-conductive substrate can be powder painted if a metal panel is temporarily placed behind and in contact with the substrate providing a charge dissipation path. However, the mechanisms for charge dissipation does not work for complicated three dimensional objects with large surface areas, awkward angles and segments.

The use of conductive primers can provide a conductive layer. When the conductive layer is grounded, it facilitates charge dissipation and provides a zero potential surface relative to the gun. The use of conductive primers to enhance the surface conductivity of substrates is a popular method in industry. Conductive primers typically contain metal as well as carbon particles and may be organic or aqueous based. Conductive primers containing nickel have been widely used in the automobile industry. Applying water based conductive primers onto non-conductive substrates takes skill since metal particles in the conductive primer are susceptible to settling and tend to slide down vertical surfaces (prior to drying) leaving areas where there is poor conductivity. Because of their high conductivity, conductive primers often result in the attenuation of RF signals and may not be acceptable in certain aerospace applications.

The practice of mixing conductive ingredients to the resin powder from which the substrate is cast has been discussed. A method for the electrostatic coating of a resin molding by mixing with the resin a complex of a specified polyether and an electrolyte salt (soluble in the polyether) has been patented [28]. The complex could be made from adding 1 part lithium perchlorate and 4 parts methanol into 20 parts polyether with stirring to obtain a homogeneous solution and then removing methanol in vacuum. The drawback with this method is that the company doing the powder painting may not be in the business of making their own resins!

The use of antistatic materials to temporarily enhance surface conductivity has been widely discussed in many aspects of plastic processing. Typically antistats can be added to the resin to be casted. After casting, the antistats may migrate to the surface providing surface conductivity. Antistats can also be applied from a solvent using a brush-on or spray-on technique [29].

Since the use of non-conductive materials in many aerospace applications is increasing, techniques for electrostatic powder coating of non-conductive substrates are being actively investigated. The objective of this paper is to report the results of a surface conductivity enhancing method to enable powder coating of polymeric substrates.

3.4.2.2 IR Curing. There are many substrates, including both conductive and non-conductive materials, which are unable to withstand the cure temperatures normally associated with powder painting. IR curing has been identified as a technology which has the potential to overcome this problem. IR ovens can be used to rapidly heat and cure the powder paint film possibly without excessively heating the substrate. The cure times for many powder paints can be reduced from approximately 20 to 40 minutes, when convection heating is used, to less than 3 minutes for IR heating. This reduction in cure time could dramatically reduce the heat effects on sensitive substrates.

While IR curing seems to offer several significant advantages including reduced cycle time, there are also several areas which required evaluation. The effects of IR curing on the powder coating properties was evaluated to insure coatings cured with IR energy maintained the same properties as those coatings cured with conventional convection heating. In addition the effects of irregular shapes could restrict the application of IR curing from some complex geometries or require combination IR/Convection ovens. Additionally, the compressed cure time from approximately 30 minutes to the short times (usually less than 3 minutes) was evaluated in reference to the careful control of the cure time required to avoid under or over cure.

There are several IR oven technologies available for use and each was investigated for powder paint curing applications. HMSC developed an IR cure evaluation plan, shown in Appendix A, for comparing the performance of IR curing of powder paint to the performance of convection ovens. The plan also evaluated the effects of irregular shapes to verify that uniform surface temperatures can be achieved to insure an even and full cure so that performance properties are not compromised.

3.5 Inhibitor Characterization and Analysis. There are two main modes of coatings failures relative to the corrosion processes: one involves rapid transport of aggressive agents through a porous or damaged coating and the other is the slow transport through an intact, effective (but not perfect) barrier coating. The consequences of these transport modes are summarized in the mechanisms of cathodic delamination [30,31], shown in Figure 1 (rapid transport) and in the mechanism of blister formation [32], shown in Figure 2 (slow transport). These mechanisms differ in establishment of a localized corrosion environment. In each mechanism, the effectiveness of the inhibitor is determined by its activity in the localized environments. It is postulated that a balance exists between coating properties which enhance coating effectiveness and those which enhance barrier properties. A barrier coating which isolates the inhibitor from the active corrosion site should not represent an effective corrosion-inhibitive coating.

When the inhibitor reaches the interface, it must interact in some manner with the metal surface in order to reduce the corrosion rate. If the electrochemical nature of the corrosion processes is considered, which constitutes at least two electrochemical partial reactions, inhibitors may also be defined on an electrochemical basis. Compounds that act as inhibitors will reduce the rates of either anodic oxidation and/or cathodic reduction. Inhibitors can affect the individual anodic and cathodic reactions or both of these chemical reactions. In addition, inhibitors may be classified as to their chemical nature, that is, if they are organic, inorganic, oxidizing or non-oxidizing materials. Their interaction can take place by means of a chemical reaction or as a barrier to a chemical reaction. The inhibitor does not have to be an integral part of the chemical product on the metal surface in order for it to function as an inhibitor.

3.5.1 Selection of Corrosion Inhibitors. An extensive literature search (See Appendix B) on corrosion inhibitors was made. The following is a list of criteria that was used to select inhibitors from those found in the literature:

1. Solid
2. Non toxic
3. Low solubility
4. Effective on aluminum
5. Commercially available

Based on these criteria, 10 inhibitors were selected for this study and are listed in Table 5.

3.5.2 Selection of Coating Materials. Extensive work was done to develop a model resin system that would resemble the resin systems used in the three different technologies mentioned earlier. Two-part epoxy systems were chosen because of the

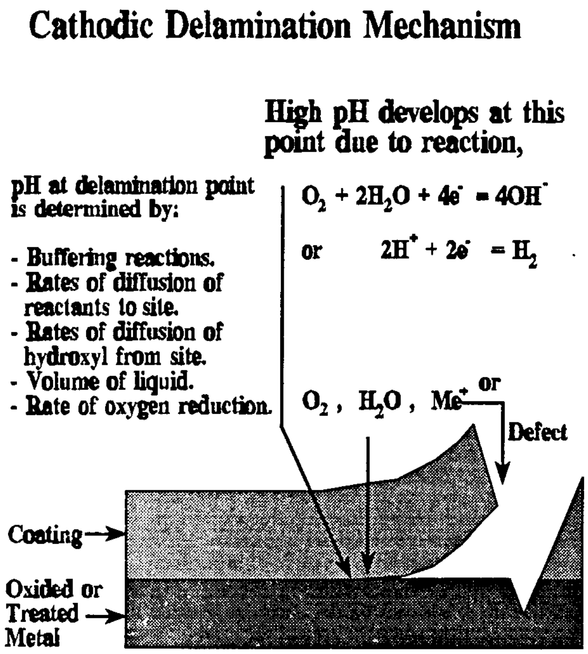


Figure 1
Schematic of Cathodic Delamination Process

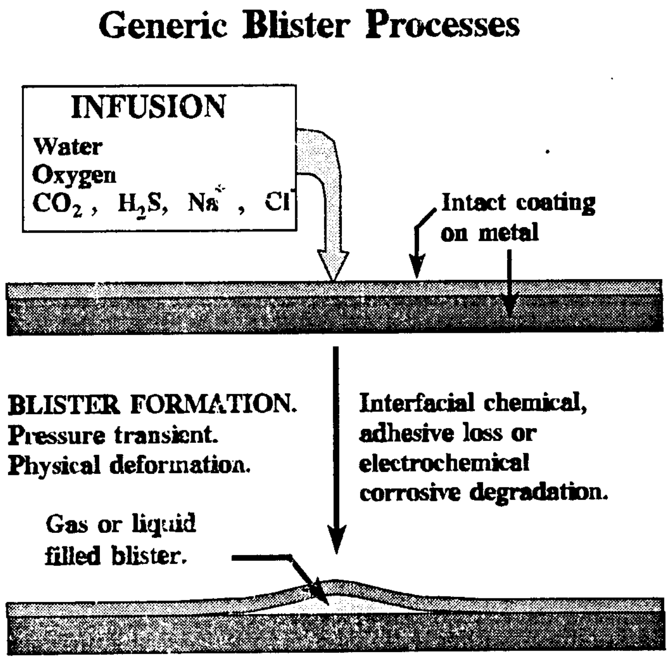


Figure 2
Schematic of Blistering Mechanism

Table 5. Inhibitor Compositions

Inhibitor Code	Inhibitor Composition
MPSi	Calcium Strontium Zinc Phosphosilicate
CaPSi	Calcium Phosphosilicate
CaSi	Calcium Modified Dioxide, Synthetic Precipitated Silicas
BaBor	Barium Metaborate Monohydrate
M1Psi	Zine Aluminum Phosphosilicate
ZnA1P	Zinc Aluminum Phosphate
MoZnP	Molybdate Zinc Phosphate
ZnoN	Zinc salts of organic Nitro compounds
ZnMoP	Basic Zinc Molybdate/Phosphate
ZnCin	Zinc Oxide and Cinnamic Acid (1:2)

impermeability to water and ions, good adhesion to aluminum substrates, and commercial availability. The specific epoxies chosen are discussed in more detail in Section 4.5.

3.5.3 Selection of Experimental Techniques. Electrochemical Impedance Spectroscopy (EIS) measurements were used to determine coating permeabilities to water and ions and to determine if a given inhibitor was effective in a particular coating-substrate-electrolyte system. Polarization resistance measurements were made for comparison to the EIS measurements to determine inhibitor effectiveness. Differential Scanning Calorimetry (DSC) and Positron Annihilation Lifetime Spectroscopy (PALS) data were obtained to determine the physical properties (degree of cure and free volume characteristics) of the various coating materials. X-Ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM) were used to determine the type, location, and percentage of chemical elements (corrosion products, components of the inhibitors, etc.) on the aluminum substrate surface. Inductively Coupled Plasma (ICP) measurements were made on inhibitor saturated aqueous solutions to determine the type and concentration of chemical elements present in these solutions.

3.6 Conversion Coating Analysis.

To resolve the problem of variations in test panels, which arose during the course of this investigation, the need for a standard method of pretreatment analysis was identified. A number of analysis techniques were evaluated for their potential to characterize the chromate conversion coating surface pretreatment used in this study. After performing a literature review on this subject, the analysis methods were selected based on this information and their perceived capability of differentiating between coating weights. Variances in coating weights and pretreatment aging were proposed as the cause of the differences in performance noted during the course of the coating evaluation.

3.7 Field Evaluations.

Following the developmental efforts for each of the coatings (powder, UV cure, and electrocoat), field tests on operational DOD components will be planned and implemented. The objectives of these field tests will be two fold: (1) confirm coating application and performance capabilities and (2) initiate transitioning of the developed materials to the commercial environment. Coatings will be applied at Naval Aviation Depots, contractor plants, and other DOD facilities during equipment manufacture, rework and overhaul. Powder and UV cure coatings will be applied to various internal and external aircraft components; the electrocoat material will be applied to internal aircraft components and/or vehicle frames. Navy aircraft components have been selected for the initial field trials, due to their severe operational exposure conditions. These field demonstrations will be conducted after the completion of this project due to time constraints. NAWCADWAR will be managing the field demonstrations following the termination of the project.

4.0 TECHNICAL RESULTS

4.1 Electrocoating Materials Development.

4.1.1 Materials Development

4.1.1.1 Evaluation of Commercially Available Materials. The first stage of this task focused on a state-of-the-art assessment of electrocoat technology. Two companies (BASF & PPG) submitted samples of commercially available electrocoat materials on pretreated aluminum panels provided by NAWCADWAR. BASF provided samples of an experimental lead free cathodic electrocoat. This material is also being investigated by McDonnell-Douglas Aerospace (MDA). All of the baseline BASF samples were processed by MDA in their 100 gallon pilot tank. PPG provided samples of two lead free materials. One sample was an anodic electrocoat (Powercron 150A), which cures at 225°F (lowest cure temperature). The other sample provided was Powercron 648LC, a cathodic electrocoat which is cured at 300°F. Both samples were coated at PPG's Springdale, PA facility.

Tables 6 and 7 contain the evaluation results for the BASF and PPG materials, respectively. The adhesion of all materials was excellent in scrape and wet tape tests. Also, these materials had excellent resistance to both water and organic fluids. Strippability was good for all materials except the PPG anodic electrocoat. The major area of concern for material performance was corrosion resistance.

Table 6. BASF Commercial Electrocoat Performance Results

			BASF Electrocoat Materials			
		Oct. '93	Mar. '94 Batch			
			Deoxidized		CCC Pretreatment	
Test Name:	**Range:**	**Batch**	**Al-2024**	**Al-7075**	**Al-2024**	**Al-7075**
Adhesion:						
Dry Scrape	0.5 - 10+ kg	4.0 kg	1.5 kg	NA	1.5 kg	NA
Wet Scrape (24 hr /RT)	0.5 - 10+ kg	3.0 kg	NA	NA	NA	NA
Dry Tape "A" method	0 - 5 (A)	5A	NA	NA	NA	NA
Wet Tape (24 hr / RT)	0 - 5 (A)	5A	5A	5A	5A	5A
Wet Tape (4 day / 120°F)	0 - 5 (A)	5A	5A	5A	5A	5A
Wet Tape (7 day / 150°F)	0 - 5 (A)	5A	5A	5A	5A	5A
Fluid/ Corrosion Resistance:						
Salt Spray (1000 hr)	P, +, -, F	+	Fail	Fail	+	+
SO2 Spray (500 hr)	P, +, -, F	Fail	Fail	Fail	Fail	Fail
H2O resistance (24 hr / RT)	P, +, -, F	Pass	Pass	Pass	Pass	Pass
H2O resistance (4 day / 120°F)	P, +, -, F	Pass	Pass	Pass	Pass	Pass
H2O resistance (7 day / 150°F)	P, +, -, F	Pass	Pass	Pass	Pass	Pass
Humidity Resistance (30 day)	P, +, -, F	Pass	Pass	NA	NA	NA
23699 Oil (24 hr / 250°F)	P, +, -, F	Pass	Pass	NA	NA	NA
83282 Hydraulic (24 hr / 150°F)	P, +, -, F	Pass	Pass	NA	NA	NA
Hydrocarbon JP-5 (7 day / RT)	P, +, -, F	Pass	Pass	NA	NA	NA
Solvent Resistance (MEK Rub)	P, +, -, F	Pass	Pass	NA	NA	NA
Heat Resistance (4 hr / 250°F)	P, +, -, F	Pass	NA	NA	NA	NA
AIA Filiform Corrosion (1000 hr)	P, +, -, F	+	NA	NA	NA	NA
EIS						
Miscellaneous:						
GE Impact test (gloss)	0.5%-60%	NA	NA	NA	NA	NA
Mandrel bend (-60°F)	0.125"...0.75"	NA	NA	NA	NA	NA
60° Gloss (gloss)	% Reflected	41.50%	59.80%	NA	53.30%	NA
Strippability (15 min.)	% Removed	100%	100%	NA	100%	NA
Cleanability	% Removed	81.17	NA	NA	NA	NA

P = Pass, + = Borderline pass, - = Borderline Fail, F = Fail, NA = Not Available

Table 7. PPG Commercial Electrocoat Performance Results

Test Name:	**Range:**	**PPG Electorcoat Materials**			
		Anodic		**Cathodic**	
		Al-2024	**Al-7075**	**Al-2024**	**Al-7075**
Adhesion:					
Dry Scrape	0.5 - 10+ kg	0.5 kg	NA	2.5 kg	NA
Wet Scrape (24 hr /RT)	0.5 - 10+ kg	2.0 kg	NA	3.5 kg	NA
Dry Tape "A" method	0 - 5 (A)	5A	5A	5A	5A
Wet Tape (24 hr / RT)	0 - 5 (A)	5A	5A	5A	5A
Wet Tape (4 day / 120°F)	0 - 5 (A)	5A	5A	5A	5A
Wet Tape (7 day / 150°F)	0 - 5 (A)	5A	5A	5A	5A
Fluid/ Corrosion Resistance:					
Salt Spray (1000 hr)	P, +, -, F	+	+	+	+
SO2 Spray (500 hr)	P, +, -, F	Fail	Fail	Fail	Fail
H2O resistance (24 hr / RT)	P, +, -, F	Pass	Pass	Pass	Pass
H2O resistance (4 day / 120°F)	P, +, -, F	Pass	Pass	Pass	Pass
H2O resistance (7 day / 150°F)	P, +, -, F	Pass	Pass	Pass	Pass
Humidity Resistance (30 day)	P, +, -, F	Pass	NA	Pass	NA
23699 Oil (24 hr / 250°F)	P, +, -, F	Pass	NA	Pass	NA
83282 Hydraulic (24 hr / 150°F)	P, +, -, F	Pass	NA	Pass	NA
Hydrocarbon JP-5 (7 day / RT)	P, +, -, F	Pass	NA	Pass	NA
Solvent Resistance (MEK Rub)	P, +, -, F	Pass	NA	Pass	NA
Heat Resistance (4 hr / 250°F)	P, +, -, F	NA	NA	NA	NA
AIA Filiform Corrosion (1000 hr)	P, +, -, F	-	NA	-	NA
EIS					
Miscellaneous:					
GE Impact test (gloss)	0.5%-60%	Would not Coat		2.00%	NA
Mandrel bend (-60°F)	0.125"...0.75"			0.125"	NA
60° Gloss (gloss)	% Reflected	64.70%	NA	87.80%	NA
Strippability (15 min.)	% Removed	85%	NA	100%	NA
Cleanability	% Removed	NA	NA	NA	NA

P = Pass, + = Borderline pass, - = Borderline Fail, F = Fail, NA = Not Available

In neutral salt spray, the panels exhibited a significant build-up of corrosion products and rundown from the scribe. At 1000 hours, all three materials were reduced to a borderline pass due to the level of scribe corrosion, however, they were free of any general surface blistering or undercutting of the film. Also, in both neutral and SO_2 salt spray tests, the 7075-T6 aluminum alloy specimens appeared to be more resistant to corrosion than the 2024-T3 alloy panels.

All three materials exhibited some blistering of the coating adjacent to the scribe before 500 hours of SO_2 salt spray exposure. However, the area away from the scribe was free of blisters in excess of the 500 hour requirement. Normally samples exposed to the SO_2 salt spray are primed and topcoated with a total coating thickness of 2.4 mils or more. However, electrocoats are applied at slightly less than one mil. While a more reasonable evaluation of electrocoats would probably include a topcoat (to bring the total system film build in line with other systems), these materials will require additional development to meet this exposure requirement.

All three materials exhibited borderline performance in the filiform corrosion evaluation. There were no filaments longer than 1/4 inch, but most filaments exceeded 1/8 inch in total length. However, many of these filaments did not extend beyond 1/8 inch from the scribe. Again, this evaluation is usually performed on a total system consisting of both a primer and a topcoat, however, these materials will still require additional development to meet this exposure requirement.

To further evaluate the baseline performance, MDA prepared two additional sets of panels with the BASF electrocoat material. One set was chromate conversion coated with the standard pretreatment and then electrocoated. The other set had the electrocoat applied directly to the deoxidized substrate. Corrosion resistance was the only property where a difference was observed between the deoxidized and chromate conversion coated panels. Table 8 lists the results for all four alloy and pretreatment combinations at 2000 hours of neutral salt spray exposure (neu) and 500 hours of SO_2 salt spray exposure (SO_2).

The performance of the PPG materials was similar to the results observed for the BASF electrocoat. A slight difference was evident between the anodic and the cathodic materials. In neutral salt spray, the cathodic material appeared to have more corrosion products in the scribe and more run down than the anodic material. In the SO_2 salt spray, the anodic material had a larger number of small blisters than the cathodic material. Table 9 lists the results for all four alloy and electrocoat material combinations at 2000 hours of neutral salt spray exposure and 500 hours of SO_2 salt spray exposure.

4.1.1.2 Relationships with Electrocoat Material Suppliers. In order to perform the electrocoat development work described in the ARPA ZDOC Program Proposal, the cooperation of electrocoat material suppliers was required. The electrocoat process is a complex system and it is difficult to start from basic materials and assemble a bath representative of current commercial technology. Ideally, numerous manufacturers would have supplied developmental materials for in-house formulation work. This would have allowed for modification of several different electrocoat resin systems in an attempt to incorporate the non-toxic corrosion inhibitors. Unfortunately, only BASF agreed to provide a cathodic material for formulation experiments. BASF supplied a standard resin emulsion to be used as-received, and a grinding resin to be used to introduce pigmentation into the electrocoat process. BASF also provided technical assistance in all aspects of the establishment of a benchtop electrocoat process line at NAWCADWAR.

Table 8. BASF Electrocoat Salt Spray Results

	Pretreatments	
Alloy	**Deoxidized**	**Chromate Conversion Coating**
2024-T3	Neu: Heavy corrosion in scribe. Many small blisters along scribe. SO_2: Heavy corrosion in scribe. Heavy blistering along scribe.	Neu: Significant corrosion in scribe with rundown. Several blisters on one panel. One blister on another. SO_2: Corrosion products in scribe. Many small blisters along scribe.
7075-T6	Neu: Heavy corrosion in scribe. Many small blisters along scribe. SO_2: Heavy corrosion in scribe. Heavy blistering along scribe.	Neu: Significant corrosion in scribe with rundown. No blisters. SO_2: Corrosion products in scribe. Many small blisters along scribe.

Neu - 2000 hours Neutral Salt Fog, SO_2 - 500 hours SO_2 Salt Fog

Table 9. PPG Electrocoat Salt Spray Results

	Electrocoat Materials	
Alloy	**Anodic Electrocoat**	**Cathodic Electrocoat**
2024-T3	Neu: Corrosion products in scribe with rundown. Couple of small blisters over four panel. SO_2: Corrosion products in scribe. Small blisters along scribe.	Neu: Corrosion products in scribe with rundown. Couple of small blisters over four panels. SO_2: Corrosion products in scribe. Small blisters along scribe.
7075-T6	Neu: Corrosion products in scribe with rundown. No blisters. SO_2: Corrosion products in scribe. Small blisters along scribe.	Neu: Corrosion products in scribe with rundown. No blisters. SO_2: Corrosion products in scribe. Small blisters along scribe.

Neu - 2000 hours Neutral Salt Fog, SO_2 - 500 hours SO_2 Salt Fog

The automotive industry prefers cathodic materials because they form a better barrier and in doing so, they provide improved corrosion protection [10]. However, the ZDOC program may have benefited from the slightly reduced barrier properties provided by anodic electrocoat materials. The reduced barrier properties may have allowed the corrosion inhibiting pigments to leach out into any defect areas and so provide protection. Cathodic materials may be such good barriers that the inhibitors are encapsulated in the coating so tightly that they are unable to leach out to provide protection.

4.1.1.3 Establish In House Electrocoat Processing. Typical voltages used for electrocoating [18] are between 200 and 300 volts with a current density between 1 and 3 amps/ft^2. A dedicated power supply is needed for the electrocoat process due to the requirement for both high voltage and high current. A Sorensen power supply (Model DCR 600 - 3B2) was selected for this requirement, since it was capable of providing 0 to 600 volts at 0 to 3 amps from an input of 115 VAC single phase current.

This unit provides sufficient power to operate a small scale (five gallon) electrocoat bath which is sufficient to coat a number of various size panels or small parts. Without enough current electrodeposition either will not begin or will not produce a properly formed film [33]. While a lower voltage would have been adequate for the resin systems considered, the higher voltage of the Sorensen model will be needed for additional pigmentation studies and to determine rupture voltages for new formulations [10]. Lastly, the low voltage single phase input allowed the electrocoat process to be plugged into a regular 115 outlet, thereby providing a flexible operation.

Initial attempts at controlling bath temperature using a hot plate proved inadequate. A dedicated temperature control system provided a quick and simple way to bring the electrocoat bath to the proper operating temperature and to maintain it during processing. The system selected for our use consisted of a 22 liter water tank with a digital immersion circulator fitted securely over a 12 x 12 inch magnetic stirrer. The circulator provided both heat and water circulation in a single unit clamped to the side of the water tank.

The panels produced in this line must be sufficiently free of film defects to allow for proper testing. Producing panels of sufficient quality requires the development of the proper techniques in both producing the bath and operating each stage of the process. All four stages of the line, which includes metal pretreatment, electrodeposition bath, rinse, and coating cure, must operate properly to produce a good quality coating.

Initial attempts at electrocoating panels with either BASF pigment pastes or NAWCADWAR pastes produced films with excessive film imperfections. Several problems associated with the electrocoat bath and the rinse stage caused the majority of the film defects. One solution employed to correct this problem was a better filtration system. Instead of filtering though a # 200 mesh sieve, the bath was passed through a # 325 mesh sieve and then through a bag filter similar to the type used by MDA. With this new system, the quality of panels significantly improved.

Another process improvement made during this investigation was in the panel handling procedures. Freshly coated panels were first immersed in a container of distilled, deionized water and soaked for approximately one minute. Then, the panels were removed and rinsed in deionized water and hung to drain. When most of the water has drained (about 5 minutes) any remainder is blown off using compressed, oil-free nitrogen. The panel were now ready for curing.

The continuous formation of seeds or of other precipitated material indicates that a problem exists with the long term stability of the electrocoat bath [34]. The manufacturer suggested that less than one gram of material should precipitate from one gallon of electrocoat during the pump stability test. This test continuously recycles electrocoat through the type of pump used in full scale process lines. Inside the pump, the material is subjected to the highest shear stress, and precipitation is most likely to occur. The magnetic stirrer used for continuous agitation of the baths, subjects the electrocoat to much less stress than in the pump. Despite this lower stress level, the baths precipitated out more material than was acceptable for the pump stability test [9]. This long term stability problem may have been caused by an insufficient amount of acid available for the electrocoat resin. The amount of available acid controls the degree of resin solubilization, called total neutralization (TN%). Measuring pH alone does not provide an accurate representation of the TN% character of an electrocoat material. TN% is determined by a potentiometric titration for both the acidic and basic milliequivalents, MEQ_a and MEQ_b respectively [35]. A sample of the potentiometric response curves is presented in Figure 3A for a bath assembled at NAWCADWAR using BASF's pigment paste. The TN% determined for the bath showed that the MEQ_a was slightly below the optimum value but not enough to account for the stability problem. After consultation with BASF, it was concluded that the resin emulsion was not within specification limits. Also, a slight pink cast, indicative of bacterial contamination, was noticed for the old emulsion. This contamination could have caused the stability problem observed.

The primary task for this effort was the formulation of corrosion inhibiting pigments into electrocoat materials. Typically, electrocoat baths are made from two separate feedstocks. The majority of the resin, or binder, is supplied as an emulsion which does not contain any pigmentation. The resin emulsion for this effort was used as-received from the supplier. The second part contains the pigments and other dry components which are dispersed in a resin paste. This pigment paste component was the focus of the formulation work.

A Dispermat System with a high-speed disk disperser blade with some additional accessories was used to grind the pigment paste to attain a Hegman grind between 7 and 7.5. Producing a batch of paste was a two step process consisting of a premilling step (using the high-speed disperser blade) and a final milling step (using a modified media mill). The premilling step allowed for a more efficient use of the media mill reducing time and improved the ultimate

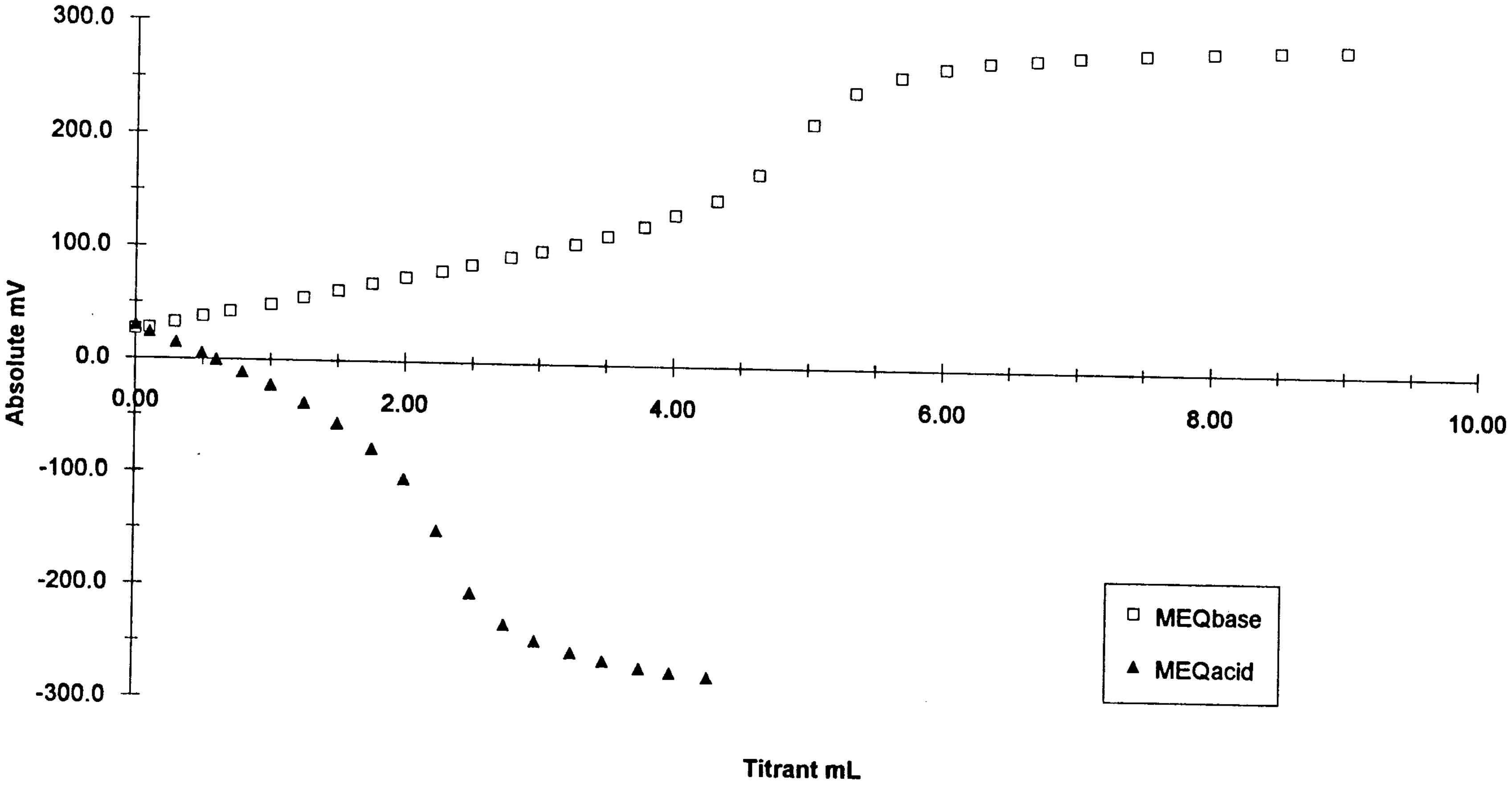


Figure 3A MEQ Potentiometric Response Curves.

dispersion [36]. A sketch of the high-speed disk disperser system attempting to disperse the small particles throughout the mill base is presented in Figure 3B [37]. The dimensional ranges indicated on the figure are those supplied by the equipment manufacturer. There is some dispute over the optimum configuration as Patton [38] suggests somewhat different ranges. Figure 4 presents a sketch of the modified media mill.

A mill base was prepared from the grind resin, an anti-foaming agent, solvent and distilled, deionized (DDI) water. This mill base was stirred for approximately 10 minutes at very low speed. Then, the dry components are slowly added to the paste. These dry components consist of color pigments and the electrocoat cure catalyst and any corrosion inhibitors desired. During this wetting and cutting-in of the pigments the rotation rate was kept just fast enough to continue stirring the paste. When all the dry components were added, the rotation rate of the blade was increased to the value required to obtain a proper dispersion. At this speed, the mill base attained a doughnut like flow pattern (laminar flow regime). During the milling process additions of water, and ethylene glycol monobutyl ether for the inhibitor containing pastes, were made as needed to maintain the correct mill base viscosity and subsequently the laminar, doughnut like flow pattern in the vessel. A high-speed disperser achieves the breakup of pigment agglomerates primarily through a smearing process although smashing plays a secondary role [39, 40]. Smearing means that the agglomerates are broken down due to the application of shear stress on the particle. The smearing action occurs across the velocity gradient present in laminar flow patterns. This steep velocity gradient exists because of the variation of shear stress through the fluid, which is then applied to the particle. Introducing turbulent flow disrupts the smearing action as pigment agglomerates become entrapped in eddies and are not subjected to sufficient shear stress [38].

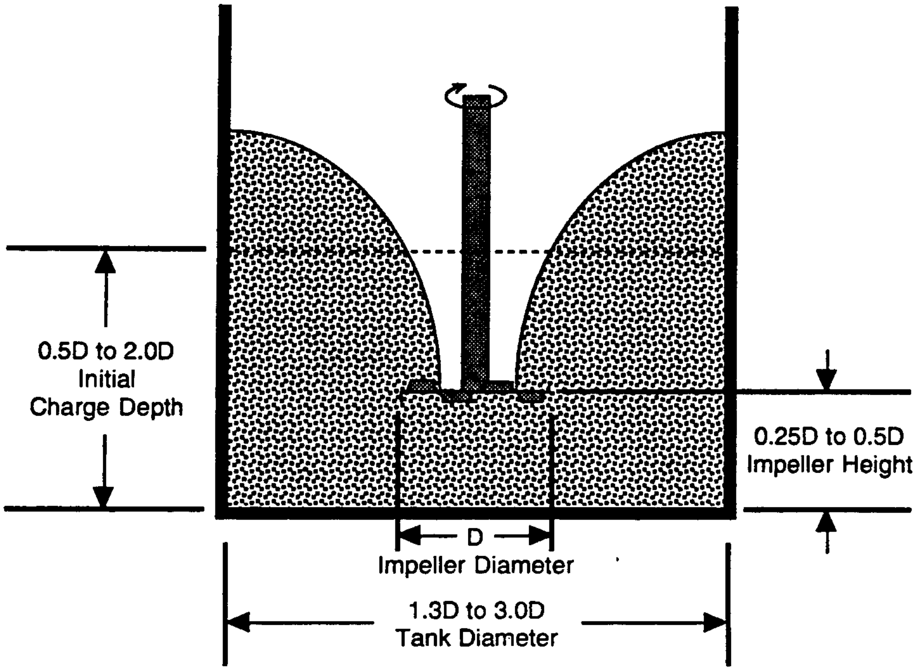


Figure 3B
High Speed Disperser System

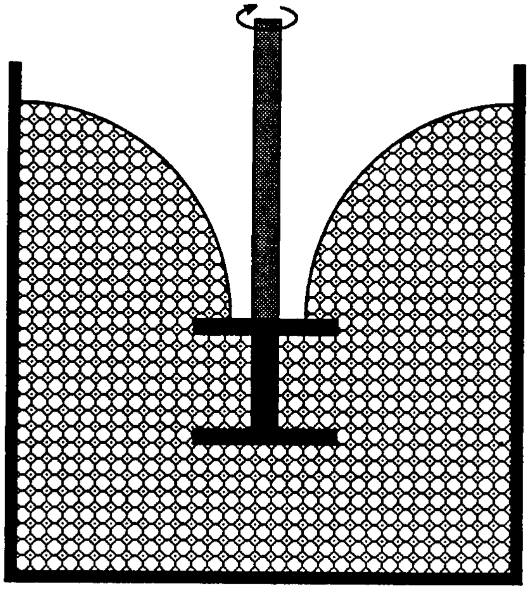


Figure 4
Modified Media Mill

The premilling in the high-speed dissolver continues for 30 minutes or until the fineness of grind (FOG) is between 5.5 and 6.0. Then, the dissolver blade is removed from the Dispermat and replaced with a 45 mm diameter, flat, dual disk impeller. Also, the vessel is charged with ZrO_2 beads which act as impinging media to further breakup the pigment agglomerates. This may be seen in Figure 4 where the impeller is the black object at the bottom of the rotating shaft and the ZrO_2 beads form a slurry with the mill base and the small pigment particles. The rotation rate was increased to obtain a doughnut like flow pattern, similar to the pattern observed in the premilling step. Additions of DDI water, and usually ethylene glycol monobutyl ether for inhibitor containing pastes, were made as needed to maintain the proper viscosity and flow pattern. Milling was continued until a FOG of 7.5 or better was obtained. At this point, the dispersion process was considered complete.

The paste was now ready for letdown [38] to the correct non-volatile level and the desired final viscosity of approximately 1000 centipoise. The rotation rate was decreased to prevent overgrinding the resin, but high enough to mix in the letdown DDI water. The water was slowly added until the correct dilution was reached. Next the paste was recovered from the ZrO_2 beads by filtering through a #20 mesh sieve.

4.1.1.4 Corrosion Inhibiting Pigments. In electrocoating, more than in most other organic coating applications, the total system must be considered when making changes. The effect of any additive on the electrocoat bath stability is as important as the performance of the additive and therefore must be selected with great care.

A significant contribution to the program was the incorporation of NAWCADWAR proprietary corrosion inhibiting pigment packages into each coating technology. These non-toxic pigment combinations were developed generically for use in a wide range of applications. A total of six inhibitors were used in assorted combinations to form five different pigment packages. Table 10 lists these six inhibitors in the section entitled, "NAWCADWAR Corrosion Inhibitors." This list includes the pigment manufacturer, its chemical composition, some selected physical property data and a shortened reference name (For example, Moly White 101 is shortened to MW-101) that will be used throughout the section. Also, listed in this table is similar information on several components used in the standard electrocoat paste formulation and several additional corrosion inhibitors that were investigated in the developmental electrocoat systems.

Some of the pigments in the NAWCADWAR packages were not compatible with the electrocoat materials. MW-101 was recommended for use in solvent borne systems, while the electrocoat system required compatibility with water borne materials. Sicron-RZ has a very high oil absorption and a low specific gravity which make this pigment difficult to properly wet and disperse into the electrocoat grinding vehicle. Finally, SZP-391 contains a significant amount of both calcium and zinc oxides which are bivalent cations.

Bivalent cations were believed to cause bath stability problems in both anodic and cathodic electrocoating systems [10]. The destabilization mechanism in anodic systems was seemingly straightforward. Anodic electrocoat material was solubilized by inducing a negative charge onto the resin. When bivalent cations were present a resin molecule attaches to each of the positive charges on the cation. When several resin molecules become bound together they will no longer remain in solution and so precipitate.

However, the destabilization mechanism in cathodic systems was not quite as straightforward. Both BASF and PPG suggested that the cations bond to the acetic acid and prevent it from solubilizing the resin, properly. Unfortunately, additional acetic acid did not appear to prevent the precipitate formation as would be expected from this simple explanation. Another explanation may be that the cations were in equilibrium with anionic acetate complexes. These complexes actually caused the precipitation from the bath and the bivalent cations indirectly caused the destabilization by forming the anionic complexes.

In addition to the NAWCADWAR pigment packages, other corrosion inhibiting pigments, which would be compatible with electrocoats, were solicited from the industry. The water solubility, pH and conductivity of these pigments under conditions similar to a working electrocoat bath were measured. These properties are important to the electrocoat process and especially to the bath stability. Table 11 presents the results of these measurements. Three sets of pH and conductivity (in mhos/cm) measurements are presented.

Standard electrocoat components were prepared in DDI water at approximately the same wt% at which they are present in the standard electrocoat bath. Both the pH and the conductivity was measured after 24 hours and after 4 days of continuous stirring. All materials quickly settled out when the agitation was stopped, except TiO_2, which remained dispersed for several days. Also, the TiO_2 left a residue on the probes that was very difficult to remove, so further testing of this material was discontinued. Finally, the pH of ASP-200 increased during these measurements.

Table 10 Pigment Manufacturers' Data.

Product Name Reference Name	Manufacturer	Chemical Composition	S.G. H_2O = 1.0	Solution pH
Standard E'coat Additives				
Ti-Pure R900 Ti-R900	Dupont	TiO_2	4.0	NA
ASP-200 ASP-200	Englehard	Aluminum Silicate	2.58	4.2
Cure Catalyst Cat.	Proprietary	NA	1.58	NA
NAWC Corrosion Inhibitors				
K-White 84 KW-84	Tayca Corp.	Aluminum Triphosphate	3.1	NA
Moly White 101 MW-101	Sherwin-Williams	Zinc Molybdate	5.06	6.5
Phos Plus Phos+	Mineral Pigment	Zinc & Barium Phosphates	3.15	4-5
Sicron-RZ Sicron-RZ	BASF Pigments	Organic Nitro Zinc Salts	2.5	7.2
SZP-391 SZP-391	Halox	Ca Sr Zn Phosphosilicate	3.01	7.0
ZMP ZMP	Heucotech LTD.	Zinc Phosphate	3.7	6.5
Others E'coat Corrosion Inhibitors				
K-White 140W KW-140W	Tayca Corp.	Aluminum Triphosphate	3.0	NA
Moly White 212 MW-212	Sherwin-Williams	Calcium Zinc Molybdate	3.0	8.5
Moly White MZAP MW-MZAP	Sherwin-Williams	Ca Zn Mo Phosphate	3.0	8.0
Moly White 501 MW-501	Sherwin-Williams	Calcium Molybdate	2.93	7.8
Heucosil ZW Hsil-ZW	Heucotech LTD.	Zinc Tungsten Boron Silicate	3.3	NA
Butrol-22 But-22	Buckman Laboratories	Barium Metaborate	3.3	8.5-9.5
Nalzin 2 Nalzin-2	Rheox Inc.	Zinc Hydroxy Phosphite	3.96	6.5-7.5

Table 11. Pigment Solution Evaluations

Pigments	24 Hours Evaluation		4 Day Evaluation		pH Adjusted Evaluations	
	pH	Λ	pH	Λ	pH	Λ
Standard E'coat Additives						
Ti R900	6.98	26.1	7.26	26.8	#	
ASP-200	4.74	24.1	5.12	23.9	-	-
Catalyst	NA	NA	-	-	-	-
NAWC Corrosion Inhibitors						
KW-84	6.83	17.2	6.85	19.9	5.61	786
MW-101 *	7.12	240.	7.03	233.	6.07	7780.
Phos Plus *	7.63	77.1	8.07	207.	4.34	670.
Sicron-RZ	7.32	83.0	7.25	90.0	5.69	3780
SZP-391	NA	NA	-	-	-	-
ZMP	6.71	62.0	6.67	65.0	5.14	4410.
Other E'coat Corrosion Inhibitors						
KW-140W	7.12	82.4	7.79	107.	5.76	1260.
MW-212	7.92	123.	7.90	121.	7.02	5210.
MW-MZAP	7.60	75.1	7.59	82.2	6.62	3430.
MW-501	7.66	124.	7.57	132.	5.44	4690.
Hsil-ZW	7.44	42.1	7.41	52.4	6.06	2970.
Butrol-22	9.76	1310.	9.31	1140.	6.25	6900.
Nalzin-2	7.40	26.4	7.14	31.5	6.15	3610.

Λ = conductivity with units µmho/cm

Evaluation Halted due to Probe Fouling.

* 4 Day Evaluation actually at 5 days due to Holiday.

Each inhibitor solution was prepared at 2% by weight in DDI water (approximate inhibitor loading level for the electrocoat baths), however, none of the inhibitors completely dissolved. Both the pH and the conductivity were measured after 24 hours and after 4 days of continuous stirring. Next, the solution pH was adjusted to between 5.8 and 6.0 (normal pH range for electrocoat operations). Glacial acetic acid (AA) was used to make pH adjustments since AA is used to solubilize the resin in the electrocoat process. Four grams of AA was added to each solution. This amount of AA in the same quantity of pure DDI would increase the solution's conductivity from less than 10 mhos/cm to 760 mhos/cm. These solutions were then stirred for another 24 hours and the measurements were taken again.

Although the target pH range was between 5.8 and 6.0, the adjusted final pH values did not lie within this range. Some solutions had subsequent changes in pH during the stirring time, while others had too much AA added and the correct range was overshot. Several solutions evidenced drifts in pH, even after more AA was added to re-adjust the pH.

As shown in Table 11, all the inhibitors except Phos+ displayed a conductivity higher than that expected from the simple addition of the acetic acid. Several of these had conductivities many times higher, indicating that these pigments were undergoing a complex dissolution when introduced into the electrocoat bath. At first appearance many of these inhibitors would appear to be compatible with anodic systems based on their solution pH and low conductivity in the slightly alkaline region [41]. However, a similar analysis should be performed using a typical anodic electrocoat solubilizing amine. In solution with the amine these inhibitors may undergo a similarly complex dissolution.

4.1.1.5 Corrosion Inhibited Electrocoats. NAWCADWAR made arrangements with both BASF and PPG to formulate the NAWCADWAR corrosion inhibiting pigment packages into their materials. BASF tried several of NAWCADWAR's inhibitor packages in their cathodic electrocoat material, while PPG tried these packages in their Powercron 150A anodic electrocoat material.

BASF attempted to incorporate several of the NAWCADWAR inhibitors individually. The MW-101 and Sicron-RZ inhibitors were incompatible with their materials in both the paste processing stage and in bath stability. Phos+ appeared somewhat compatible with the materials but did not improve the corrosion performance. BASF also tried to incorporate lead silicochromate, a traditional anodic electrocoat inhibitor, however, this inhibitor was incompatible and completely gelled the paste during the dispersion process.

PPG attempted to incorporate the Z-14L, Z-18L, Z-51, and Z-MM5 NAWCADWAR inhibitor packages directly into their anodic system at the typical levels used for their electrocoat. Several of these packages were incompatible with their water based pigment paste. They investigated a solvent based paste by substituting the water with ethylene glycol monobutyl ether, which successfully produced the pigment pastes, however, the resulting baths precipitated on overnight stirring.

Introducing corrosion inhibiting pigments into these materials is more complex than processing standard coating formulations. The high speed dissolver and the modified media mill, used to obtain the desired fineness of grind, require a specific range of viscosities to operate. If the mill base viscosity falls outside the proper range, the dispersion process will not proceed and the resin may even undergo degradation. Maintaining the correct viscosity while dispersing the inhibitive pigments requires additions of ethylene glycol monobutyl ether solvent and/or water. These additions differ in quantity and order for each of the different corrosion inhibitors.

Further formulation work at NAWCADWAR resulted in the successful production of individual inhibitor containing electrocoat pigment pastes. These pastes were based on the standard BASF formulation with 75% by weight of the TiO_2 replaced with one of the inhibitors. Once the inhibitor containing pastes were produced, electrocoat baths were assembled in the usual manner. Besides evaluating the electrocoated panels for the usual performance properties, the compatibility of the inhibitors with the electrocoat materials must be consider. Any incompatibilities will cause the bath to precipitate material at an accelerated rate. Table 12 summarizes the paste processing and electrocoat stability results for these materials. The actual paste and bath formulations are included in Appendix C. Finally, the resultant electrocoat baths still did not meet the manufacturer's stability requirements.

The following is a description of the incorporation of the individual corrosion inhibiting pigments. The SZP-391 pigment appeared to grind in the normal manner, however, after two days the paste gelled into a solid mass. The MW-101 proved difficult to grind and the addition of 10g of solvent into the 400g batch of paste was required to complete the process. Surprisingly, this paste still remained a liquid with approximately the correct viscosity. The Phos Plus also proved difficult to properly grind. Although only a small amount of additional

Table 12 Corrosion Inhibiting Pigment - Electrocoat Compatibility Results.

Pigments	**Pigment Pastes**		**E'coat Baths**
	Processing *	Storage	
KW-84	Easy Grinding. Viscosity Low. Added B-C-S.	Separated one month. Could not recover	Some precipitate recovery with a few large particles. Somewhat easy filtration.
MW-101	Gelled during Grinding. Recovered with B-C-S.	Good stability.	Worst bath stability: greatest precipitate recovery. Very difficult filtration.
Phos +	Pseudoplastic Rheology.	Pseudoplastic but stable.	Best bath stability. Little precipitate recovery. Easy filtration.
Sicron-RZ	Very Difficult. Very low Loading. Added a lot B-C-S.	Good stability.	Some precipitate recovery mostly large clumps. Somewhat easy filtration.
SZP-391	Easy grinding. No B-C-S.	Gelled solid in two days.	Significant precipitate recovery. Somewhat difficult filtration.
ZMP	Pseudoplastic behavior problem . Added B-C-S.	Pseudoplastic with high yield point but stable.	Some precipitate recovery. Somewhat easy filtration.
Hsil-ZW	Pseudoplastic. Difficult letdown. Added B-C-S.	May be Flocculating. Pseudoplastic.	Little precipitate recovery. Easy filtration.

* B-C-S = Butyl Cellosolve

solvent was required, the rheological behavior of the paste during the grinding was wrong. This paste exhibited pseudoplastic behavior with a very high yield point during the grinding and when checked after one week this paste also had gelled. Processing the KW-84 pigment went smoothly although maintaining the correct viscosity required several solvent additions. However, after one month, this pigment settled out as a hard sediment that could not be recovered.

The Sicron-RZ proved to be the most difficult to properly grind. This pigment's low specific gravity and high oil absorption value, make high loading levels difficult to disperse. The first attempt replaced only 50% by weight of the TiO_2 with this inhibitor in the standard formulation. The pigment was hard to cut in and eventually the paste completely gelled. Additions of water and solvent could not recover this batch. The reason this first attempt failed was probably because the volume of dry components exceeded the wetting capacity of the grind resin. The second attempt at producing this paste incorporated 25% by weight of the usual amount of TiO_2 as Sicron-RZ and 25% of the usual amount of curing catalyst. At this significantly reduced loading level, the processing went smoothly although maintaining the correct viscosity required several solvent additions. This paste also remains a liquid with approximately the correct viscosity.

Finally, there was an excessive loss of material during processing with the average yield less than 50%. Also, the viscosity of the standard paste was twice the suggested value. This indicates that the pastes were not being letdown sufficiently. Most of the pastes made prior to this analysis, including the first three inhibited pastes, were probably at too high a viscosity. The subsequent batches of standard paste were subsequently letdown to the correct viscosity.

These pastes were used to make working electrocoat baths. After 24 hours of stirring, the baths were filtered into a clean vessel and then brought to the desired operating temperature. A voltage ladder determined the correct voltage for the desired film thickness for each inhibited bath. A total of 20 3x4 inch panels were coated from each bath. Also, the bath non-volatile content and the pigment to binder ratio were monitored to check the bath stability. All five inhibitor containing baths lost approximately a gram of material from a one liter bath during overnight stirring. This amount is significantly more than that lost from the standard formulation bath and does not meet manufacturer's requirements.

Table 13 presents the performance results for the five inhibitor systems and the standard formulation. These panels and panels coated with the standard electrocoat formulation produced at NAWCADWAR and by MDA (controls) were tested. As reported for the current commercial materials all of the above systems pass water resistance and tape adhesion tests. Chemical resistance was not tested, but all systems pass the solvent resistance test which is actually a measure of sufficient cure. Also, sample panels from selected systems were evaluated with atomic absorption to analyze of the film. These systems appear to have deposited the inhibitors in the correct proportions.

Corrosion resistance was the primary performance property targeted for improvement. Sets of panels were exposed to SO_2 salt fog for 1000 hours and to neutral salt fog for 2000 hours. Unfortunately, none of the five inhibitors unequivocally improved the corrosion resistance of the electrocoat materials. Table 14 summarizes the SO_2 and neutral salt fog exposure performance. Several of the inhibitors slightly improved the SO_2 salt fog performance, but none improved the neutral salt fog performance, and two actually degraded this property. Both the MDA panels and the NAWCADWAR produced electrocoat panels performed as expected. These two standard formulas resisted blistering in the neutral salt fog but exhibited a build up of corrosion products at the scribe along with rundown from the scribe.

Table 13 Corrosion Inhibited Electrocoat Performance Results.

Test Name:	Range:	Standard	Corrosion Inhibitor Containing E'coats.				
		E'coat	KW-84	MW-101	Phos +	Sicron-RZ	SZP-391
Adhesion:							
Dry Scrape	0.5 - 10+ kg	NA	NA	NA	NA	NA	NA
Wet Scrape (24 hr /RT)	0.5 - 10+ kg	NA	NA	NA	NA	NA	NA
Dry Tape "A" method	0 - 5 (A)	5A	5A	5A	5A	5A	5A
Wet Tape (24 hr / RT)	0 - 5 (A)	5A	5A	5A	5A	5A	5A
Wet Tape (4 day / 120°F)	0 - 5 (A)	5A	5A	5A	5A	5A	5A
Wet Tape (7 day / 150°F)	0 - 5 (A)	5A	5A	5A	5A	5A	5A
Fluid/ Corrosion Resistance:							
Salt Spray (1000 hr)	P, +, -, F	+	+	Fail	+	Fail	+
SO2 Spray (500 hr)	P, +, -, F	Fail	Fail	Fail	Fail	Fail	Fail
H2O resistance (24 hr / RT)	P, +, -, F	Pass	Pass	Pass	Pass	Pass	Pass
H2O resistance (4 day / 120°F)	P, +, -, F	Pass	Pass	Pass	Pass	Pass	Pass
H2O resistance (7 day / 150°F)	P, +, -, F	Pass	Pass	Pass	Pass	Pass	Pass
Humidity Resistance (30 day)	P, +, -, F	NA	NA	NA	NA	NA	NA
23699 Oil (24 hr / 250°F)	P, +, -, F	NA	NA	NA	NA	NA	NA
83282 Hydraulic (24 hr / 150°F)	P, +, -, F	NA	NA	NA	NA	NA	NA
Hydrocarbon JP-5 (7 day / RT)	P, +, -, F	NA	NA	NA	NA	NA	NA
Solvent Resistance (MEK Rub)	P, +, -, F	Pass	Pass	Pass	Pass	Pass	Pass
Heat Resistance (4 hr / 250°F)	P, +, -, F	NA	NA	NA	NA	NA	NA
AIA Filiform Corrosion (1000 hr)	P, +, -, F	NA	NA	NA	NA	NA	NA
EIS							
Miscellaneous:							
GE Impact test (gloss)	0.5%-60%	NA	NA	NA	NA	NA	NA
Mandrel bend (-60°F)	0.125"...0.75"	NA	NA	NA	NA	NA	NA
60° Gloss (gloss)	% Reflected	NA	NA	NA	NA	NA	NA
Strippability (15 min.)	% Removed	NA	NA	NA	NA	NA	NA
Cleanability	% Removed	NA	NA	NA	NA	NA	NA

P = Pass, + = Borderline pass, - = Borderline Fail, F = Fail, NA = Not Available

Table 14 Corrosion Inhibited Electrocoat Salt Spray Results.

E'coat Composition	**Neutral Salt Spray** 2000 Hours	**SO_2 Salt Spray**	
		500 hours	1000 Hours
Mac-Air Produced Panels	Corrosion products in scribe with rundown. One blister on 3 panels.	Corrosion products in scribe. Small blisters along scribe.	Blister size increased. White corr. under blisters dark corr. in scribe.
Standard Formulation	Corrosion products in scribe with rundown. No Blisters	Corrosion products in scribe. Small blisters along scribe.	Blister size increased. White corr. under blisters dark corr. in scribe.
KW-84	Corrosion products in scribe with rundown. One blister on 3 panels.	Little dark underfilm corrosion present. Small blisters along scribe.	Many more blisters at scribe and in field. Dark corr. present at scribe.
MW-101	Corrosion products in scribe with rundown. Several blisters each panel.	Most dark underfilm corrosion present. Small blisters along scribe.	No change in blisters or in dark corr. Appears as if degradation stopped.
Phos +	Corrosion products in scribe with rundown. No Blisters	Little dark underfilm corrosion present. Small blisters along scribe.	Blister size increased. White corr. under blisters dark corr. in scribe.
Sicron-RZ	Corrosion products in scribe with rundown. Many small blisters each panel.	Least dark underfilm corrosion present. Small blisters along scribe.	Blister size increased. White corr. under blisters dark corr. in scribe.
SZP-391	Corrosion products in scribe with rundown. No Blisters	Little dark underfilm corrosion present. Small blisters along scribe.	Many small blisters at and away from scribe. Corr. products near scribe.

The coatings containing the inhibitors did not perform any better in the neutral salt fog than the standard formulation. They all exhibited a build up of corrosion products at the scribe with rundown from the scribe. Two of the inhibited systems also had blisters along the scribes on all three panels submitted for salt fog evaluation. While one small blister out of three panels is not unusual, as has happened with the MDA baseline panels, the MW-101 and the Sicron-RZ containing systems had blistering on all three panels which began before the 1000 hour point.

The performance of the inhibitor containing systems in the SO_2 salt fog exposure was not quite as straightforward an evaluation. At 500 hours, all systems had small blisters along the scribe, but several of the inhibitor systems had fewer blisters than the standard formulations. Unfortunately, all the inhibited systems also exhibit dark spots along the scribe. Evaluation of these specimens under a 10X microscope showed very aggressive corrosion penetrating into the metal. This dark underfilm corrosion does not appear to uplift the coating, at least initially, but produces dark corrosion products which appear as dark spots through the film. MW-101 contained the highest amount of this corrosion, although, all the inhibitor containing systems had some of this type of corrosion. The standard system had surface corrosion under the blisters, but none of this dark underfilm corrosion.

After 1000 hours, the blisters on the standard system grew larger but few additional blisters formed. However, the corrosion at and near the scribe blisters began to form dark corrosion products where originally there had been only white surface corrosion. This dark corrosion may have been the same as seen in the underfilm corrosion discussed above. While no chemical analysis of these corrosion products was performed, it is possible that this dark corrosion begins to form in the inhibitor containing systems through a different mechanism than in the standard system. Similar changes had occurred in most of the inhibitor systems. The size of the blisters had increased somewhat but not as much as in the standard system. Also, the dark corrosion did not increase very much. At 1000 hours, both the inhibited and the standard systems had nearly the same amount of pitting and surface corrosion. The KW-84 and SZP-391 systems had more small blisters than at 500 hours and some were away from the scribe. Finally, the MW-101 produced an unusual result. It appeared as through the degradation completely stopped at 500 hours. Very little difference was evident between the 500 hour panels and the 1000 hour panels. In all other systems, these two test durations were easily differentiated.

In addition to the above inhibitor studies, two additional pigments were formulated into pastes. One pigment was ZMP (another inhibitor from the NAWCADWAR packages) and the other pigment was Hsil-ZW (an inhibitor claimed to be compatible with electrocoats). BASF reported that pigment pastes, made with Hsil-ZW, produce a stable bath but fouls ultrafiltration systems. Neither inhibitor behaved ideally during the paste processing. Both exhibited pseudoplastic behavior, required additions of ethylene glycol monobutyl ether, and proved very difficult to process.

Only bath stability was analyzed for these new paste materials. The Hsil-ZW appeared to be as stable as the current standard formulation, however the compatibility with ultrafiltration systems was not evaluated. The ZMP inhibitor failed the stability evaluation, although it did not precipitate as much material as some of the other baths. Additional testing was restricted due to time limitations of this program.

4.1.2 Electrochemical Impedance Spectroscopy Analysis. The literature does not appear to contain any EIS studies of electrocoated aluminum. There is relatively little published information on EIS of aluminum painted in any fashion.

Therefore, to establish baseline information, a pigmented (but "uninhibited") cathodic type electrocoat was evaluated. The electrocoat was supplied by BASF and processed at McDonnell

Douglas Aircraft Co. in their 100 gallon electrocoat bath. This electrocoat was based on an amine epoxy resin. MDA supplied "full system" level specimens for EIS evaluations as well as unpainted pretreated specimens.

The full system specimens were of several types. Aluminum alloys used were bare 2024-T3 and bare 7075-T6. Two pretreatments were used, chromate conversion coating and hot water-sealed thin film sulfuric acid anodization. Nominally, only one type of electrocoat was used to paint the pretreated aluminum, although some adjustment of bath chemistry and application parameters were made by McDonnell Douglas engineers during the course of this program.

The most common type of EIS experimental program for painted metal surfaces involves measuring spectra at open circuit as a function of immersion time. This approach was not very revealing for the systems of interest here. Therefore, other approaches were developed based on the dependence of circuit element values on test electrolyte and bias potential. The composition of each test electrolyte studied is given in the experimental section of this report. The electrolytes were selected to provide variation in pH and corrosivity. The selection of bias potentials was guided by consideration of the polarization curves of unpainted pretreated aluminum.

4.1.2.1 Experimental. An electrochemical measurement cell was formed by clamping an O-ring glass joint to a metal panel. The inside diameter of the O-ring was 1.25 in. giving a calculated working electrode area of 7.91 cm^2. Thirty milliliters of test electrolyte was placed in the cell. A high purity graphite rod served as counter electrode and a commercial reference electrode was used. A few confirmatory experiments were done using an EG&G flat cell with a 1 cm^2 working electrode area.

The commercial reference electrode used in most experiments had a very slow draining ceramic plug junction and appeared to be an SCE. However, periodic measurement of its potential versus genuine SCE's showed it to be -513 +/- 2mv versus the SCE at room temperature. Despite this peculiar fact, the reference electrode did not cause any problems. Hereafter, potentials quoted versus this electrode are designated versus (REF) or versus user electrode.

Impedance spectra were measured under potentiostatic control using an EG&G Model 273A potentiostat and a Schlumberger Model 1255 frequency response analyzer. An IBM PS/2 Model 70 386 computer controlled the experiment using EG&G software.

Typical measurement parameters used for electrocoated samples are as follows:

Single Sine Technique
Room temperature
10 mV amplitude
5 points/decade
10^5 H_z to 0.01 H_z
Cell open to air

Unpainted pretreated aluminum samples were measured using a 5 mV amplitude. Linear polarization scans of unpainted pretreated aluminum were controlled with an EG&G software package.

Three electrolytic test solutions were used:

1) 3.5% NaCl
2) 0.1M sodium borate adjusted to pH = 7 with boric acid
3) 1% sodium carbonate, 0.2% sodium silicate

The NaCl electrolyte is often used in studies of painted surfaces. The borate electrolyte was adopted from a literature report [42]. The use of the carbonate/silicate electrolyte for EIS is believed to be original to this work. Boukamp's computer program was used to fit equivalent circuit models to the data [43].

4.1.2.2 Long Term Immersion. As a first step in the program, various electropainted panels were assembled as EIS cells and committed to 3.5% NaCl electrolyte. The EIS of the immersed panels was measured every week or two for six months. All of the panels showed capacitive behavior which did not change with immersion time. The electropaint was behaving as an ideal barrier coating.

Meanwhile, methods to accelerate coating degradation were being studied. That work led to the discovery that some electropainted specimens exhibiting capacitive behavior can be made to show multiple time constant behavior by an "activation" procedure. The "activation" procedure will be discussed further in the next section.

Table 15 is a summary of observations made on the long term specimens after nine months immersion. Without activation all the specimens were capacitive at nine months. Only the 2024 chromated sample showed a large effect from activation. It is suspected that this exceptional result may be due to faulty preparation technique. In any event, the results of Table 15 as a whole strongly suggest that electropainted aluminum can withstand long immersion in 3.5% NaCl without degradation or under film corrosion. It is noteworthy that even 2C1, showed no visible underfilm corrosion.

4.1.2.3 Activation. Electropainted specimens were subjected to a 10 mV amplitude sine wave from 10^5 Hz to 0.01 Hz while maintaining a negative DC bias voltage. It was thought that this procedure might cause degradation in analogy with the effect of cathodic polarization observed for certain coated systems by others [44]. Bias potentials were stepped from -1 V (REF) to -4 V (REF). The treatment invariably had no effect on the open circuit EIS measured immediately after the treatment, when freshly assembled electropainted panels were used.

In another attempt to measure accelerated degradation, the EIS measurement was linked to the SO_2/salt spray test (ASTM G-85). Several authors have used EIS in conjunction with one or another accelerated test. The work by Hirayama and Haruyama is one example [45].

Panels (3"x6") were scribed and placed in the SO_2/salt spray cabinet at 15° for various times. Visible corrosion eventually occurs in the scribe. Given enough time small blisters which

TABLE 15. Degradation/Corrosion for Electropainted Aluminum Surfaces Immersed in 3.5% NaCl at Room Temperature for Nine Months.

Sample Code	Alloy	Pretreatment	Degradation when Activated	Visible Corrosion after Chemical Stripping	Thickness (mil)
7D	7075	Deoxidized	None	None	0.76
7D7	7075	Deoxidized	Slight	None	0.68
2D9	2024	Deoxidized	None	None	0.94
2D12	2024	Deoxidized	Very Slight	None	0.92
7C6	7075	Chromated	None	None	1.34
7C8	7075	Chromated	Very Slight	None	1.01
2C1	2024	Chromated	Degraded	None	0.88

appear to contain white aluminum hydroxide corrosion product form very near the scribe. The SO_2 exposed panels used for EIS did not contain any visible degradation in the unscribed area where the EIS cell was assembled. In addition, no appreciable delamination from the scribe could be detected by scraping.

Panels removed from the SO_2/salt spray were immediately assembled as EIS cells and subjected to one of the test electrolytes. Multiple time constants were sometimes observed without activation, but activation was usually required. Activation is apparently a temporary phenomenon. When an activated electrode is left at open circuit for a few days, it generally will appear to be a capacitor when EIS is again performed. Activation can be repeated on the electrode and the same or very similar impedance spectrum is obtained.

Although the activation process is not well understood at this time, it may be useful to offer some tentative explanations. An activated electrode behaves as if the electropaint has a microporous structure through which electrolyte can penetrate to the surface at the base of the pores. At equilibrium the conductivity of the bulk test solution is much greater than the conductivity within the pores. If the pores do not provide a sufficiently conductive pathway capacitive behavior is expected.

During the activation process pore conductivity increases through electromigration and/or other processes. If the conductivity is sufficiently high, multiple time constants can be observed. The deactivation process is slow enough to allow the recording of steady state impedance spectra.

4.1.2.4 Pretreatments. A knowledge of the EIS and DC polarization behavior of unpainted pretreated aluminum should prove helpful in understanding the painted systems. Tables 16 and 17, and Figures 5 and 6 give EIS results for hot water sealed anodized aluminum 2024 in borate electrolyte. Some relevant electrochemical data on the test electrolyte (including borate) are included for reference in Table 18.

Impedance spectra of anodized aluminum in borate were measured as a function of potential in the range -500 mV (REF) to +700 mV (REF). The two time constant equivalent circuit model shown in Figure 7 was fit to the data. The basic physical explanation for the two time constant behavior is to assign the high frequency time constant to a relatively thick outer porous layer, while the low frequency time constant is assigned to the thin inner barrier layer [46].

The fit is shown in Figure 5. A nearly perfect looking fit was obtained by using three or even four parallel RC elements in series, but this greatly inflated the relative per cent error values. Perhaps the legitimacy of using a more complex model than shown in Figure 7 can be determined with the measurement model approach [47].

The important point to be made here using the two time constant model is that all the circuit element values except one remain constant as the bias potential is changed. The one variable element is the barrier layer resistance which increases by about an order of magnitude from -500 mV to -200 mV (REF) and fluctuates somewhat thereafter. This behavior is qualitatively consistent with the DC polarization curves in Figures 7A and 7B which show a sharp increase in cathodic faradaic current beginning at potentials somewhat negative of the reversible hydrogen potential. The constant porous layer resistance is thus apparently ohmic in character, while the variable barrier layer resistance must be attributable at least in part to a charge transfer process.

As shown in Table 17, the capacitance associated with the barrier resistance has a value of 7.9 x 10^{-7} F/cm^2. (The units "mho" are artifacts of the computer program and can be ignored).

```
Sample: 2024 SAA HWS/BORATE
Date: 052295
Temp (C): M388       2.71
Ambient:  -500
Electrode:  7.5440E+00

Freq. range:  1.000E-03 -  1.000E+05 Herz
Data set   :    40 frequencies

CircuitCode: R(QR)(QR)

Chi-Squared:  2.33E-03

Resistance    - 1=  1.014E+02      11.79 %   [ohm]
C-P Elmnt, Yo- 2=  7.826E-07       1.64 % ["mho"]
Freq power, n- 2=  0.9537          0.82 %
Resistance    - 3=  6.454E+06      2.00 %   [ohm]
C-P Elmnt, Yo- 4=  4.457E-08       6.66 % ["mho"]
Freq power, n- 4=  0.8491          0.76 %
Resistance    - 5=  6.521E+04      2.21 %   [ohm]
```

```
Correlation factors of NLLS-fit parameters:

Par.-#    R- 1   Q- 2   n- 2   R- 3   Q- 4   n- 4   R- 5
R- 1:     1.00
Q- 2:    -0.01   1.00
n- 2:    -0.07  -0.30   1.00
R- 3:    -0.02  -0.12   0.32   1.00
Q- 4:    -0.46   0.02   0.14   0.04   1.00
n- 4:     0.50  -0.01  -0.16  -0.05  -0.98   1.00
R- 5:     0.17   0.02  -0.42  -0.13  -0.38   0.38   1.00
```

Table 16. Sample computer output Fit of equivalent circuit model to EIS data for Anodized Al 2024 in Borate electrolyte at -500 mv (REF).

-500 mv (REF)

Resistance	- 1= 1.018E+02	11.13 %	[ohm]
C-P Elmnt	Yo -2= 7.859E-07	1.59%	[“mho”]
Freq power	n -2= 0.9475	0.85%	
Resistance	-3= 6.904E+06	3.97%	[ohm
C-P Elmnt	Yo -4= 4.407E-08	6.35%	[“mho”]
Freq power	n -4= 0.8502	0.73%	
Resistance	-5= 6.485E+04	2.13%	[ohm]

-350 mv (REF)

Resistance	-1= 1.018E+02	10.85%	[ohm]
C-P Elmnt	Yo -2= 7.950E-07	1.39%	[“mho”]
Freq power	n -2= 0.9426	0.76%	
Resistance	-3= 1.684E+07	6.97%	[ohm]
C-P Elmnt	Yo -4= 4.386E-08	6.16%	[“mho”]
Freq power	n -4= 0.8505	0.71%	
Resistance	- 5= 6.532E+04	2.05%	[ohm]

Table 17. Fit of two time constant models to EIS data for Anodized Al 2024 in Borate as a function of potential.

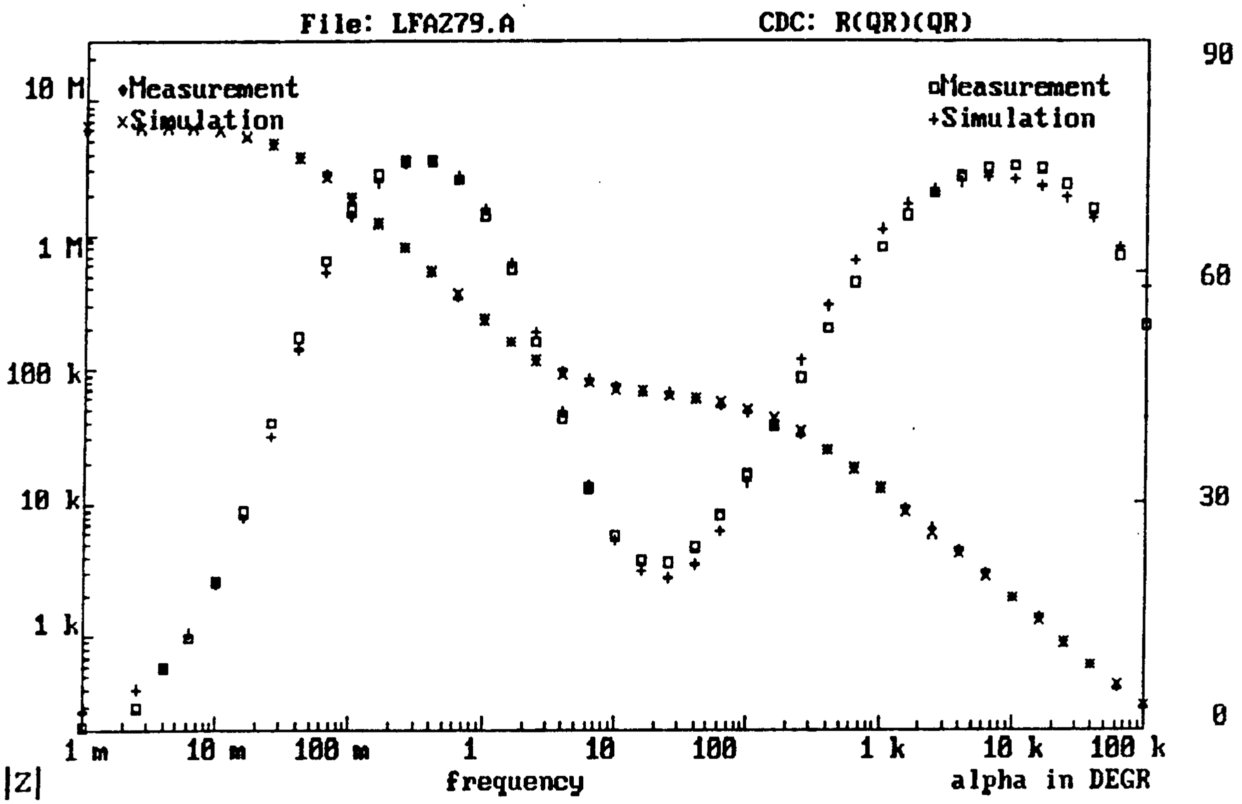


Figure 5. Graphical representation from Table 16.

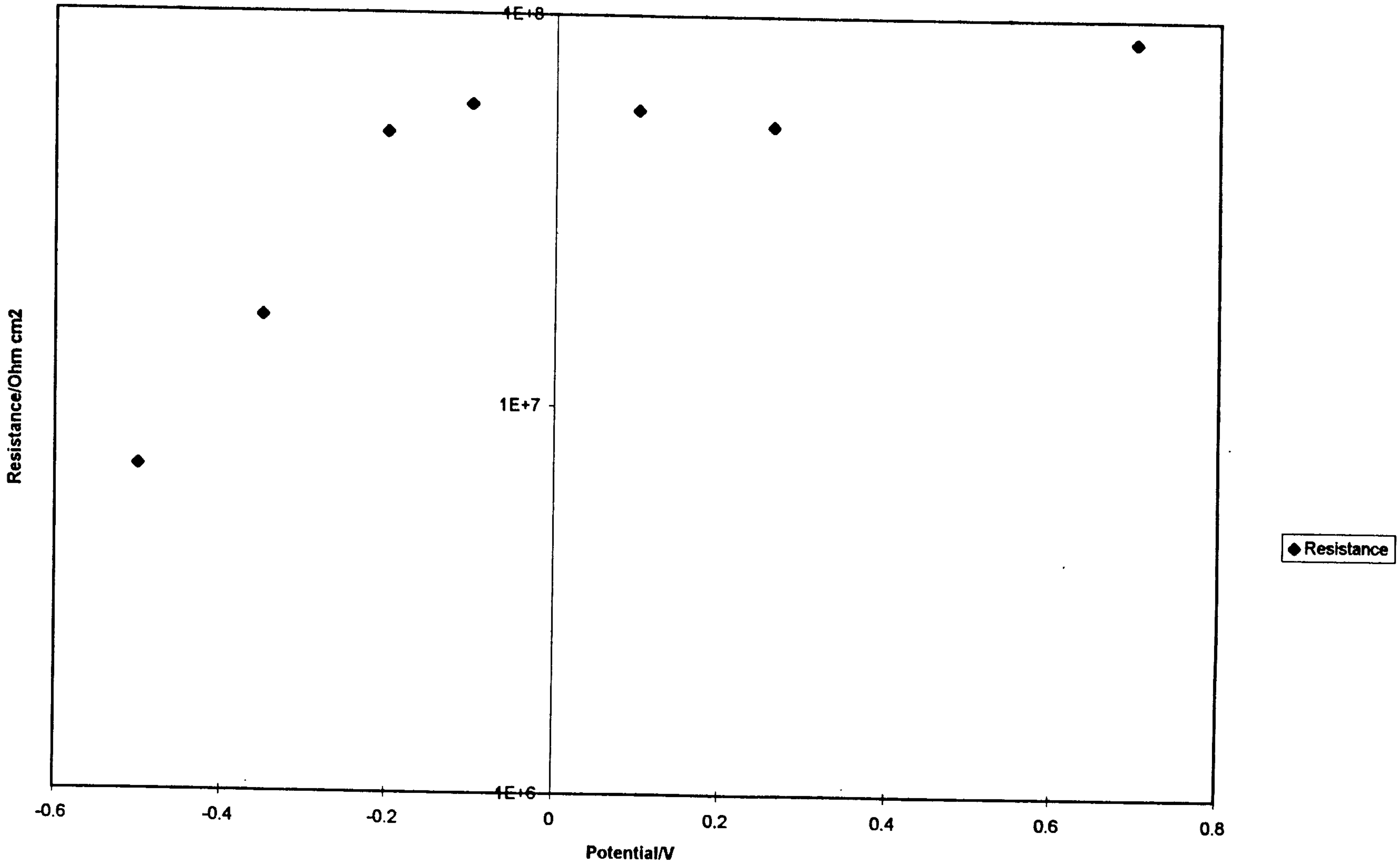


Figure 6. Variation of Barrier Layer Resistance with Potential for Anodized Al 2024 in Borate Electrolyte

TABLE 18. Calculated potentials for Reversible Hydrogen Electrode (RHE) and Reversible Oxygen Electrode (ROE) in test electrolyte at 25°.

Electrolyte Solution	pH	RHE (mv vs SCE)	ROE (mv vs SCE)
Sodium Chloride	6.5	-624	606
Sodium Borate/Boric Acid	7.0	-654	576
Sodium Carbonate/Sodium Silicate	11.5	-920	310

Using an anodization voltage of 15V and the empirical value 14 A°/V, the thickness of the barrier layer is estimated as 210 A°. Thus the dielectric constant calculated from the plate capacitor equation is 18.7, in rough agreement with the expected value of about 10.

There is an apparent problem here because a charge transfer resistance should be coupled to a surface electrolyte double layer capacitance and not to the capacitance of a solid dielectric. Likewise, a solid dielectric capacitance should be coupled to the resistance of the solid. The resistance of the solid probably wouldn't vary much with potential and it certainly could not lead to the cathodic faradaic current observed in the polarization curve.

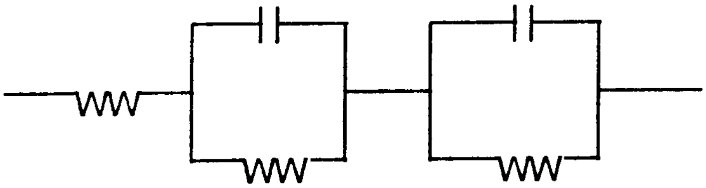


Figure 7
Equivalent Circuit Diagram

```
Model 352/252 Corrosion Analysis Software. v.   2.01
Pstat:   M273A [92, 96] Ver 200              LP LINEAR POLARIZATION
Date Run:   05-30-95                          Time Run:   09: 22: 17
Cond. Time      CT   pass           s         Initial Pot.    IP  -20.00E-3      V oc
Cond. Pot.      CP   pass           V         Final Pot.      FP  -0.6000        V
Initial Delay   ID   pass           s         Scan Rate       SR   1.000         mV/s
Curr. Range     CR   Auto                     Scan Incr.      SI   1.000         mV
Step Time       ST   1.000          s         No. of Points   NP   402
GI Time Const.  TC   Off                      Line Sync.      LS   no
IR Mode         IR   none                     Rise Time       RT   high stability
Filter          FL   Off                      Working Elec.   WE   Solid
Ref. Elec.      RE   User  0.0000   V         Sample Area     AR   7.910         cm^2
Equiv. Wt.      EW   27.00          g         Density         DE   2.700         g/ml
Open Circuit    OC  -0.1790         V
```

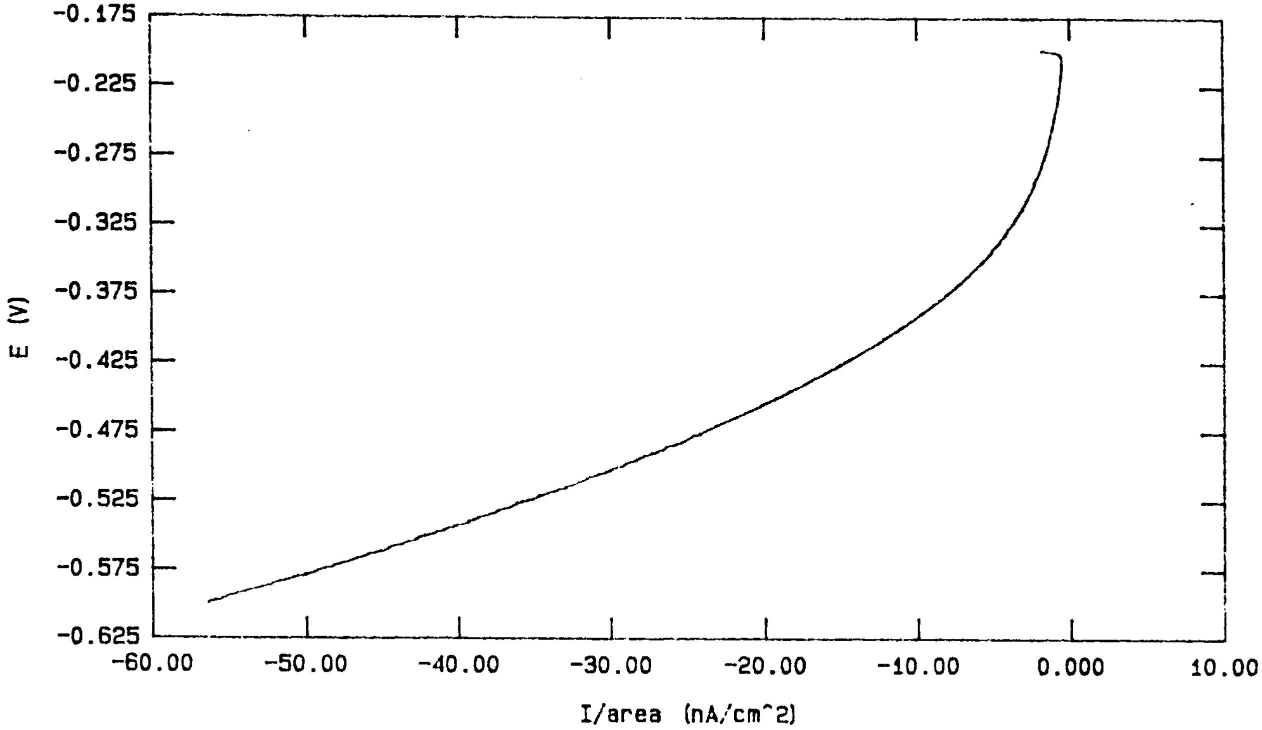


Figure 7A. Initial Cathodic Polarization curve of Hot Water Sealed Sulfuric Acid Anodized Al 2024-T3. (Borate test electrolyte)

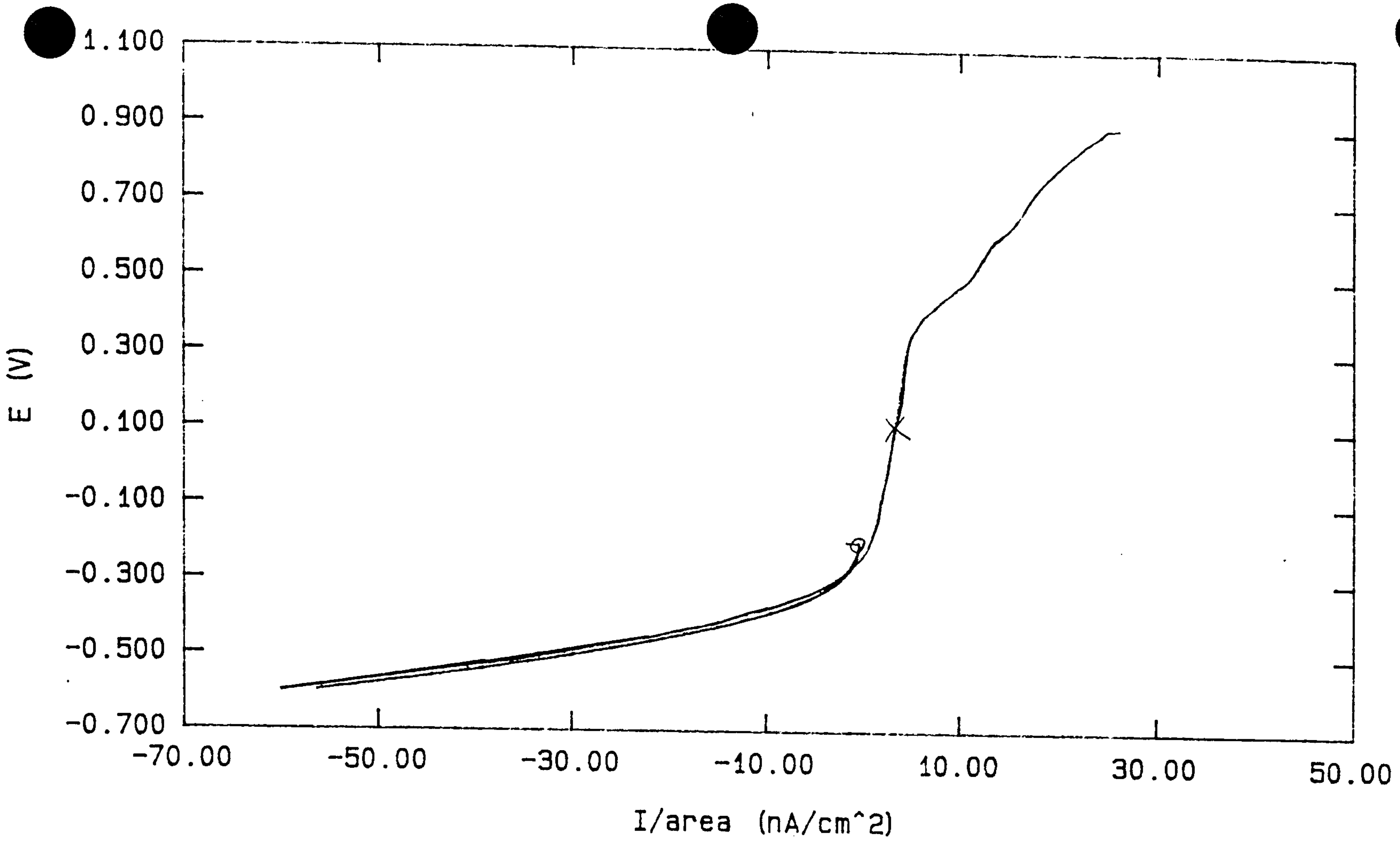
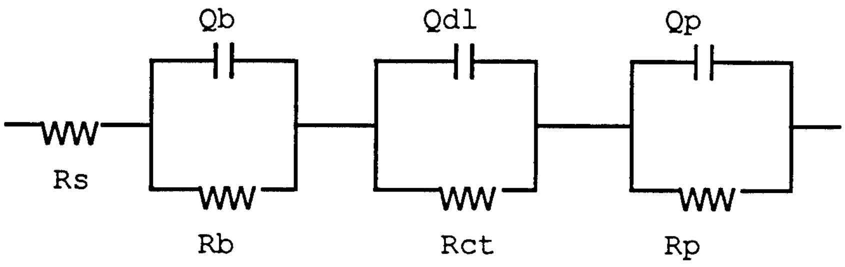


Figure 7B. Overlay of Initial Cathodic Polarization curve and complete Polarization curve of Hot Water Sealed Sulfuric Acid Anodized Al 2024-T3. (Borate test electrolyte)

Legend: X = Initial Cathodic
O = Complete

The problem is resolved for the more cathodic potentials when one realizes the "true" model is as follows:



Rs = solution resistance

Qb = barrier capacitance

Rb = barrier resistance

Qdl = double layer capacitance

Rct = charge transfer resistance

Qp = porous layer capacitance

Rp = porous layer resistance

A simulation of this three time constant model was run assuming a reasonable value for Qdl of 2×10^{-5} F/cm^2. The charge transfer resistance of 6.9×10^{6} ohm cm^2 from Table 17 was coupled with Qdl. The barrier capacitance of 7.9×10^{-7} F/cm^2 from Table 17 was coupled with a parameterized Rb. At Rb equal to 3×10^{7} ohm cm^2 the simulation shown in Figure 7C looks like a two time constant plot and a fit of the simulated data to the two time constant model produces values very close to those shown for real data in Table 17. Qb is now coupled with Rct for cathodic potentials. More work is required to explain the complete range of potentials and that anodic processes need to be considered.

Figures 8, 9, 10 and11 show polarization curves of anodized aluminum 2024 in carbonate/silicate test electrolyte and compare them to polarization curves obtained in borate. Higher anodic currents are evident in the case of carbonate/silicate. There is not much difference evident in the cathodic current for the two electrolytes when comparison is made at the same potential (Figure 10). However, the open circuit potential and the reversible hydrogen electrode (RHE) vary for the two electrolytes. If cathodic currents are compared at equal overvoltages with respect to the RHE, one sees that greater currents are obtained in the carbonate/silicate electrolyte.

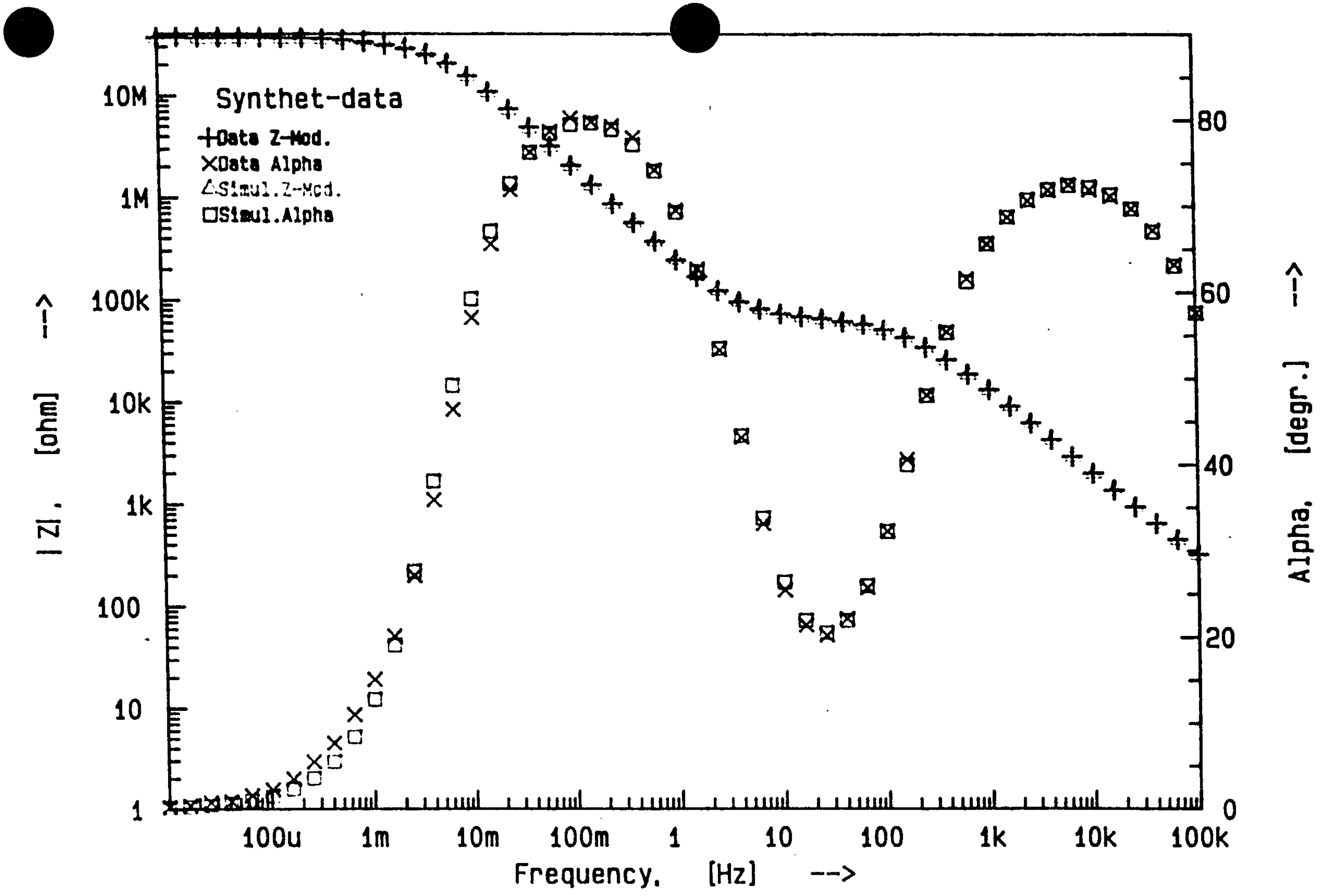


Figure 7C. Fit of 3 time constant simulated data to 2 time constant model (anodized AL 2024 in Borate)

```
Model 352/252 Corrosion Analysis Software, v.   2.01
Pstat:   M273A [92, 96]  Ver 200                 LP LINEAR POLARIZATION
Date Run:   06-01-95                             Time Run:   12: 34: 42
Cond. Time       CT   120            s           Initial Pot.    IP   -0.9000       V
Cond. Pot.       CP   -0.9000        V           Final Pot.      FP   0.6000        V
Initial Delay    ID   pass           s           Scan Rate       SR   1.000         mV/s
Curr. Range      CR   Auto                       Scan Incr.      SI   1.000         mV
Step Time        ST   1.000          s           No. of Points   NP   1501
6I Time Const.   TC   Off                        Line Sync.      LS   no
IR Mode          IR   none                       Rise Time       RT   high stability
Filter           FL   Off                        Working Elec.   WE   Solid
Ref. Elec.       RE   User  0.0000   V           Sample Area     AR   7.910         cm^2
Equiv. Wt.       EW   27.00          g           Density         DE   2.700         g/ml
Open Circuit     OC   -0.7190        V
```

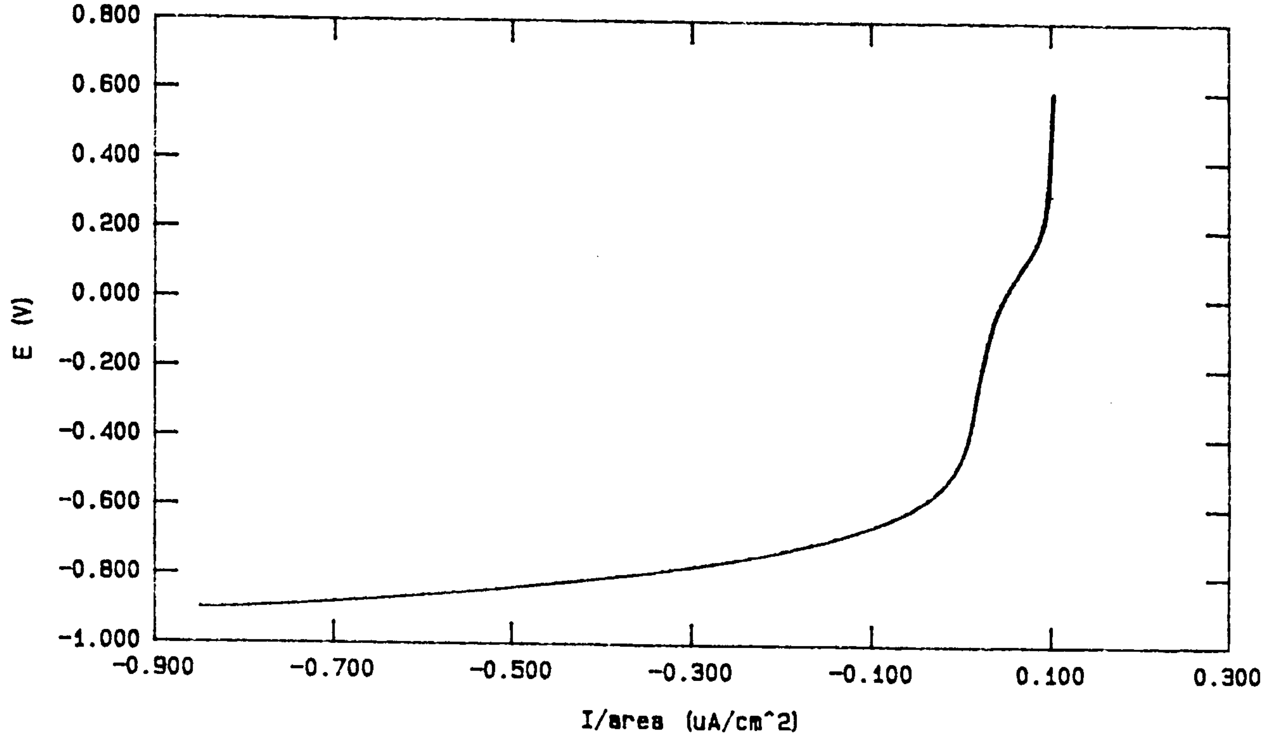


Figure 8. Complete Polarization curve of Anodized Al 2024-T3 in Carbonate /Silicate test electrolyte.

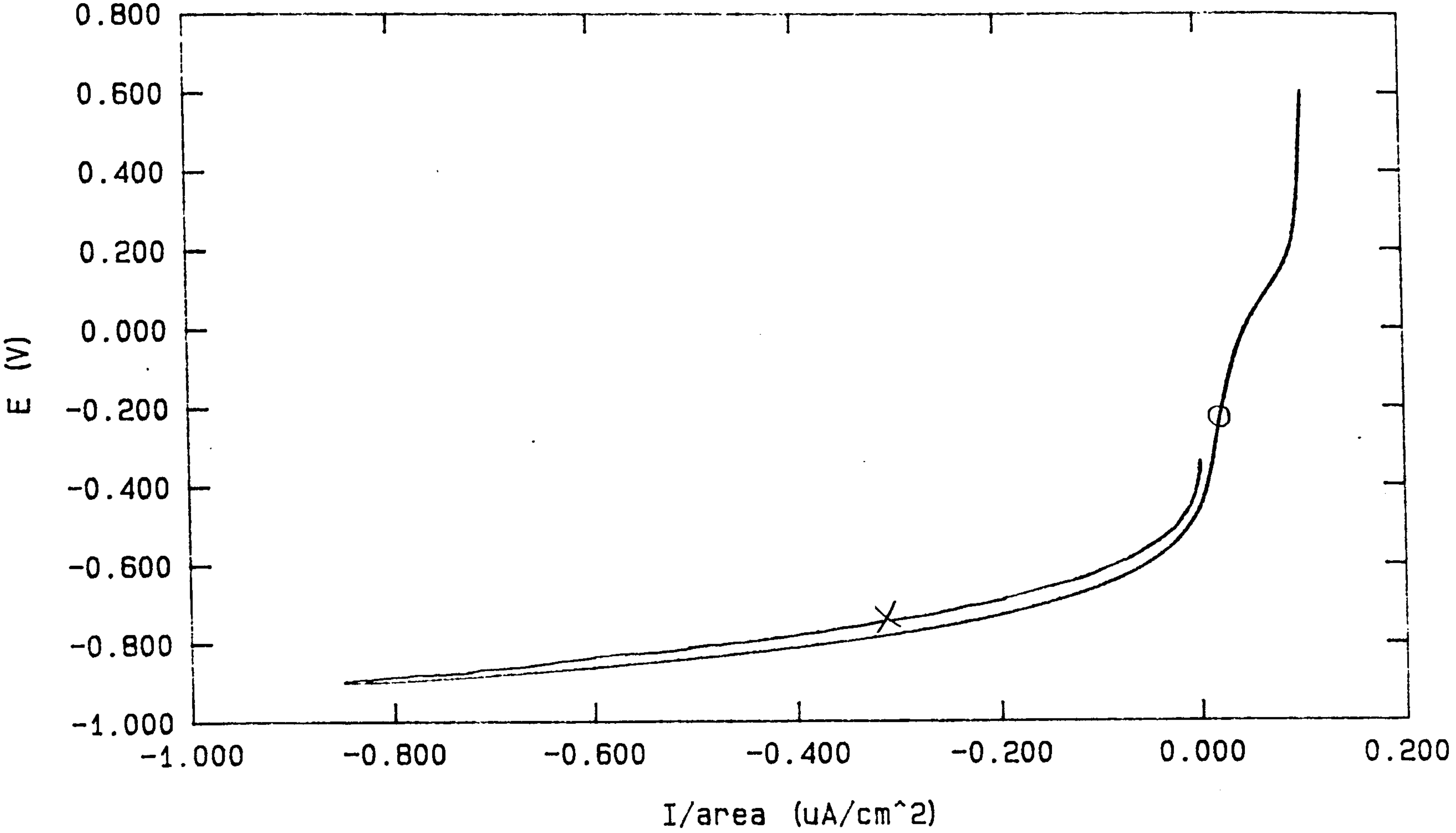


Figure 9. Overlay of Initial Cathodic and complete Polarization curves of Anodized Al 2024-T3 in Carbonate/Silicate electrolyte.

Legend: X= Initial Cathodic
O= Complete

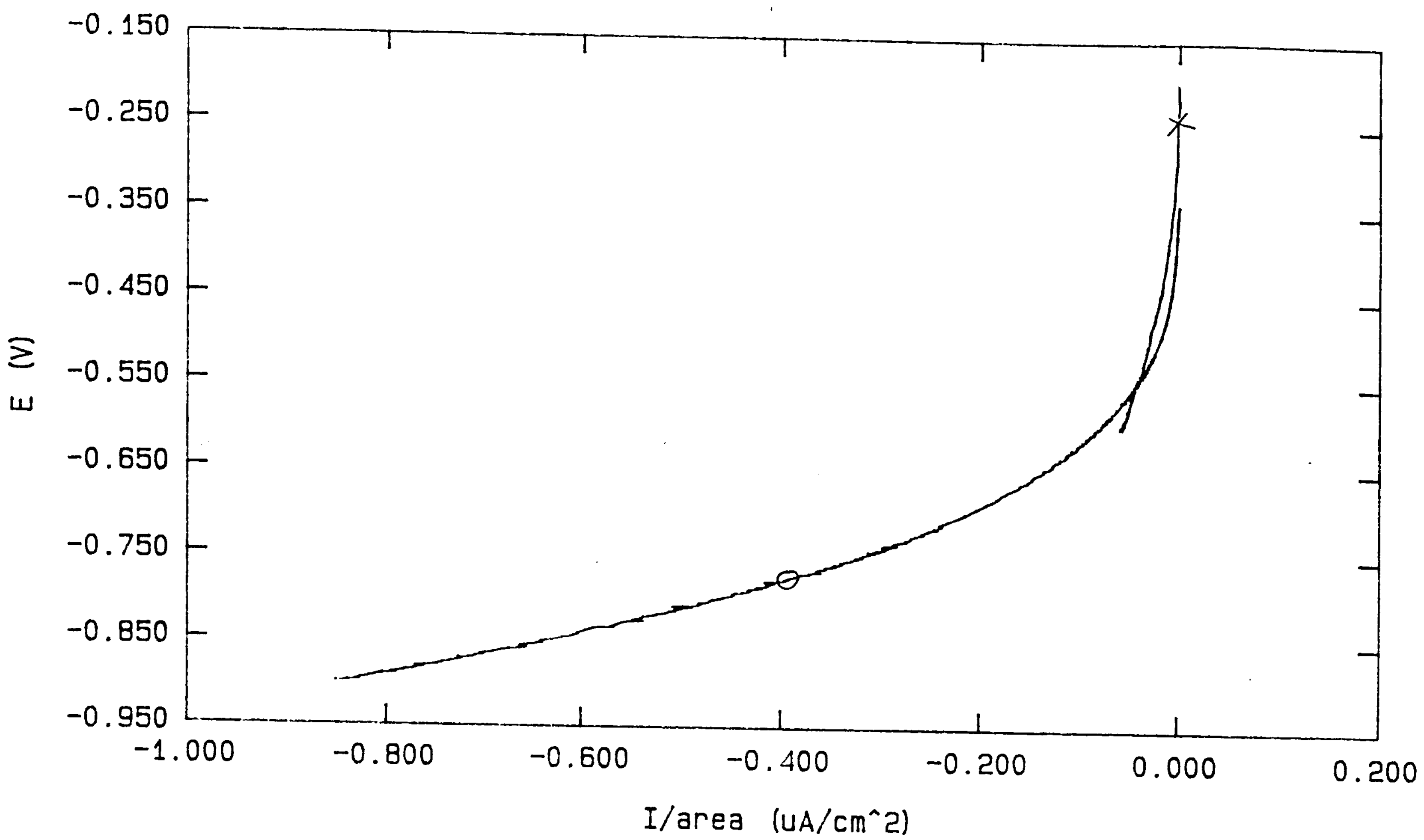


Figure 10. Overlay of Initial Cathodic Polarization curves of Anodized Al 2024-T3 in Borate and Carbonate/Silicate electrolyte.

Legend: X= Borate
O= Carbonate/Silicate

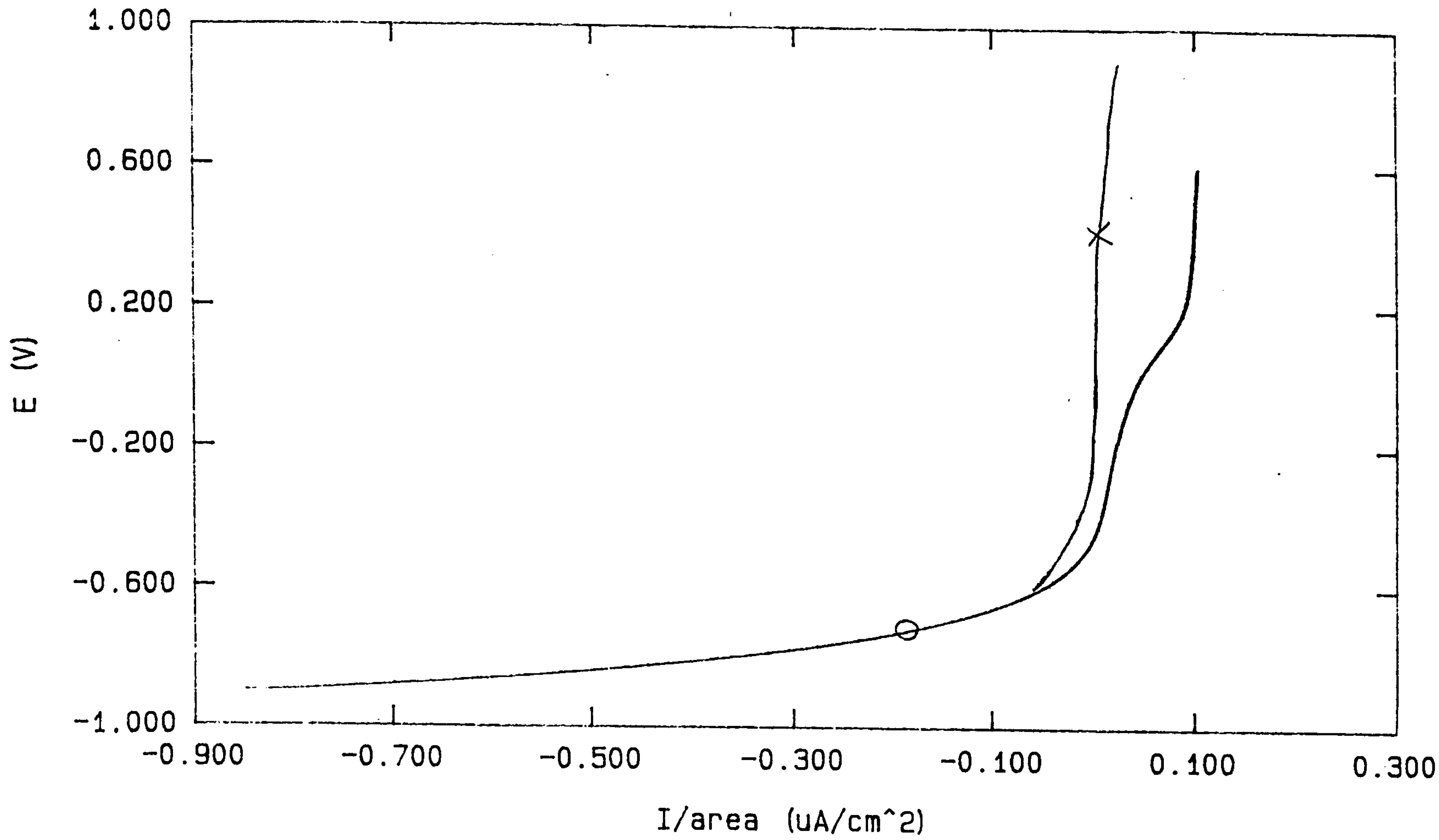


Figure 11. Overlay of complete Polarization curves of Anodized Al 2024-T3 in Borate and Carbonate/Silicate test electrolyte.

Legend: X= Borate
O= Carbonate/Silicate

Figures 12 and 13 show polarization curves of chromate conversion coated aluminum 2024 in borate electrolyte and a comparison with anodized aluminum 2024 in that same electrolyte. It is clear that the chromated electrode is less polarizable in both the cathodic and anodic sense than the anodized electrode. However, the chromated electrodes' behavior in borate is not very much different from the behavior of the anodized electrode in carbonate/silicate. In sum, Figures 7A-13 indicate passive type behavior, very low corrosion rates, and a cathodic charge transfer process. The cathodic process may be partly or even entirely hydrogen evolution. In fact, in the case of the chromated aluminum, gas bubbles are visible on the electrode at potentials where the net current is cathodic.

EIS measurements were performed on chromated aluminum 2024 in borate electrolyte as a function of potential from -500 mV to +300 mV (REF). The data were fit to the two time constant model shown in Figure 7 just as had been done for anodized aluminum. In the chromated case, however, the high frequency time constant is associated with a shoulder in the spectrum rather than the fairly well resolved feature seen in the anodized spectrum.

The resistance of the low frequency time constant is plotted as a function of potential in Figure 14. The values increase monotonically from 1.8 x 10^5 ohm cm^2 at 0.5 v (REF) to greater than 1 x 10^6 ohm cm^2 at 0 v, and fluctuate a bit after that. This should be compared to the behavior of the "barrier layer" resistance of anodized aluminum given in Figure 6. Both surfaces exhibit a sharp monotonic decrease in resistance over the same potential range, but the value of the resistance is roughly an order of magnitude less for conversion coated compared to anodized aluminum 2024.

The other circuit element values for the chromated case are probably independent of potential, just as observed for anodized. However, there is more scatter in the chromate data and this inference is less certain than in the anodized case.

The value for the capacitance coupled to the variable resistance for chromated aluminum 2024 is about 4 x 10^{-6} F/cm2. This is about an order of magnitude too low for a double layer capacitance and about an order of magnitude larger than found for the anodized barrier layer capacitance. More work would be needed to give a physical interpretation.

4.1.2.5 Electrodeposited Coatings. The most common equivalent circuit models for painted metal surfaces are given in Figures 15 and 16. The nested parallel capacitor/resistor or capacitor/resistor/Warburg networks usually are assigned to interfacial processes. The outer capacitor/resistor combination is related to properties of the paint. These models were not satisfactory for the systems studied here and the three time constant model shown in Figure 17 was often used.

It was usually possible to find an excellent fit to data from the visibly undamaged electrocoated pretreated aluminum samples which had been degraded in SO_2 salt spray and subsequently activated. Although a purely mathematical characterization of the electrocoated systems may be useful, it would be even more desirable to assign physical processes to the circuit elements. As a result of this work some but not all of the circuit elements can be given a physical meaning.

As a case in point, computer printouts and associated Bode plots of data and fits are discussed. All the results shown refer to an electrocoated conversion coated aluminum 2024 specimen which was scribed and exposed to SO_2 salt spray for 20 days. After 10 days immersion in borate electrolyte the electrode was activated and spectra were recorded at several bias voltages. The order of presentation of data is the same as the order of experimentation. An attempt was made to model the data from each experiment with two different equivalent circuits. The two

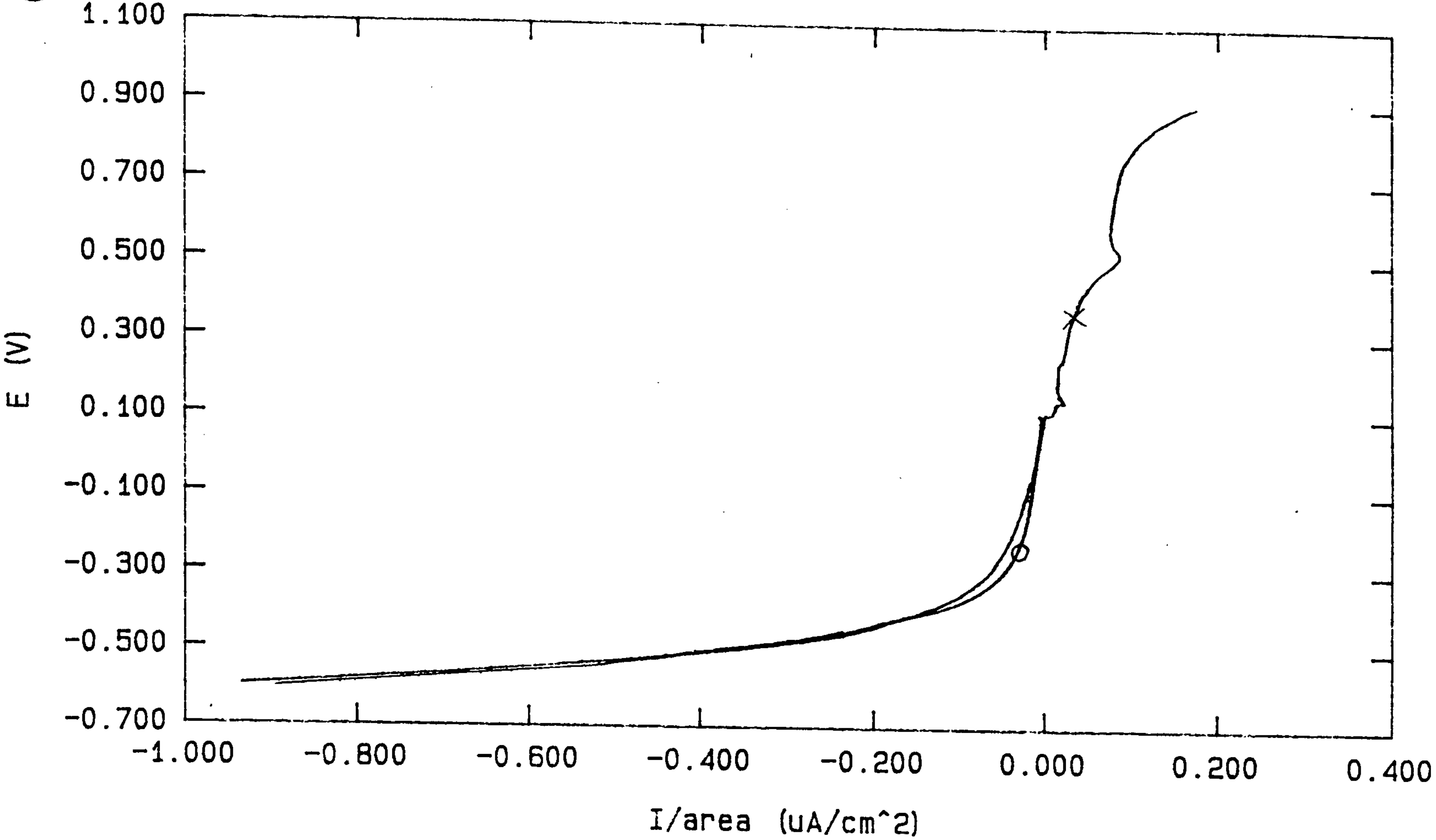


Figure 12. Overlay of Initial and Complete Polarization curves of Chromate Conversion Coated Al 2024-T3. (Borate test electrolyte).

Legend: X= Complete
O= Initial

Approved for public release; distribution is unlimited

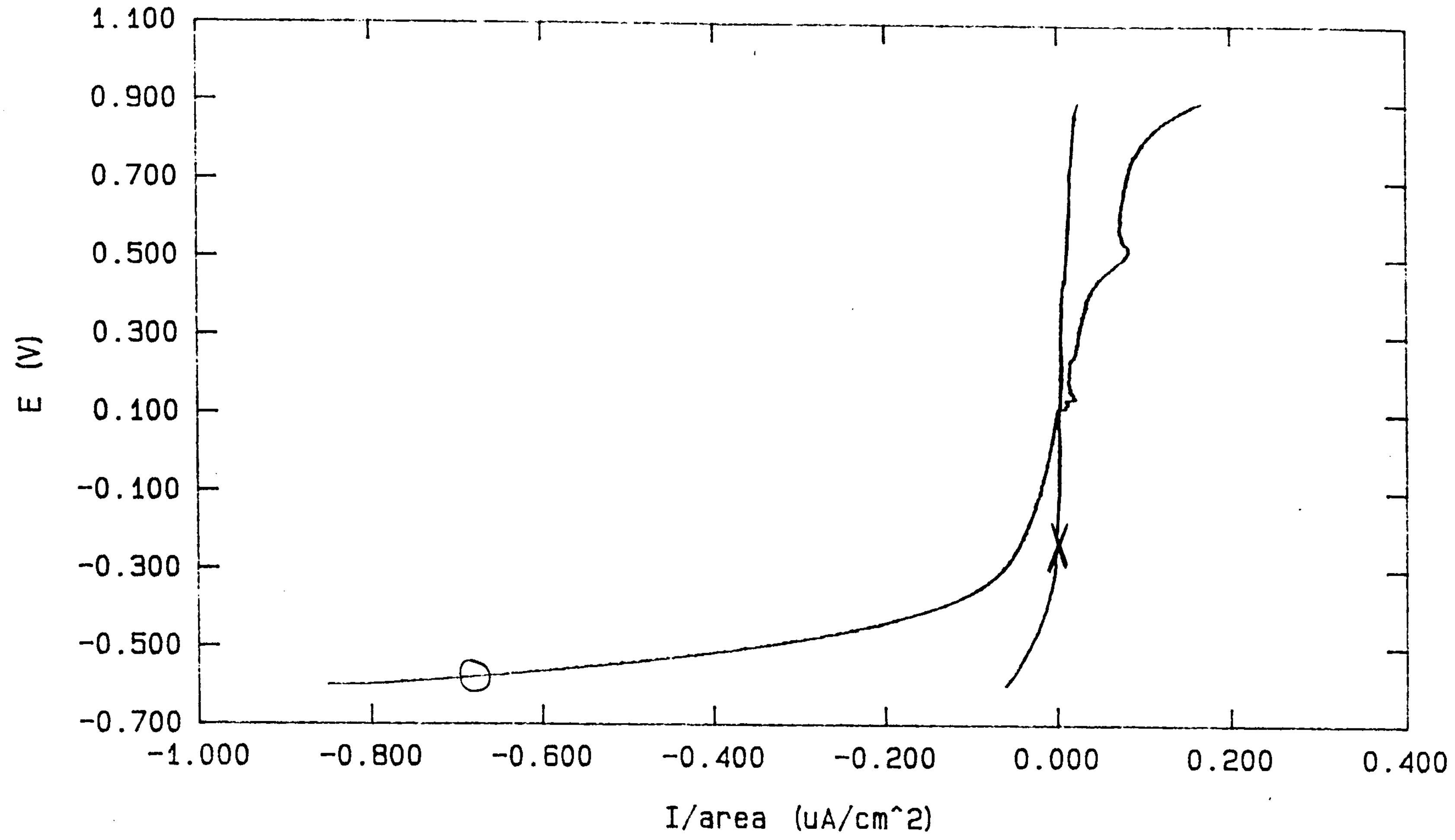


Figure 13. Comparison of complete Polarization curves of Chromate Conversion Coated and Sulfuric Acid Anodized Al 2024-T3. (Borate test electrolyte).

Legend: X= Anodized
O= Chromate Conversion Coated

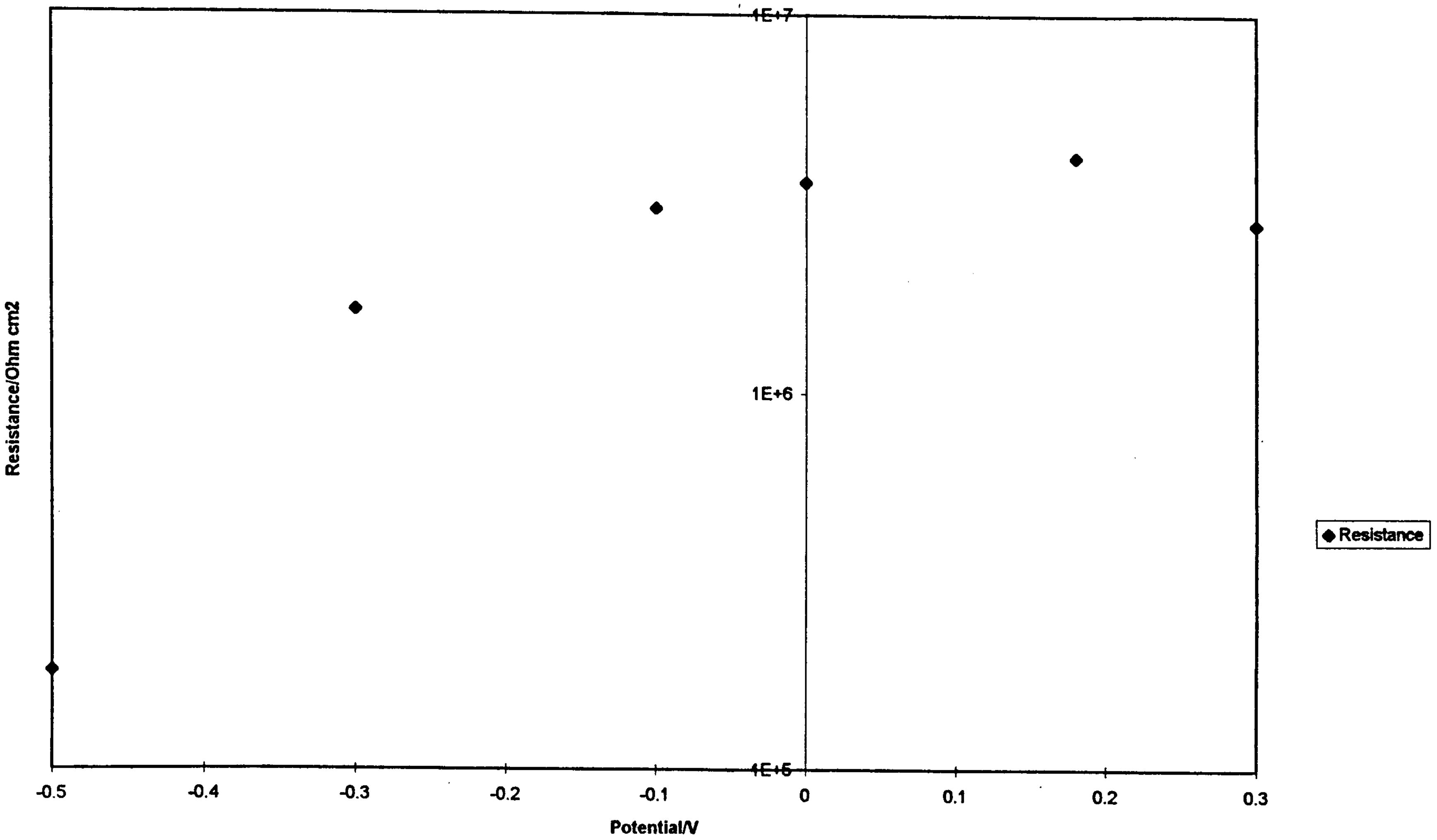


Figure 14. Variation of Resistance with Potential for Chromated Al 2024 in Borate Electrolyte

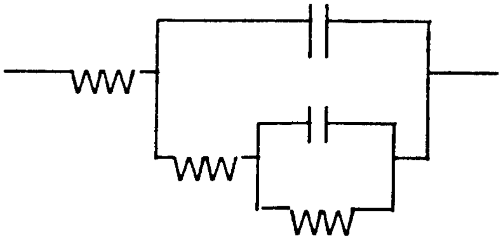


Figure 15
Equivalent Circuit Diagram

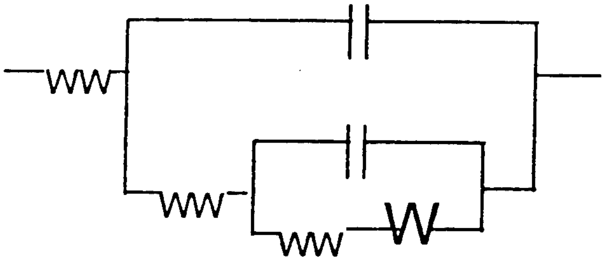


Figure 16
Equivalent Circuit Diagram

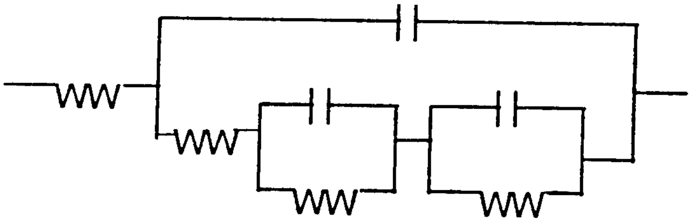


Figure 17
Equivalent Circuit Diagram

time constant model in Figure 15 was used to test data from 1Hz to 10^5 Hz and the three time constant model in Figure 17 was used for the complete data sets.

Tables 19 to 21 and Figures 18 to 20, shown in Appendix D, represent three successive scans at -700 mV (REF). The middle scan was extended to 1 x 10^{-3} Hz as is shown more clearly in Table 22 and Figure 21, shown in Appendix D. The very close agreement of all the circuit values for the successive scans demonstrates that a steady state has been achieved. This is a fundamental requirement for meaningful impedance spectra.

Tables 23 to 25 and Figures 22 to 24, shown in Appendix D, represent three successive scans at -500 mV (REF), the middle scan again having been extended to 1 x 10^{-3} Hz. A big difference is noted in the nested resistance which is about 2 x 10^8 ohm cm^2 for -500 mV and 2 x 10^7 ohm cm^2 for -700 mV. It is tempting to attribute this change to a small area fraction of conversion coated aluminum exposed to electrolyte at the base of pores extending through the paint. However, data for direct comparison at -700 mV is lacking. Also there seems to be a significant change in the value of the associated capacitance, while for unpainted conversion coated aluminum this was not observed (at least in the potential range investigated).

The result for -1000 mV shown in Table 26 and Figure 25, in Appendix D, allows some speculation about the dilemma just raised. Note that the resistance goes down somewhat compared to -700 mV, but the capacitance becomes smaller. Remember the order of measurement was -700 mV, -500 mV, and -1000 mV. One speculates that the changes seen at -1000 mV could be due to loss of active pore area due to hydrogen evolution.

One fairly well understood feature of the data is the constancy of the outer capacitance and resistance. These are assigned to coating capacitance and resistance in analogy with the traditional models of painted metal surfaces. However, these values are retained over many cycles with time and do not vary with immersion time in the manner reported in many studies of other materials. Tables 27 to 31 and Figures 26 to 30, shown in Appendix D, illustrate that a three time constant model does a good job of explaining the data over the full frequency range. Two of the time constants show values which match very well with the two time constant potential fit. The third time constant is definitely necessary to the fit, but unfortunately it is not well resolved enough to assess its dependence on electrode potential.

4.2 UV Curable Coatings.

4.2.1 Supplier Summary. Twenty as-received UV curable coatings were applied to various test panel substrates and screen tested. The UV curable coating/substrate variables that were subjected to screen tests at HAC are summarized in Table 32. For comparative evaluation, the Z14L proprietary pigment formulation was added to eight of the most promising of these coatings and tested on the various substrates described in Table 4. In addition, several variables of a pigmented UV curable powder coating, applied to test panels by Herberts Powder Coatings, Inc., and coated panels prepared by NSWC, were submitted.

4.2.1.1 Sokol Enterprises. Sokol Enterprises has been developing a line of 100% solids coatings which is being targeted for the automotive industry [48]. The very low viscosity of this material makes it particularly unique among the coatings evaluated in this study. Sokol is not experienced in formulating pigmented paints that conform to Military specifications. Consequently, HAC worked closely with Sokol to provide formulation guidance for their submissions.

The candidate coatings from Sokol were submitted to HAC on a progressive basis. Initial submissions were screen tested on conversion-coated aluminum and the results were provided

Table 32. Summary of UV Curable Coating/Substrate Variables

MANUFACTURER	MATERIAL DESIGNATION	RESIN TYPE	PIGMENT TYPE	SUBSTRATE TESTED *	COMMENTS
CASCHEM	NONE	URETHANE/ ACRYLATE	NONE	ALUMINUM, CONVERSION COATED	Modified conformal coating
DYMAX	986	URETHANE/ ACRYLATE	NONE	ALUMINUM, CONVERSION COATED	
DYMAX	984 TC	URETHANE/ ACRYLATE	Z14L	ALL IN TABLE 4	Modified conformal coating
HERBERTS POWDER COATINGS	VARIOUS	EPOXY OR ACRYLIC	Z14L	1.ALUMINUM, BARE 2.ALUMINUM, CONVER-SION COATED 3. ZN-PH STEEL	Powder coating
HERBERTS POWDER COATINGS	EXPERIMENTAL	EPOXY OR ACRYLIC	TiO2	ALUMINUM, CONVERSION COATED	Powder coating
MICRO-LITE	3010M	URETHANE/ ACRYLATE	NONE	ALUMINUM, CONVERSION COATED	
MILES	3919	POLYESTER/ ACRYLATE	NONE	ALUMINUM, CONVERSION COATED	Contains water
NSWC	NONE	EPOXY	Z14L	1. ALUMINUM CONVERSION COATED 2. ZN-PH STEEL 3. GRIT BLASTED STEEL 4. TIGHT RUSTED STEEL	
NSWC	NONE	POLYURETHANE	TiO2	ALUMINUM, CONVERSION COATED	
SOKOL	1189	URETHANE/ ACRYLATE	NONE	ALUMINUM, CONVERSION COATED	
SOKOL	908-15	URETHANE/ ACRYLATE	NONE	ALUMINUM, CONVERSION COATED	
SOKOL	15XX SERIES (6 Variables)	URETHANE/ ACRYLATE	Z14L	ALL IN TABLE 4	Experimental formulations
3M	DUAL CURE	URETHANE/ ACRYLATE	TiO2	ALUMINUM, CONVERSION COATED	Developed under DOE contract
3M	631	POLYESTER/ ACRYLATE	Z14L	ALL IN TABLE 4	Three component

* See Table 4 for substrate and surface treatment specifications

to Sokol. The most promising coating, Sokol 1516, was then formulated into five additional compositions, 1510-1515. These compositions, including the 1516, were each pigmented with the Z14L proprietary pigment formulation to a level of 10% pigment volume concentration (PVC), and applied to each of the six substrates being tested. In addition, Sokol 1516 was also pigmented with 27.6% PVC of the Z14L pigment and applied to conversion coated aluminum.

The comparative results of the unpigmented vs. pigmented Sokol 1500 series coatings on conversion coated aluminum are presented in Table 32. The adhesion of both the clear and 10% PVC pigmented compositions was good. The conical mandrel flexibility remained good for all except the 1514 and 27.6% PVC pigmented compositions, although the impact flexibility decreased significantly when pigment was added. Solvent resistance was also adversely affected by the addition of the pigment, even at the low 10% PVC level.

The six compositions that were pigmented with 10% Z14L were also applied to five other substrates, and these results are presented in Tables 33 through 37. On the steel substrates, primed surfaces generally resulted in better performance of the pigmented UV topcoats than unprimed surfaces. Of the tests conducted, the results on bare and primed aluminum surfaces were not significantly different, with the exception of gloss, which was better on bare aluminum. Solvent resistance on all substrates was poor.

Based upon the results of these evaluations, Sokol was supplied with a small amount of the Z14L pigment, and conducted additional research to improve their formulation. It is noteworthy that when Sokol received the Z14L pigment, they found that an inherent incompatibility existed between pigment components and certain components of the coating formulation. Therefore, Sokol began developing a new formulation that would be compatible with the Z14L pigment. They performed extensive in-house testing using substrate panels supplied by HAC. Reportedly, improvements in flexibility, solvent resistance, heat resistance, and fluid resistance were achieved. Evaluation of the improved formulation was not able to be conducted by HAC because of the imminent end of this phase of the ZDOC project.

4.2.1.2 Dymax Corporation. Dymax submitted two UV curable coatings for evaluation. One of these, Dymax 984 TC, was previously an experimental coating designated as X256-16-1 in early quarterly reports. Its formulation is based on UV curable conformal coating technology for electronic circuit boards, and is now a commercial product. This is a urethane/acrylic copolymer that cures in UV light and in shadows with a secondary cure mechanism using atmospheric moisture. This material was pigmented with 25% PVC of the Z14L pigment, applied to each of the six test substrates (see Table 4) and subjected to screen tests.

The comparative results of the unpigmented vs. pigmented coating on conversion coated aluminum are presented in Table 38. When the unpigmented coating was applied at a thickness of 0.5 mil, the coating exhibited good impact flexibility and the remaining screening test results were good. When applied at a thickness of 1.0 mil, the impact flexibility was significantly reduced; addition of 25% PVC Z14L pigment resulted in a further decrease in impact flexibility. The solvent resistance and conical mandrel flexibility of the pigmented coating remained good.

The test results of the 25% PVC pigmented coating on the remaining five substrates are presented in Tables 33 through 37. The adhesion and solvent resistance was generally good. Although the conical mandrel flexibility was somewhat better on primed surfaces, the impact flexibility on all test substrates was poor.

Table 33. Screen Test Results of UV Curable Coatings on Zn-Ph Steel

TEST	MEK RESISTANCE	PENCIL HARDNESS	DRY ADHESION	WET ADHESION	IMPACT, FORWARD, IN-LBS	IMPACT, REVERSE, IN-LBS	CONICAL MANDREL	GLOSS
TEST DESCRIPTION	50 Wipes	ASTM D3363	3M 250 Tape	24 hour immersion	ASTM D2794	ASTM D2794	1/4"conical mandrel bend	FED-STD-141,Method 6101.1
REQUIREMENT	No removal of coating	None	No delamination	No delamination	40% elongation	40% elongation	No cracking	> 90
SOKOL 1510, Z14L:10% pvc	Gloss Loss-5 rubs; Thk Loss-40 rubs	9H	PASS	PASS	10	<2	FAIL	67.3
SOKOL 1511 Z14L:10% pvc	Gloss Loss-5 rubs; Thk Loss-40 rubs	9H	PASS	PASS	14-18	<2	FAIL	75.9
SOKOL 1513, Z14L:10% pvc	Gloss Loss-5 rubs; Thk Loss-40 rubs	9H	PASS	PASS	10	<2	FAIL	73.3
SOKOL 1514, Z14L:10% pvc	Gloss Loss-5 rubs; Thk Loss-40 rubs	9H	PASS	PASS	8	<2	FAIL	33.5
SOKOL 1515, Z14L:10% pvc	Gloss Loss-5 rubs; Thk Loss-40 rubs	9H	PASS	PASS	10	<2	FAIL	74.6
SOKOL 1516, Z14L:10% pvc	Gloss Loss-5 rubs; Thk Loss-40 rubs	9H	PASS	PASS	12	<2	FAIL	63

Table 33. Screen Test Results of UV Curable Coatings on Zn-Ph Steel - Continued

TEST	MEK RESISTANCE	PENCIL HARDNESS	DRY ADHESION	WET ADHESION	IMPACT, FORWARD, IN-LBS	IMPACT, REVERSE, IN-LBS	CONICAL MANDREL	GLOSS
TEST DESCRIPTION	50 Wipes	ASTM D3363	3M 250 Tape	24 hour immersion	ASTM D2794	ASTM D2794	1/4"conical mandrel bend	FED-STD-141,Method 6101.1
REQUIREMENT	No removal of coating	None	No delamination	No delamination	40% elongation	40% elongation	No cracking	> 90
3M 631 Z14L: 37% pvc	PASS	5H	PASS	PASS	60, stress marks @ 30	60, stress marks @ 30	PASS	96
DYMAX 984 TC, Z14L:25% pvc	PASS	9H	PASS	PASS	0	0	FAIL	46.6
HERBERTS 094-58-1 1.3-1.6 MILS	Not Tested	Not Tested	PASS	Not Tested	14	<2	FAIL	Not Tested
NSWC Epoxy Acrylate Z14L: none	Not Tested	Not Tested	PASS	Not Tested	0	0	FAIL	Not Tested
NSWC Epoxy Acrylate Z14L: 20%	PASS	7H	PASS	PASS	4	4	FAIL	49

Table 34. Screen Test Results of UV Curable Coatings on: Zn-Ph Steel + Wash Primer

TEST	MEK RESISTANCE	PENCIL HARDNESS	DRY ADHESION	WET ADHESION	IMPACT, FORWARD, IN-LBS	IMPACT, REVERSE, IN-LBS	CONICAL MANDREL	GLOSS
TEST DESCRIPTION	50 Wipes	ASTM D3363	3M 250 Tape	24 hour immersion	ASTM D2794	ASTM D2794	1/4"conical mandrel bend	FED-STD-141,Method 6101.1
REQUIREMENT	No removal of coating	None	No delamination	No delamination	40% elongation	40% elongation	No cracking	> 90
SOKOL 1510, Z14L:10% pvc	Gloss Loss-5 rubs; Thk Loss-40 rubs	9H	Good@UV/primer Fail@primer/steel	PASS	14	<2	Fail@Primer/steel interface	56
SOKOL 1511, Z14L:10% pvc	Gloss Loss-5 rubs; Thk Loss-40 rubs	9H	Good@UV/primer Fail@primer/steel	PASS	8	<2	Fail@Primer/steel interface	64.5
SOKOL 1513, Z14L:10% pvc	Gloss Loss-5 rubs; Thk Loss-40 rubs	9H	Good@UV/primer Fail@primer/steel	PASS	18-22	2	Fail@Primer/steel interface	74.8
SOKOL 1514, Z14L:10% pvc	Gloss Loss-5 rubs; Thk Loss-40 rubs	9H	Good@UV/primer Fail@primer/steel	PASS	8	<2	Fail@Primer/steel interface	30
SOKOL 1515, Z14L:10% pvc	Gloss Loss-5 rubs; Thk Loss-40 rubs	9H	Good@UV/primer Fail@primer/steel	PASS	14	0	Fail@Primer/steel interface	79.4
SOKOL 1516, Z14L:10% pvc	Gloss Loss-5 rubs; Thk Loss-40 rubs	9H	Good@UV/primer Fail@primer/steel	PASS	8	<2	Fail@Primer/steel interface	58.3

Table 34. Screen Test Results of UV Curable Coatings on: Zn-Ph Steel + Wash Primer - Continued

TEST	MEK RESISTANCE	PENCIL HARDNESS	DRY ADHESION	WET ADHESION	IMPACT, FORWARD, IN-LBS	IMPACT, REVERSE, IN-LBS	CONICAL MANDREL	GLOSS
TEST DESCRIPTION	50 Wipes	ASTM D3363	3M 250 Tape	24 hour immersion	ASTM D2794	ASTM D2794	1/4"conical mandrel bend	FED-STD-141,Method 6101.1
REQUIREMENT	No removal of coating	None	No delamination	No delamination	40% elongation	40% elongation	No cracking	> 90
3M 631 Z14L:37% pvc	Good	5H	PASS	PASS	60	60	PASS	92.8
DYMAX 984 TC, Z14L:25% pvc	Good	9H	PASS	PASS	0	0	FAIL	52.6

Table 35. Screen Test Results of UV Curable Coatings on: Zn-Ph Steel + Wash Primer + Primer

TEST	MEK RESISTANCE	PENCIL HARDNESS	DRY ADHESION	WET ADHESION	IMPACT, FORWARD, IN-LBS	IMPACT, REVERSE, IN-LBS	CONICAL MANDREL	GLOSS
TEST DESCRIPTION	50 Wipes	ASTM D3363	3M 250 Tape	24 hour immersion	ASTM D2794	ASTM D2794	1/4"conical mandrel bend	FED-STD-141,Method 6101.1
REQUIREMENT	No removal of coating	None	No delamination	No delamination	40% elongation	40% elongation	No cracking	> 90
SOKOL 1510, Z14L:10% pvc	Gloss Loss-5 rubs; Thk Loss-40 rubs	9H	Good@UV/primer Fail@primer/steel	FAIL	20	<2	PASS	57.8
SOKOL 1511, Z14L:10% pvc	Gloss Loss-5 rubs; Thk Loss-40 rubs	9H	Good@UV/primer Fail@primer/steel	FAIL	34	4	Fail@Primer/steel interface	71.4
SOKOL 1513, Z14L:10% pvc	Gloss Loss-5 rubs; Thk Loss-40 rubs	9H	Good@UV/primer Fail@primer/steel	FAIL	34	2	PASS	75.8
SOKOL 1514, Z14L:10% pvc	Gloss Loss-5 rubs; Thk Loss-40 rubs	9H	Good@UV/primer Fail@primer/steel	FAIL	30	2	PASS	60.8
SOKOL 1515, Z14L:10% pvc	Gloss Loss-5 rubs; Thk Loss-40 rubs	9H	Good@UV/primer Fail@primer/steel	FAIL	38	6	PASS	72.8
SOKOL 1516, Z14L:10% pvc	Gloss Loss-5 rubs; Thk Loss-40 rubs	9H	Good@UV/primer Fail@primer/steel	FAIL	16-18	<2	PASS	64.3

Table 35. Screen Test Results of UV Curable Coatings on: Zn-Ph Steel + Wash Primer + Primer - Continued

TEST	MEK RESISTANCE	PENCIL HARDNESS	DRY ADHESION	WET ADHESION	IMPACT, FORWARD, IN-LBS	IMPACT, REVERSE, IN-LBS	CONICAL MANDREL	GLOSS
TEST DESCRIPTION	50 Wipes	ASTM D3363	3M 250 Tape	24 hour immersion	ASTM D2794	ASTM D2794	1/4"conical mandrel bend	FED-STD-141,Method 6101.1
REQUIREMENT	No removal of coating	None	No delamination	No delamination	40% elongation	40% elongation	No cracking	> 90
3M 631, Z14L: 37% pvc	Good	5H	PASS	PASS	60	60	PASS	93.1
DYMAX 984 TC, Z14L:25% pvc	Good	9H	PASS	PASS	12	2	PASS	52.9

Table 36. Screen Test Results of UV Curable Coatings on: 2024 Aluminum, TO, Bare

TEST	MEK RESISTANCE	PENCIL HARDNESS	DRY ADHESION	WET ADHESION	IMPACT, FORWARD, IN-LBS	IMPACT, REVERSE, IN-LBS	CONICAL MANDREL	GLOSS
TEST DESCRIPTION	**50 Wipes**	**ASTM D3363**	**3M 250 Tape**	**24 hour immersion**	**ASTM D2794**	**ASTM D2794**	**1/4"conical mandrel bend**	**FED-STD-141,Method 6101.1**
REQUIREMENT	**No removal of coating**	**None**	**No delamination**	**No delamination**	**40% elongation**	**40% elongation**	**No cracking**	**> 90**
SOKOL 1510, Z14L:10% pvc	Gloss Loss-5 rubs: Thk Loss-40 rubs	9H	PASS	FAIL	32	2	PASS	98.7
SOKOL 1511, Z14L:10% pvc	Gloss Loss-5 rubs: Thk Loss-40 rubs	9H	PASS	FAIL	8	<2	PASS	98.1
SOKOL 1513, Z14L:10% pvc	Gloss Loss-5 rubs: Thk Loss-40 rubs	9H	PASS	FAIL	6	<2	PASS	113.9
SOKOL 1514, Z14L:10% pvc	Gloss Loss-5 rubs: Thk Loss-40 rubs	9H	PASS	FAIL	4	<2	FAIL	79
SOKOL 1515, Z14L:10% pvc	Gloss Loss-5 rubs: Thk Loss-40 rubs	9H	PASS	FAIL	6	<2	PASS	113.5
SOKOL 1516, Z14L:10% pvc	Gloss Loss-5 rubs: Thk Loss-40 rubs	9H	PASS	FAIL	14	2	PASS	84.6

Table 36. Screen Test Results of UV Curable Coatings on : 2024 Aluminum, TO, Bare - Continued

TEST	MEK RESISTANCE	PENCIL HARDNESS	DRY ADHESION	WET ADHESION	IMPACT, FORWARD, IN-LBS	IMPACT, REVERSE, IN-LBS	CONICAL MANDREL	GLOSS
TEST DESCRIPTION	50 Wipes	ASTM D3363	3M 250 Tape	24 hour immersion	ASTM D2794	ASTM D2794	1/4"conical mandrel bend	FED-STD-141,Method 6101.1
REQUIREMENT	No removal of coating	None	No delamination	No delamination	40% elongation	40% elongation	No cracking	> 90
3M 631, Z14L: 37% pvc	PASS	5H	FAIL	FAIL	60	60	PASS	111.8
DYMAX 984 TC, Z14L:25% pvc	PASS	9H	PASS	FAIL	4	0	FAIL	49.3
HERBERTS ULTRAFAST WHITE 200F+UV	Gloss Loss-1 rub	Not Tested	Not Tested	PASS	32	2	Not Tested	Not Tested
HERBERTS ULTRAFAST WHITE 260F+UV	Gloss Loss-1 rub	Not Tested	Not Tested	PASS	26	2	Not Tested	Not Tested
HERBERTS UV CURE#30, 1.1-1.4MILS	Gloss Loss-1 rub	Not Tested	Not Tested	PASS	36	26	Not Tested	Not Tested
HERBERTS UV CURE#30 1.2-1.5MILS	Gloss Loss-1 rub	Not Tested	Not Tested	PASS	34	18	Not Tested	Not Tested

Table 36. Screen Test Results of UV Curable Coatings on : 2024 Aluminum, TO, Bare - Continued

TEST	MEK RESISTANCE	PENCIL HARDNESS	DRY ADHESION	WET ADHESION	IMPACT, FORWARD, IN-LBS	IMPACT, REVERSE, IN-LBS	CONICAL MANDREL	GLOSS
TEST DESCRIPTION	**50 Wipes**	**ASTM D3363**	**3M 250 Tape**	**24 hour immersion**	**ASTM D2794**	**ASTM D2794**	**1/4"conical mandrel bend**	**FED-STD-141,Method 6101.1**
REQUIREMENT	**No removal of coating**	**None**	**No delamination**	**No delamination**	**40% elongation**	**40% elongation**	**No cracking**	**> 90**
HERBERTS UV CURE#30 1.6-1.9MILS	Gloss Loss-1 rub	Not Tested	Not Tested	FAIL	16	6	Not Tested	Not Tested
HERBERTS 094-58-1 1.3-1.6MILS	Not Tested	Not Tested	PASS	Not Tested	22	12	PASS	Not Tested

Table 37. Screen Test Results of UV Curable Coatings on: Aluminum + Conversion Coat + Primer

TEST	MEK RESISTANCE	PENCIL HARDNESS	DRY ADHESION	WET ADHESION	IMPACT, FORWARD, IN-LBS	IMPACT, REVERSE, IN-LBS	CONICAL MANDREL	GLOSS
TEST DESCRIPTION	50 Wipes	ASTM D3363	3M 250 Tape	24 hour immersion	ASTM D2794	ASTM D2794	1/4"conical mandrel bend	FED-STD-141,Method 6101.1
REQUIREMENT	No removal of coating	None	No delamination	No delamination	40% elongation	40% elongation	No cracking	> 90
SOKOL 1510, Z14L:10% pvc	Gloss Loss-5 rubs: Thk Loss-40 rubs	9H	Good@UV/primer Fail@primer/ Al	FAIL	14	2	PASS	46.8
SOKOL 1511, Z14L:10% pvc	Gloss Loss-5 rubs: Thk Loss-40 rubs	9H	Good@UV/primer Fail@primer/ Al	FAIL	14-16	4	PASS	60.8
SOKOL 1513, Z14L:10% pvc	Gloss Loss-5 rubs: Thk Loss-40 rubs	9H	Good@UV/primer Fail@primer/Al	FAIL	12	2	PASS	74.2
SOKOL 1514, Z14L:10% pvc	Gloss Loss-5 rubs: Thk Loss-40 rubs	9H	Good@UV/primer Fail@primer/Al	FAIL	4	<2	PASS	61
SOKOL 1515, Z14L:10% pvc	Gloss Loss-5 rubs: Thk Loss-40 rubs	9H	Good@UV/primer Fail@primer/ Al	FAIL	16	16	PASS	78.5
SOKOL 1516, Z14L:10% pvc	Gloss Loss-5 rubs: Thk Loss-40 rubs	9H	Good@UV/primer Fail@primer/ Al	FAIL	10	2	PASS	59.2
3M 631, Z14L: 37 % pvc	Good	5H	PASS	PASS	60	60	PASS	95

Table 37. Screen Test Results of UV Curable Coatings on: Aluminum+Conversion Coat+Primer-Continued

TEST	MEK RESISTANCE	PENCIL HARDNESS	DRY ADHESION	WET ADHESION	IMPACT, FORWARD, IN-LBS	IMPACT, REVERSE, IN-LBS	CONICAL MANDREL	GLOSS
TEST DESCRIPTION	50 Wipes	ASTM D3363	3M 250 Tape	24 hour immersion	ASTM D2794	ASTM D2794	1/4"conical mandrel bend	FED-STD-141,Method 6101.1
REQUIREMENT	No removal of coating	None	No delamination	No delamination	40% elongation	40% elongation	No cracking	> 90
DYMAX 984 TC, Z14L:25% pvc	PASS	9H	PASS	PASS	6	0	Adhesion Good, Stress marks	46.3

Table 38. ZDOC SCREEN TEST RESULTS
COMPARISON OF PIGMENTED VS.UNPIGMENTED UV COATINGS ON CONVERSION COATED ALUMINUM

Test	Test Description	Requirement	Sokol 1510, Unpigmented	Sokol 1510, Pigmented, Z14L: 10% PVC	Sokol 1511, Unpigmented	Sokol 1511, Pigmented Z14L: 10%PVC
Thickness (mils)			1.8	2.5	1.7	2.5
Color	Visual	N/A	Clear	Translucent white	Clear	Translucent White
1. Dry tape adhesion 2. Wet tape adhesion	1. 3M 250 tape 2. 24 hour immersion	No delamination No delamination	PASS PASS	PASS PASS	PASS PASS	PASS PASS
Impact flexibility	ASTM D2794	40% elongation	Forward: 10 in-lb Reverse: 2 in-lb	Forward: 6 in-lb Reverse: <2 in-lb	Forward: 18 in-lb Reverse:12 in-lb	Forward: 6 in-lb Reverse: 2 in-lb
MEK resistance	50 wipes	No removal of coating	PASS	Fail	PASS	FAIL
Pencil hardness	ASTM D3363	None	4H	9H	4H	9H
Skydrol 500 resistance	7 day immersion	<2 Pencil hardness change	FAIL (flaked off panel)	Not tested	FAIL (coating rmvd)	Not tested
Lube oil resistance (MIL-L-23699)	24 hour, 250°F	Pencil hardness, appearance	PASS	Not tested	PASS	Not tested
Hydraulic fluid resistance (MIL-H-83282)	25 hour, 150°F	Pencil hardness, appearance	PASS	Not tested	PASS	Not tested
Salt fog (5%)	500 hours	No corrosion	Corrosion in scribe lines only	Not tested	Corrosion in scribe lines only	Not tested
Flexibility	Conical Mandrel	No cracking	PASS	PASS	FAIL	PASS
Gloss (60°)	FED-STD-141, Method 6101.1	90 or greater	97	65.8	99	54.5
Heat resistance	4 hours at 300°F	Meet gloss and impact requirements	Gloss =100 38 in-lb (fwd) 32 in-lb (rev)	Not tested	Gloss =98 16 in-lb (fwd) 18 in-lb (rev)	Not tested

Table 38. ZDOC SCREEN TEST RESULTS - Continued
COMPARISON OF PIGMENTED VS.UNPIGMENTED UV COATINGS ON CONVERSION COATED ALUMINUM

Test	**Test Description**	**Requirement**	**Sokol 1513, Unpigmented**	**Sokol 1513, Pigmented, Z14L: 10% PVC**	**Sokol 1514, Unpigmented**	**Sokol 1514, Pigmented, Z14L: 10%PVC**
Thickness (mils)			1.8	2.5	1.7	2.5
Color	Visual	N/A	Clear	Translucent white	Clear	Translucent white
1. Dry tape adhesion 2. Wet tape adhesion	1. 3M 250 tape 2. 24 hour immersion	No delamination No delamination	PASS PASS	PASS PASS	PASS PASS	PASS PASS
Impact flexibility	ASTM D2794	40% elongation	Forward: 24 in-lb Reverse: 22 in-lb	Forward: 8 in-lb Reverse: <2 in-lb	Forward: 14 in-lb Reverse: 4 in-lb	Forward: 4 in-lb Reverse: <2 in-lb
MEK resistance	50 wipes	No removal of coating	PASS	FAIL	PASS	FAIL
Pencil hardness	ASTM D3363	None	4H	9H	4H	9H
Skydrol 500 resistance	7 day immersion	<2 Pencil hardness change	PASS	Not tested	PASS	Not tested
Lube oil resistance (MIL-L-23699)	24 hour, 250°F	Pencil hardness, appearance	PASS	Not tested	PASS	Not tested
Hydraulic fluid resistance (MIL-H-83282)	25 hour, 150°F	Pencil hardness, appearance	PASS	Not tested	PASS	Not tested
Salt fog (5%)	500 hours	No corrosion	FAIL	Not tested	Corrosion in scribe lines only	Not tested
Flexibility	Conical Mandrel	No cracking	PASS	Pass	PASS	FAIL
Gloss (60°)	FED-STD-141, Method 6101.1	90 or greater	96	72.7	98	58.4
Heat resistance	4 hours at 300°F	Meet gloss and impact requirements	Gloss =100 38 in-lb (fwd) 44 in-lb (rev)	Not tested	Gloss =100 36 in-lb (fwd) 22 in-lb (rev)	Not tested

Table 38. ZDOC SCREEN TEST RESULTS - Continued
COMPARISON OF PIGMENTED VS.UNPIGMENTED UV COATINGS ON CONVERSION COATED ALUMINUM

Test	Test Description	Requirement	Sokol 1515, Unpigmented	Sokol 1515, Pigmented, Z14L: 10% PVC	Sokol 1516, Unpigmented	Sokol 1516, Pigmented, Z14L: 10% PVC
Thickness (mils)			1.6	2.5	1.7	2.5
Color	Visual	N/A	Clear	Translucent white	Clear	Translucent white
1. Dry tape adhesion 2. Wet tape adhesion	1. 3M 250 tape 2. 24 hour immersion	No delamination No delamination	PASS PASS	PASS PASS	PASS PASS	PASS PASS
Impact flexibility	ASTM D2794	40% elongation	Forward: 30 in-lb Reverse: 24 in-lb	Forward: 6 in-lb Reverse: <2 in-lb	Forward: 26 in-lb Reverse: 4 in-lb	Forward: 8 in-lb Reverse: <2 in-lb
MEK resistance	50 wipes	No removal of coating	PASS	FAIL	PASS	FAIL
Pencil hardness	ASTM D3363	None	4H	9H	4H	9H
Skydrol 500 resistance	7 day immersion	<2 Pencil hardness change	PASS	Not tested	PASS	Not tested
Lube oil resistance (MIL-L-23699)	24 hour, 250°F	Pencil hardness, appearance	PASS	Not tested	PASS	Not tested
Hydraulic fluid resistance (MIL-H-83282)	25 hour, 150°F	Pencil hardness, appearance	PASS	Not tested	PASS	Not tested
Salt fog (5%)	500 hours	No corrosion	Corrosion in scribe lines only	Not tested	Corrosion in scribe lines only	Not tested
Flexibility	Conical Mandrel	No cracking	FAIL	PASS	PASS	PASS
Gloss (60°)	FED-STD-141, Method 6101.1	90 or greater	100	79.4	100	58.3
Heat resistance	4 hours at 300°F	Meet gloss and impact requirements	Gloss =100 42 in-lb (fwd) 34 in-lb (rev)	Not tested	Gloss =100 50 in-lb (fwd) 44 in-lb (rev)	Not tested

Table 38. ZDOC SCREEN TEST RESULTS - Continued
COMPARISON OF PIGMENTED VS.UNPIGMENTED UV COATINGS ON CONVERSION COATED ALUMINUM

Test	**Test Description**	**Requirement**	**Sokol 1516, Pigmented, Z14L: 27.6 % PVC**	**Dymax 984TC, Unpigmented**	**Dymax 984TC, Unpigmented**	**Dymax 984TC, Pigmented, Z14L:25% PVC**
Thickness (mils)			1.9	0.5	1.0	2.5
Color	Visual	N/A	Translucent white	Clear	Clear	Translucent white
1. Dry tape adhesion 2. Wet tape adhesion	1. 3M 250 tape 2. 24 hour immersion	No delamination No delamination	FAIL FAIL	PASS PASS	PASS PASS	PASS PASS
Impact flexibility	ASTM D2794	40% elongation	Forward: 2 in-lb Reverse: 2 in-lb	Forward: 50 in-lb Reverse: 60 in-lb	Forward: 20 in-lb Reverse: 20 in-lb	Forward: 4 in-lb Reverse: 0 in-lb
MEK resistance	50 wipes	No removal of coating	PASS	PASS	FAIL	PASS
Pencil hardness	ASTM D3363	None	SH	4H	9H	9H
Skydrol 500 resistance	7 day immersion	<2 Pencil hardness change	FAIL Delamination in solution.	PASS (4H)	PASS (7H)	Not tested
Lube oil resistance (MIL-L-23699)	24 hour, 250°F	Pencil hardness, appearance	FAIL Delamination in solution.	Not tested	Not tested	Not tested
Hydraulic fluid resistance (MIL-H-83282)	25 hour, 150°F	Pencil hardness, appearance	FAIL Delamination in solution.	Not tested	Not tested	Not tested
Salt fog (5%)	500 hours	No corrosion	Not tested	Extensive corrosion	Extensive corrosion	Not tested
Flexibility	Conical Mandrel	No cracking	FAIL	PASS	FAIL	PASS
Gloss (60°)	FED-STD-141, Method 6101.1	90 or greater	34.2	100	100	Not tested
Heat resistance	4 hours at 300°F	Meet gloss and impact requirements	Gloss =16.3 2 in-lb (fwd) 2 in-lb (rev)	Gloss=100 50 in-lb (fwd) 50 in-lb (rev)	Gloss=100 14 in-lb (fwd) 10 in-lb (rev)	

Table 38. ZDOC SCREEN TEST RESULTS - Continued
COMPARISON OF PIGMENTED VS.UNPIGMENTED UV COATINGS ON CONVERSION COATED ALUMINUM

Test	Test Description	Requirement	3M 631, Unpigmented	3M 631, Z14L pigment, 37% PVC
Thickness (mils)			1.6	2.5
Color	Visual	N/A	Clear	
1. Dry tape adhesion 2. Wet tape adhesion	1. 3M 250 tape 2. 24 hour immersion	No delamination No delamination	PASS PASS	PASS PASS
Impact flexibility	ASTM D2794	40% elongation	Forward: >80in-lb Reverse: >80in-lb	Forward: >60in-lb Reverse:>60in-lb
MEK resistance	50 wipes	No removal of coating	PASS	PASS
Pencil hardness	ASTM D3363	None	3H	5H
Skydrol 500 resistance	7 day immersion	<2 Pencil hardness change	3H (PASS)	Not tested
Lube oil resistance (MIL-L-23699)	24 hour, 250°F	Pencil hardness, appearance	PASS (3H) appearance-good	Not tested
Hydraulic fluid resistance (MIL-H-83282)	25 hour, 150°F	Pencil hardness, appearance	PASS (3H)	Not tested
Salt fog (5%)	500 hours	No corrosion	Corrosion in scribe lines only	Very slight corrosion in scribe line
Flexibility	Conical Mandrel	No cracking	PASS	PASS
Gloss (60°)	FED-STD-141, Method 6101.1	90 or greater	100	Not tested
Heat resistance	4 hours at 300°F	Meet gloss and impact requirements	Gloss=100 80+ in-lb (fwd) 80+ in-lb (rev)	Not tested

The other submission from Dymax, 986 Darc Cure, was applied only to conversion coated aluminum. It was not tested with pigment, since initial adhesion and solvent resistance results were poor for a coating thickness of only 0.5 mil, as reported in Table 39.

4.2.1.3 3M. The 3M Corporate Research Lab had been working on a dual cure, photocurable coating for several years under a DOE contract. The goals of that program were similar in many ways to the ZDOC program, with several exceptions; their study did not include non-chromated corrosion inhibitors.

For the ZDOC program, 3M initially submitted a dual cure urethane/acrylate formulation with titanium dioxide (TiO_2) pigment. The incorporation of TiO_2 in this material is particularly noteworthy since TiO_2-pigmented coatings are difficult to cure in UV light. This difficulty is caused because TiO_2 absorbs light strongly below 380 nanometers and reflects strongly over 420 nanometers. These properties make it very difficult for the UV light to penetrate into the coating and thoroughly cure at the substrate/coating interface. However, 3M has found a photoinitiator which reacts in the small band range of 380-420 nanometers, thus promoting cure of the coating.

In addition to submitting their dual-cure, TiO_2-pigmented coating , 3M also submitted a three component unpigmented formulation, 3M 631, based on the same photoinitiator system as the dual cure coating discussed above. When the 631 material was pigmented to 37% PVC with the Z14L pigment, the screen test results on all six test substrates were excellent, as indicated in Table B-5 and Tables 33 through 37. In addition, when subjected to 1000 hours of salt fog exposure per ASTM B117, this coating performed well on conversion coated aluminum and primed aluminum substrates (data not recorded in tables). This coating passed extensive testing in the unpigmented version; based upon excellent test results when the coating was pigmented with Z14L and subjected to limited screen testing, it would be expected to pass more extensive testing.

There is a major drawback with this coating, however, in that it has a VOC content of approximately 120g/l. In addition, the high viscosity of the grind resin (the resin component into which the pigment is ground prior to mixing the components together) required the addition of solvent before the pigment could be incorporated. A Hegman grind of 6 1/2 was achieved. After the pigment was incorporated, the solvent was driven off.

4.2.1.4 Herberts Powder Coatings, Inc. Herberts is a producer of powder coatings, and has formulated a unique formulation that fuses at 160°F and is UV curable. This combination of properties could be very useful for temperature sensitive substrates that cannot withstand the 250°F to 350°F fusion temperatures of most low cure-temperature powder coatings.

Herberts submitted several coating candidates, all of which were powder coatings applied to test panels by Herberts. Each of the Herberts formulations contained TiO_2 or Z14L pigment. As they received screening test results from HAC, Herberts worked extensively to improve the characteristics of their submissions, and conducted concurrent screen testing with several European laboratories prior to submitting their last formulation. There were never enough samples of a particular coating/substrate combination to conduct a full set of even the most basic screen tests.

Most of their coatings were submitted on bare aluminum, and these results are presented in Table 36. The solvent resistance was poor; when Herberts attempted to improve this, a decrease in flexibility was observed. The coating identified as UV Cure #30 exhibited the best impact flexibility results on bare aluminum. As expected however, this characteristic decreased

Table 39. ZDOC Screen Test Results

AS-RECEIVED UV CURABLE COATINGS ON CONVERSION COATED ALUMINUM

Test	Test Description	Requirement	Sokol 908-15	Sokol 1512	Sokol 1189 Coating	Dymax 986 Darc Cure	3M Dual Cure Polyurethane Coating
Thickness (mils)			0.7	1.8		0.5	2.5
Color	Visual	N/A	Clear	Clear	Clear	Clear	White
1. Dry tape adhesion 2. Wet tape adhesion	1. 3M 250 tape 2. 24 hour immersion	No delamination No delamination	PASS FAIL	PASS PASS	PASS PASS	FAIL FAIL	FAIL FAIL
Impact flexibility	ASTM D2794	40% elongation	Forward: 10 in-lb Reverse: 10 in-lb	Forward: 16 in-lb Reverse: 2 in-lb	Forward: 10 in-lb Reverse: 4 in-lb	Forward: 40 in-lb Reverse: 40 in-lb	Forward: 80 in-lb Reverse:>100 in-lb
MEK resistance	50 wipes	No removal of coating	PASS (slight removal)	PASS	PASS	FAIL	PASS
Pencil hardness	ASTM D3363	None	8H	4H	5H	5H	4H
Skydrol 500 resistance	7 day immersion	<2 Pencil hardness change	7H	FAIL (flaked off panel)	4H (PASS) appearance-good	PASS (3H)	3H (PASS) appearance-good
Lube oil resistance (MIL-L-23699)	24 hour, 250°F	Pencil hardness, appearance	Not tested	PASS	Not tested	Not tested	Not tested
Hydraulic fluid resistance (MIL-H-83282)	25 hour, 150°F	Pencil hardness, appearance	Not tested	PASS	Not tested	Not tested	Not tested
Salt fog (5%)	500 hours	No corrosion	Corrosion in scribe lines only	Corrosion in scribe lines only	Extensive corrosion	Extensive corrosion	Corrosion in scribe line only
Flexibility	Conical Mandrel	No cracking	PASS	PASS	PASS	PASS	PASS
Gloss (60°)	FED-STD-141, Method 6101.1	90 or greater	100	93	91	86	91
Heat resistance	4 hours at 300°F	Meet gloss and impact requirements	Gloss=100 <10 in-In (fwd) <10 in-lb (rev)	Gloss =100 22 in-lb (fwd) 24 in-lb (rev)	Gloss=45 (FAIL) 6 in-lb (fwd) 4 in-lb (rev)	Gloss=88 40 in-lb (fwd) 35 in-lb (rev)	Gloss=90 >100 in-lb (fwd) 80 in-lb (rev)

Table 39. ZDOC Screen Test Results - Continued

AS-RECEIVED UV CURABLE COATINGS ON CONVERSION COATED ALUMINUM

Test	Test Description	Requirement	Herberts UV Powder	Herberts 094-58-1	NSWC Epoxy	NSWC Polyurethane	NSWC Epoxy-Acrylate
Thickness (mils)			1.2-1.9	1.3-1.6	1.2-3.4 mils	1.2-3 mils	2.5
Color	Visual	N/A	White	White	Gray	Gray	Clear
1. Dry tape adhesion 2. Wet tape adhesion	1. 3M 250 tape 2. 24 hour immersion	No delamination No delamination	PASS PASS	Not tested PASS	FAIL FAIL	FAIL FAIL	Not tested Not tested
Impact fexibility	ASTM D2794	40% elongation	Forward: 4 in-lb Reverse: 0 in-lb	Forward:>80 in-lb Reverse:>80 in-lb	Forward:<10 in-lb Reverse:<10 in-lb	Forward:<10 Reverse:<10	Reverse: 0 in-lb
MEK resistance	50 wipes	No removal of coating	PASS	Not tested	PASS	PASS	Not tested
Pencil hardness	ASTM D3363	None	4H	Not tested	7H	6H	Not tested
Skydrol 500 resistance	7 day immersion	<2 Pencil hardness change	FAIL	Not tested	PASS	PASS	Not tested
Lube oil resistance (MIL-L-23699)	24 hour, 250°F	Pencil hardness, appearance	PASS	Not tested	Not tested	not tested	Not tested
Hydraulic fluid resistance (MIL-H-83282)	25 hour, 150°F	Pencil hardness, appearance	PASS	Not tested	Not tested	not tested	Not tested
Salt fog (5%)	500 hours	No corrosion	Corrosion in scribe lines and some other areas.	PASS (1000 hours)	Extensive corrosion	Extensive corrosion	FAIL
Flexibility	Conical Mandrel	No cracking	FAIL	PASS	FAIL	FAIL	FAIL
Gloss (60°)	FED-STD-141, Method 6101.1	90 or greater	86	Not tested	86	85	Not tested
Heat resistance	4 hours at 300°F	Meet gloss and impact requirements	Gloss=83 6 in-lb (fwd) 0 in-lb (rev)	Not tested	Gloss=88 <10 in-lb (fwd) <10 in-lb (rev)	Gloss=77 <10 in-lb (fwd) <10 in-lb (rev)	Not tested

Table 39. ZDOC Screen Test Results - Continued

AS-RECEIVED UV CURABLE COATINGS ON CONVERSION COATED ALUMINUM

Test	Test Description	Requirement	Miles 3919	Caschem	Microlite 3010
Thickness (mils)			1.3	3.0	1.5
Color	Visual	N/A	Clear	Clear	Clear
1. Dry tape adhesion 2. Wet tape adhesion	1. 3M 250 tape 2. 24 hour immersion	No delamination No delamination	FAIL FAIL	FAIL FAIL	FAIL FAIL
Impact flexibility	ASTM D2794	40% elongation	Forward: 40 in-lb Reverse: 26 in-lb	Forward: 4 in-lb Reverse: 2 in-lb	Forward: 12 in-lb Reverse: 8 in-lb
MEK resistance	50 wipes	No removal of coating	PASS	PASS	PASS
Pencil hardness	ASTM D3363	None	5H	5H	7H
Skydrol 500 resistance	7 day immersion	<2 Pencil hardness change	4H (PASS)	3H (PASS) appearance-good	4H (PASS) appearance-good
Lube oil resistance (MIL-L-23699)	24 hour, 250°F	Pencil hardness, appearance	PASS (5H) appearance-good	Not tested	PASS
Hydraulic fluid resistance (MIL-H-83282)	25 hour, 150°F	Pencil hardness, appearance	PASS (5H)	Not tested	PASS
Salt fog (5%)	500 hours	No corrosion	Extensive corrosion	Extensive corrosion	Extensive corrosion
Flexibility	Conical Mandrel	No cracking	PASS	FAIL	FAIL
Gloss (60°)	FED-STD-141, Method 6101.1	90 or greater	97	PASS	115
Heat resistance	4 hours at 300°F	Meet gloss and impact requirements	Gloss=96 32 in-lb (fwd) 32 in-lb (rev)	Gloss=95 4 in-lb (fwd) <2 in-lb (rev)	Gloss=100 16 in-lb (fwd) 4 in-lb (rev)

with increasing film thickness. Although not included in Table 36, when the UV Cure #30 was applied to bare aluminum and subjected to 1000 hours of salt fog exposure per ASTM B117, the results were very promising.

The screen test results of the Herberts' coatings that were applied to conversion coated aluminum are shown in Table 39. When subjected to 1000 hours of salt fog exposure per ASTM B117, the 094-58-1 coating performed well on conversion coated aluminum. As indicated, the impact flexibility of the 094-58-1 formulation was exceptionally good in comparison to other UV curable coatings evaluated for this program. When this coating was applied at the same film thickness to bare aluminum and Zn-Ph treated steel, the flexibility properties were significantly less, as indicated in Tables 39 and 33 respectively.

4.2.1.5 Naval Surface Warfare Center (NSWC). From a literature survey it was determined that NSWC was conducting related research on a UV curable, gray pigmented paint for touch-up use on Navy submarines. Their work was particularly applicable to the ZDOC program because the requirement for low toxicity on a submarine mandated a 100% solids paint. The paint developed by NSWC has a pigment loading of only 5%. The TiO_2 pigment that was used strongly absorbs UV light below 350 nanometers and strongly reflects above 390 nanometers. This characteristic necessitates the use of a UV source with an unconventional spectral output. The spectral output of a Xenon bulb, about 380 nanometers, not only meets the requirements of the pigment, but is a non-mercury based system. This is significant since mercury is not allowed on a submarine.

A contract was issued to NSWC to formulate a paint for this program. The Navy application being worked on required an epoxy paint that would adhere to steel. When this coating was applied to conversion coated aluminum, the screen test results were not acceptable, as indicated in Table 39. Due to the flexibility requirements of this program and the requirement to adhere to conversion coated aluminum, an acrylic modified polyurethane resin system was subsequently chosen for development. The formulation effort was based on similar work done by Henry Miller of Sartomer which exhibited good adhesion to aluminum and good flexibility. Photoinitiators were chosen to provide UV absorption and activation in ranges close to the visible region, so curing could occur in the presence of pigments, especially the commonly used titanium dioxide pigment.

After the coating was applied to conversion coated aluminum, photoinitiator incompatibility was exhibited with Ciba Geigy's 1173 photoinitiator. This was replaced with BAPO, a photoinitiator from Sartomer. Incompatibility was observed in the form of ridges and lumps after the clear coating was applied to the aluminum substrate. The addition of a surfactant did not help, nor did heating the substrate either prior to or after the coating was applied. The screen test results, as indicated in Table 39, were not acceptable since the coating failed adhesion, flexibility, solvent resistance, and corrosion resistance requirements.

Because of these problems, the study with NSWC subsequently focused on an epoxy acrylate formulation which reportedly worked well on steel substrates. This coating was pigmented and applied by NSWC to two different steel substrate variables. In addition, a small sample of the formulation, unpigmented, was submitted to HAC for evaluation.

The as-received unpigmented epoxy-acrylate coating was applied to conversion coated aluminum, and subjected to reverse impact and conical mandrel flexibility tests. As shown in Table 39, the coating failed both of these tests. This coating/substrate combination also failed the 1000 hour salt fog exposure test, which was expected since the as-received unpigmented coating contained no corrosion inhibiting pigments.

The screening test results of the coated panels submitted by NSWC are presented in Table 40. The grit blasted steel and tight rusted steel substrates used were those of particular importance to NSWC, since they are the substrates most likely to be encountered on submarines. Dry adhesion and solvent resistance were acceptable, but impact flexibility and conical mandrel flexibility were poor. On Zn-Ph steel, the flexibility was also poor. However, this is usually not a major concern for steel substrates. Although not included in Table 40, the results of the 1000 hour salt fog exposure test, on each of the above-mentioned steel substrates, were marginal.

4.2.1.6 Miles Laboratories. The literature review showed that Miles Laboratories was very active in producing paints with a lower environmental impact. The Miles Defense Sector has a significant formulation capability, and has worked extensively on ultra low VOC military topcoats for ZDOC team member NAWCADWAR. The Miles' Wood Products Sector has been making very significant progress on zero VOC waterbased UV curable coatings for wood products. For these reasons it appeared that Miles would be a valuable contributor of test coatings to this program.

Miles initially submitted a water-based conventionally cured polyester/acrylate coating for evaluation, and the results are presented in Table 39. This material exhibited poor wetting when applied to conversion coated aluminum, and had poor adhesion. It was also determined to be inappropriate to further consider non-UV curable, ultra low VOC coatings in this program.

Subsequently, Miles decided not to continue participation in this program, since an analysis indicated that the potential market was insufficient to justify the necessary effort required to combine the technologies of their Defense and Wood Products Sectors.

4.2.1.7 Caschem, Inc. A dual cure UV curable conformal coating, for which the secondary cure is fairly rapid (< 24 hours), was modified by Caschem to meet the requirements of the ZDOC program. When the unpigmented formulation was applied to conversion coated aluminum and subjected to screen tests, impact flexibility, conical mandrel flexibility, and adhesion results did not meet the requirements, as indicated in Table 39. Caschem did not submit further coating formulations for evaluation.

4.2.1.8 Microlite. Microlite works with the government on Air Force and submarine applications, in addition to working with NSWC. Their candidate UV curable coating for the ZDOC program was applied to conversion coated aluminum. As shown in Table 39, this coating did not pass flexibility or adhesion tests, although solvent and fluid resistance were good.

4.2.2 Pigments. The UV light absorbance at different wavelengths of various non-chromated corrosion inhibiting pigments was determined and the results are presented in Table 41, shown in Appendix E. Using this data, the percent transmission of UV energy for each pigment was calculated, and is presented in Table 42. The transmission properties of most of the pigments in the 250 nanometer to 450 nanometer wavelength range was limited. Although the Phosplus pigment exhibited 100% transmission in this band range, it dissolved in the glycerol carrier to produce a clear liquid, unlike the other pigments which were suspended solids. The solute characteristics of the Phosplus pigment would probably be undesirable for applications requiring opacity.

The UV transmission properties of several non-chromated corrosion inhibiting pigments, at various concentrations in glycerin, was determined. As shown in Figures 31 through 33, the percent of UV energy transmission decreased with increasing concentration.

Table 40. Screen Test Results of UV Curable Epoxy Acrylate, NSWC, Pigmented

TEST	**MEK RESISTANCE**	**PENCIL HARDNESS**	**DRY ADHESION**	**WET ADHESION**	**FORWARD IMPACT, IN-LBS**	**REVERSE IMPACT, IN-LBS**	**CONICAL MANDREL**	**60 GLOSS**
TEST DESCRIPTION	**50 Wipes**	**ASTM D3363**	**3M 250 Tape**	**24 hour immersion**	**ASTM D2794**	**ASTM D2794**	**1/4" conical mandrel bend**	**FED-STD-141,Method 6101.1**
REQUIREMENT	**No removal of coating**	**None**	**No delamination**	**No delamination**	**40% elongation**	**40% elongation**	**No cracking**	**> 90**
SUBSTRATE: Grit Blasted Steel	PASS	7H	PASS	PASS	12	2	FAIL	48.7
SUBSTRATE: Tight Rusted Steel*	PASS	7H	PASS	FAIL	8	2	FAIL	46.1

* Tight rested steel is described as rusty steel that has been wire brushed to remove all loosely adherent rust.

TABLE 42

Percent Transmittance of UV Energy
(250 thru 450 nanometers)

	Molywhite	Sicorin	Phosplus	Ifochou	Halox	ZWP	Sicorin	Halox	Mix (3)	Sicorin	Itochou
Concentration	0.14	0.1	0.1	0.13	0.11	0.1	0.2	0.31	0.3	2	2
Wavelengths											
450	60.3	57.5	100.0	64.6	57.5	66.1	38.0	23.4	33.9	0.35	0.36
440	60.3	55.0	100.0	63.1	56.2	66.1	36.3	22.9	33.1	0.34	0.35
430	61.7	53.7	100.0	63.1	56.2	66.1	34.7	22.4	32.4	0.32	0.34
420	61.7	52.5	100.0	63.1	55.0	64.6	32.4	21.9	31.6	0.30	0.32
410	63.1	50.1	100.0	63.1	55.0	64.6	30.9	21.4	30.9	0.29	0.31
400	63.1	49.0	100.0	63.1	53.7	64.6	28.8	20.9	29.5	0.26	0.29
390	63.1	46.8	100.0	63.1	53.7	63.1	26.9	20.4	28.8	0.21	0.26
380	63.1	44.7	100.0	64.6	53.7	63.1	24.5	20.0	27.5	0.14	0.07
370	64.6	41.7	100.0	66.1	55.0	64.6	21.9	21.4	26.3	0.07	0.06
360	64.6	38.9	100.0	67.6	55.0	64.6	19.5	21.4	24.5	0.03	0.07
350	64.6	36.3	100.0	67.6	55.0	64.6	17.0	20.9	22.9	0.00	0.08
340	66.1	33.1	100.0	69.2	55.0	64.6	14.1	20.9	20.9	0.00	0.09
330	66.1	28.8	100.0	69.2	55.0	64.6	11.5	20.4	19.1	0.00	0.09
320	66.1	25.1	100.0	69.2	55.0	63.1	9.1	20.0	17.0	0.00	0.10
310	67.6	24.0	100.0	69.2	53.7	63.1	7.9	19.5	16.2	0.00	0.10
300	67.6	24.0	100.0	69.2	53.7	63.1	7.8	19.1	15.8	0.00	0.10
290	69.2	24.5	100.0	70.8	52.5	63.1	8.1	18.6	16.6	0.00	0.10
280	69.2	25.7	100.0	70.8	52.5	63.1	8.7	18.2	17.0	0.00	0.10
270	69.2	25.7	100.0	70.8	51.3	61.7	9.1	17.8	17.0	0.00	0.09
260	69.2	24.5	100.0	70.8	50.1	60.3	8.5	17.0	16.6	0.00	0.09
250	70.8	22.4	100.0	70.8	50.1	60.3	7.2	16.2	15.1	0.00	0.09

"Mix" is formulation Z-14L

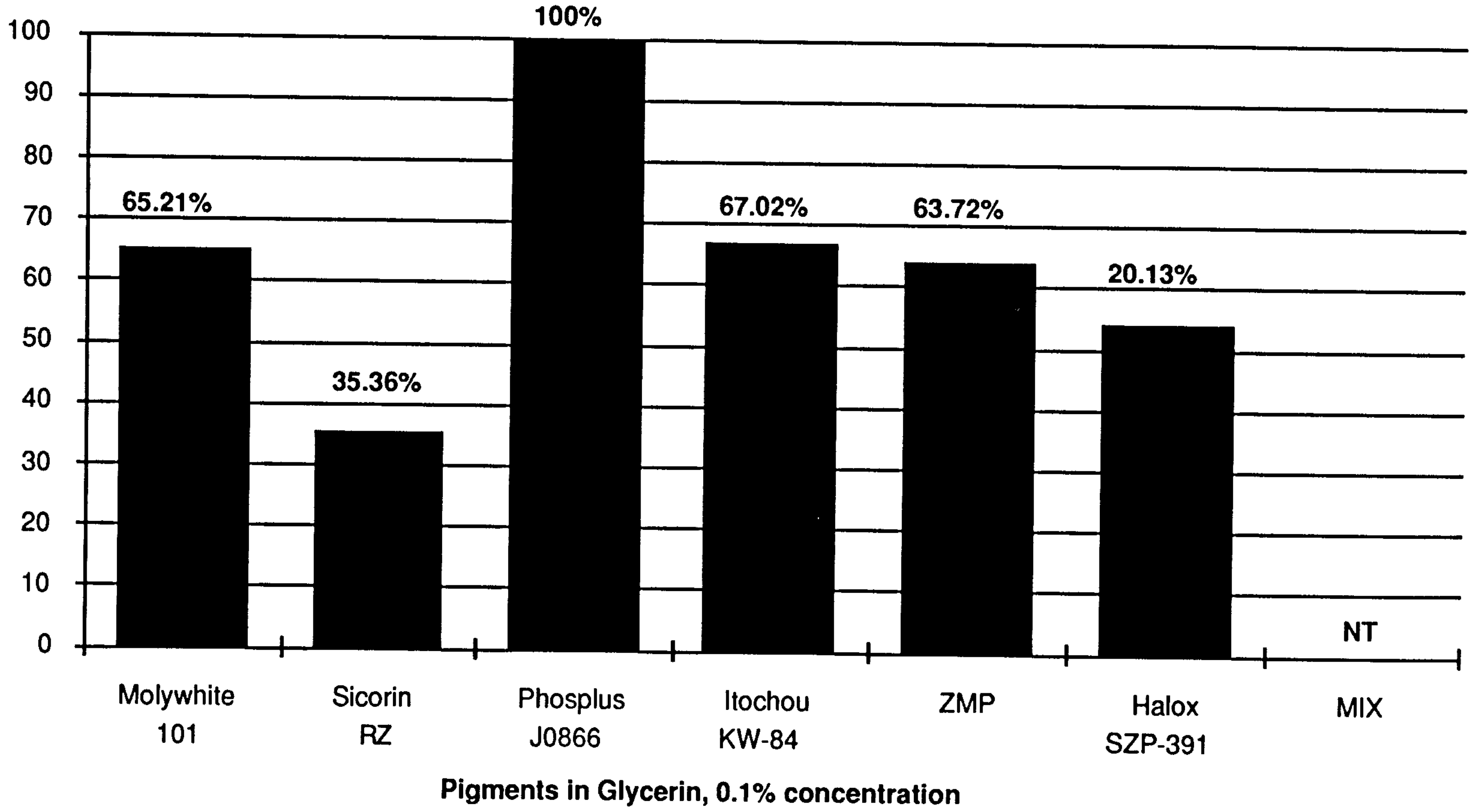


FIGURE 31
UV Transmission of Chromate Free Corrosion Inhibiting Pigments

Approved for public release; distribution is unlimited

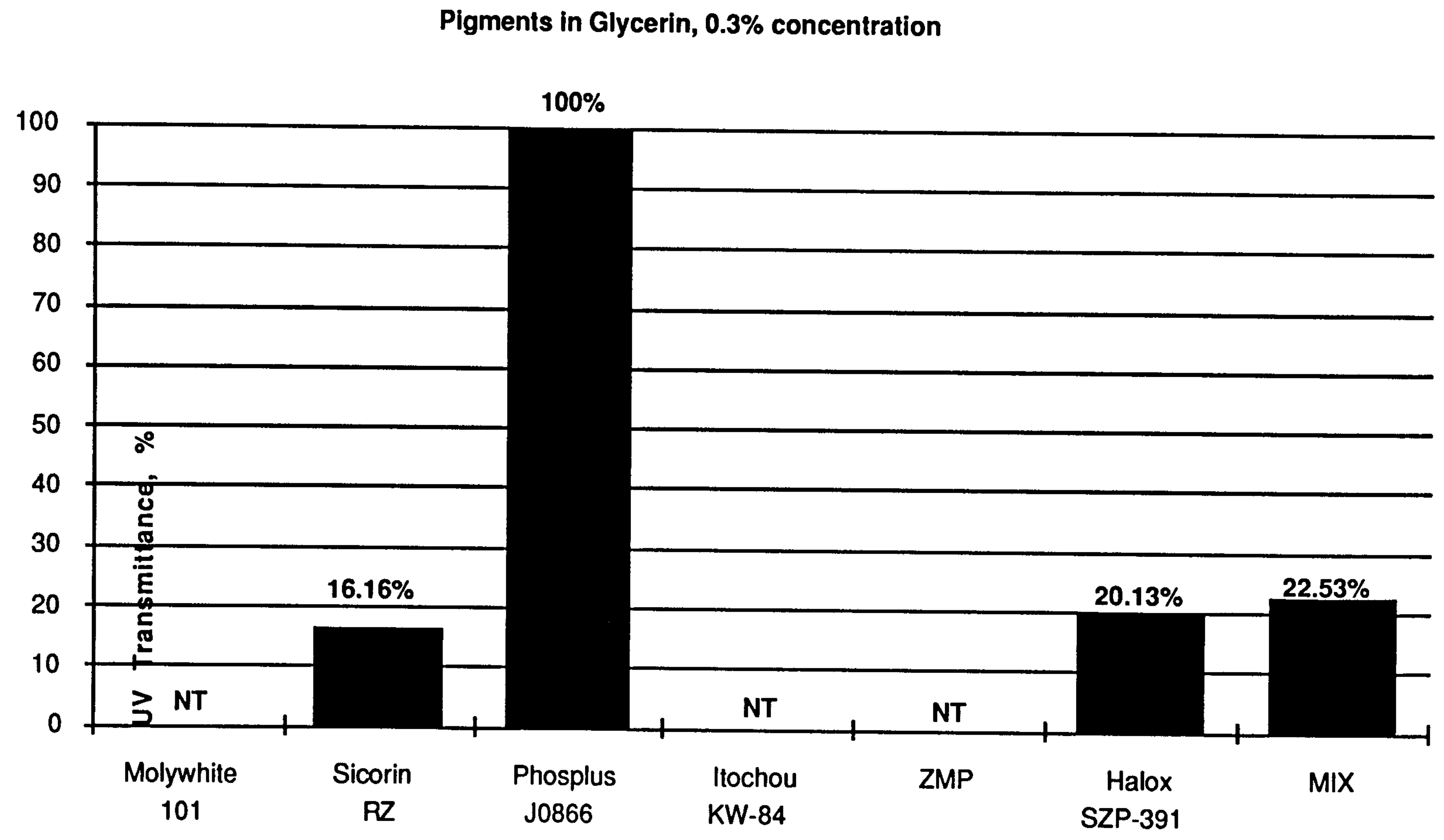


Figure 32
UV Transmission of Chromate Free Corrosion Inhibiting Pigments

Approved for public release; distribution is unlimited

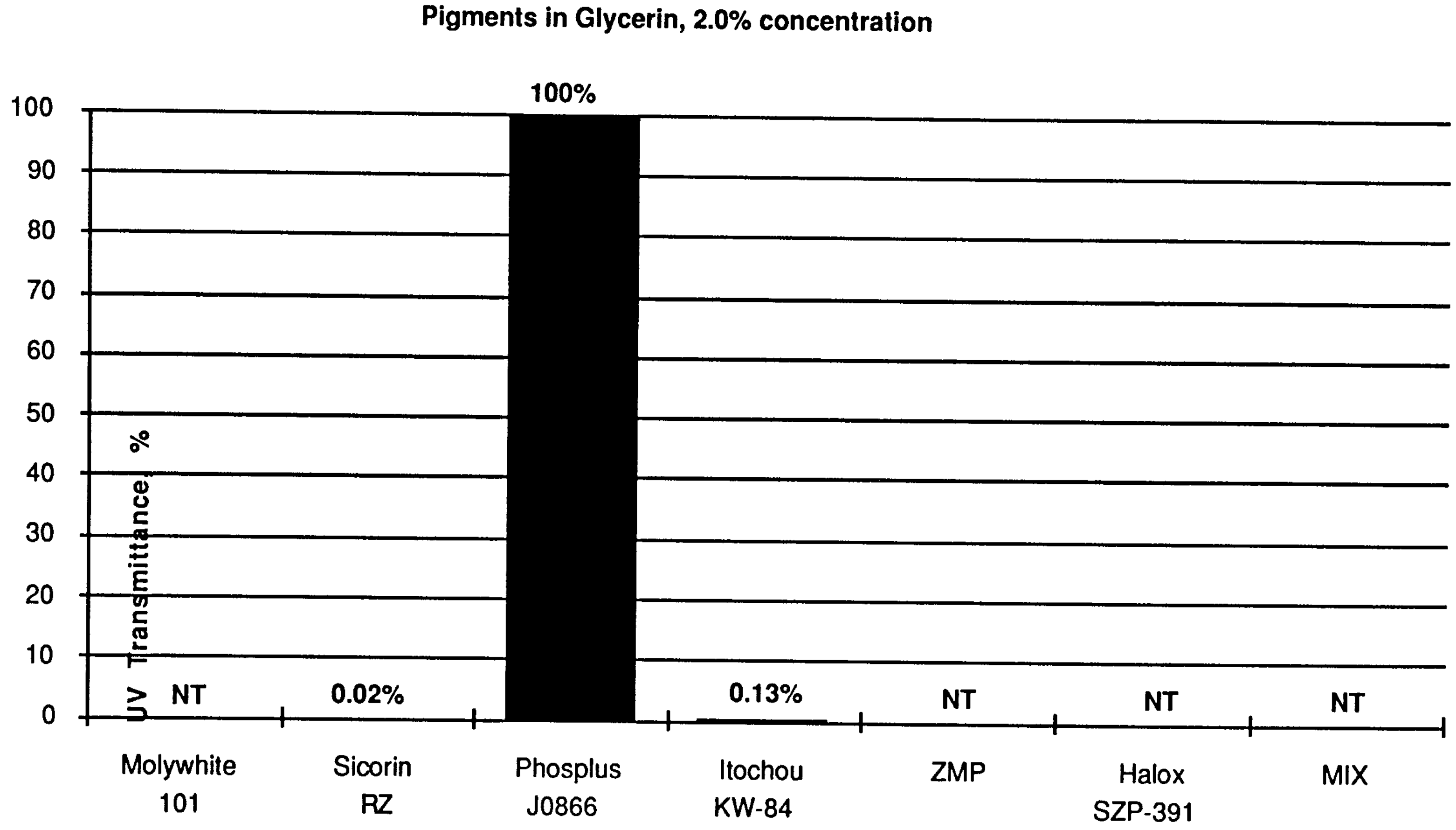


Figure 33
UV Transmission of Chromate Free Corrosion Inhibiting Pigments

4.3 Powder Coatings Development. The first coating development iteration was performed by HMSC, in order to determine the baseline properties of the various powder coating resin chemistries available in the industry. Prior to the initiation of this effort, NAWCADWAR developed the Z14L pigment system in a liquid polyurethane coating system, and demonstrated its effectiveness in both the lab and in field demonstrations [6]. This inhibitive pigment system was utilized extensively in the powder coating development effort. A non-corrosion inhibited pigment system was used as a negative control and consisted of either titanium dioxide (TiO_2) or TiO_2 combined with a small amount of carbon black (TiO_2-C). Since the Z14L pigment system has very low contrast ratio (ability to mask the substrate), it was combined or mixed with the high contrast ratio non-corrosion inhibited system to form a more practical formulation for exterior purposes. These three basic pigment packages (non-corrosion inhibited, Z14L, and Z14L/TiO_2 mixture system) were individually compounded into the epoxy & acrylic powder resins from Herberts and into the epoxy, epoxy-phenolic hybrid, acrylic, & low temp epoxy powder resins from Morton during the second coating development iteration. In the third coating development iteration, the Herberts epoxy and the Morton epoxy-phenolic hybrid were combined with these three pigment packages but at a decreased pigment volume concentration (PVC) level in an effort to increase the flexibility of these coatings. It is a generally accepted principle that flexibility is inversely related to PVC. The formulation parameters and the coating performance test data for the second iteration are provided in Tables 43 through 46. The formulation parameters and the test data for the third iteration are provided in Tables 47 through 49. Detailed test descriptions and rating systems are provided in Appendix F. The corrosion total performance evaluation (CTPE) data is provided in Tables 50 for the second iteration and in Table 51 for the third iteration.

4.3.1 Permeability. The ability of coatings to resist harsh operational fluids is typically a prerequisite for the selection of a potential protective coating system. Water, humidity, and operational aircraft fluid resistance tests were used to characterize the permeability properties of these coatings. The elevated exposure temperatures and varied durations, as listed in the test data tables and in Appendix F, were used to accelerate coating effects by increasing water ion mobility and/or the potential for chemical bond breakage. None of the coatings, on any of the three substrates, displayed coating defects (blisters, uplifting, softening, etc.) except for the M255-92-3 acrylic mixture formulation which failed the solvent (methyl ethyl ketone) resistance rub test. This failure can be attributed to the high PVC level (30%) of this formulation which exacerbated the already high level of porosity. In general, the powder coatings tested in this effort exhibited excellent permeability resistance regardless of the pigmentation composition or concentration.

4.3.2 Flexibility. Flexibility, and the ability to resist chipping and cracking, plays an important role in the durability and long term service life of protective coating systems. This is particularly true for aerospace applications since these coating systems are typically exposed to regular abuse from maintenance procedures, flight-induced rain impingement/erosion, and substrate flexing. Impact flexibility and low temperature (-60°F) cylindrical mandrel bend tests were used to characterize flexibility. For aerospace equipment, 10% for primers and 20% for topcoats and self-priming topcoats are acceptable minimum values. Mandrel bend requirements can range from 0.25 inch to 2 inches depending on the coating gloss and the coating function. The Morton epoxy-phenolic hybrid displayed excellent flexibility, with 10 to 40% for the second iteration and 60% across the board for the third iteration. The non-inhibited coatings generally displayed superior flexibility compared to the inhibited coatings.

4.3.3 Adhesion. Adhesion affects not only the ability of a coating system to remain in intimate contact with the underlying substrate, but also the ability of the coating system to resist corrosion. As discussed by Leidheiser [49], the onset of corrosion can occur after the

Table 43. Total Performance Evaluation (TPE) Comparison Results for the Second Iteration of Inhibited Powder Coatings.

		H070-70-1	H073-63-2	H073-63-3	H089-18-1	H089-18-2	H073-72-4	M255-89-1	M255-89-2	M255-89-3	M255-89-4	M255-90-1	M255-90-2	M255-90-3	M255-92-1	M255-92-2	M255-92-3	M255-95-1	M255-95-2	M255-95-3
FORMULATION DATA	RESIN SYS	EPOXY			ACRYLIC			EPOXY			EPOXY	EPOXY-PHENOLIC			ACRYLIC			LOW TEMP EPOXY		
	PVC (%)	25	30	25	15	15	15	23	22	30	28	23	22	30	23	22	30	23	22	30
	PIGMT SYS	14L	MIX	TiO	14L	MIX	TiO	TiO-C	14L	MIX	SZP391	TiO-C	14L	MIX	TiO-C	14L	MIX	TiO-C	14L	MIX
	CURE (°F)	250	250	250	275	275	275	300	300	300	300	300	300	300	300	300	300	300	300	300
TPE DATA	Al	90.30	87.00	81.00	88.90	88.90	80.50	93.10	90.40	95.10	90.30	94.50	95.80	92.90	87.50	92.60	88.50	88.40	92.30	92.30
	BG Steel	39.60	53.80	78.70	39.60	48.30	48.30	62.10	70.00	62.10	43.50	71.60	43.50	62.10	57.40	40.80	60.90	62.10	48.30	62.10
	ZPG Steel	92.90	100.00	78.70	85.80	85.80	92.90	92.90	88.20	92.90	66.90	92.90	85.80	95.30	78.70	63.40	60.90	66.90	85.80	92.90
	Substrate Avg	74.27	80.27	79.47	71.43	74.33	73.90	82.70	82.87	83.37	66.90	86.33	75.03	83.43	74.53	65.60	70.10	72.47	75.47	82.43

NOTE: Herberts epoxy mixture formulation consists of [25% Z14L / 5% TiO]
Herberts acrylic mixture formulation consists of[10% Z14L / 5% TiO]
Morton mixture formulations consist of [20% Z14L / 10% TiO]

Table 44. Test Results of the Second Iteration of Herberts Powder Coatings

ADHESION:	**Range:**	**Subtrate:**	H070-70-1	H073-63-2	H073-63-3	H089-18-1	H089-18-2	H073-72-4
Dry Tape "A" Method	0 - 5 (A)	std	5A	5A	4A	5A	5A	5A
Wet Tape (24 hr / RT)	0 - 5 (A)	std	5A	5A	5A	5A	5A	5A
Wet Tape (4 day / 120°F)	0 - 5 (A)	std	5A	5A	5A	5A	5A	5A
Wet Tape (7 day / 150°F)	0 - 5 (A)	std	5A	5A	4A	5A	5A	5A
Dry Tape "A" Method	0 - 5 (A)	BG-St	5A	5A	5A	5A	5A	5A
Wet Tape (7 day / 150°F)	0 - 5 (A)	BG-St	0A	1A	0A	2A	1A	1A
Dry Tape "A" Method	0 - 5 (A)	ZPG-St	5A	5A	5A	5A	5A	5A
Wet Tape (7 day / 150°F)	0 - 5 (A)	ZPG-St	4A	5A	2A	4A	4A	5A
FLUID/CORROSION RESISTANCE:								
Salt Spray (2000 hr)	P, +, -, F	std	P	P	P	P	P	F
SO2 Spray (500 hr)	P, +, -, F	std	-	-	-	-	-	-/F
Filiform Corrosion	P, +, -, F	alclad	P	P/-	P/F	P	P	P
Salt Spray (500 hr)	P, +, -, F	BG-St	F	+ [1]	P	F	-	-
SO2 Spray (96 hr)	P, +, -, F	BG-St	F	F [1]	P	F	-	-
Salt Spray (500 hr)	P, +, -, F	ZPG-St	P	P [1]	P	+	+	+
SO2 Spray (96 hr)	P, +, -, F	ZPG-St	P	P [1]	P	P	P	P
H2O Resistance (24 h/RT)	P, +, -, F	std	P	P	P	P	P	P
H2O Resistance (4 d/120°F)	P, +, -, F	std	P	P	P	P	P	P
H2O Resistance (7 d/150°F)	P, +, -, F	std/B/Z	P/P/P	P/P/P	P/P/P	P/P/P	P/P/P	P/P/P
Humidity Resistance	P, +, -, F	std	P	P	P	P	P	P
Xe Weatherometer (500 hr)	60° Gloss	std	56.6	32.4	70.4	53.3	71.3	88.8
Xe Weatherometer (500 hr)	Delta E	std	7.11	7.59	3.19	4.22	2.8	0.31
23699 Oil (24 hr / 250°F)	P, +, -, F	std	P	P	P	P	P	P
83282 Hydraulic(24 h/150°F)	P, +, -, F	std	P	P	P	P	P	P
Hydrocarbon JP-5(7d/RT)	P, +, -, F	std	P	P	P	P	P	P
Solvent Resistance	P, +, -, F	std	P	P	P	P	P	P
FLEXIBILITY:								
GE Impact	0.5%-60%	flex	10/5	2	2	0.5	0.5	0.5
Mandrel Bend (-60°F)	0.125".....1"	flex	0.25	>0.25	>0.5	0.125	>0.5	>0.5
MISCELLANEOUS:								
60° Gloss		std	85.8	89.8	94.5	63.5	72.2	82.2
Color (L/a/b)		std	61/2.4/1.6	77/-0.8/-1.4	97/-1.2/2.1	61/1.1/1.5	89/-1.2/0.2	96/-1.2/0.5
DFT Range (mils)			1.8 - 2.2	1.8 - 2.2	1.8 - 2.2	1.8 - 2.2	1.8 - 2.2	1.8-2.2

Note: std = 2024 T3 with CCC, alclad = 2024 T3 Alcad with CCC, flex = 2024 T0 with CAA
BG-St = 1010 Steel Bare Ground On One Side, ZPG-St = 1010 Steel with Zinc Phosphate Ground On One Side
For corrosion tests: Overall Rating [# of samples if other than the normal 2]
P = pass, + = borderline pass, - = borderline fail, F = fail
Single diagonal scribe (positive slope) for corrosion test on steel substrates.
DFT Range data was provided by manufacturer.

Table 45 Test Results of the Second Iteration of Morton Powder Coatings

ADHESION:	Range:	Subtrate:	M255-89-1	M255-89-2	M255-89-3	M255-89-4	M255-90-1	M255-90-2	M255-90-3
Dry Tape "A" Method	0 - 5 (A)	std	5A	5A	5A	5A	5A	5A	5A
Wet Tape (24 hr / RT)	0 - 5 (A)	std	5A	5A	5A	5A	5A	5A	5A
Wet Tape (4 day / 120°F)	0 - 5 (A)	std	5A	5A	5A	5A	5A	5A	5A
Wet Tape (7 day / 150°F)	0 - 5 (A)	std	5A	5A	5A	5A	5A	5A	5A
Dry Tape "A" Method	0 - 5 (A)	BG-St	5A	5A	5A	5A	5A	5A	5A
Wet Tape (7 day / 150°F)	0 - 5 (A)	BG-St	0A	1A	1A	1A	0A	0A	1A
Dry Tape "A" Method	0 - 5 (A)	ZPG-St	5A	5A	5A	4A	5A	5A	5A
Wet Tape (7 day / 150°F)	0 - 5 (A)	ZPG-St	5A	4A	5A	3A	5A	4A	5A
FLUID/CORROSION RESISTANCE:									
Salt Spray (2000 hr)	P, +, -, F	std	P	P	P	P	P	P	P/+
SO2 Spray (500 hr)	P, +, -, F	std	-	P/+	P	-	-	+	+
Filiform Corrosion	P, +, -, F	alclad	P	+	P	P	P	P	P
Salt Spray (500 hr)	P, +, -, F	BG-St	+/-	P/+	-	F	+ [1]	F	-
SO2 Spray (96 hr)	P, +, -, F	BG-St	P	P/+	P	-	P [1]	-	P
Salt Spray (500 hr)	P, +, -, F	ZPG-St	+	P/+	+	+	+	+	P/+
SO2 Spray (96 hr)	P, +, -, F	ZPG-St	P	P	P	+	P	P	P
H2O Resistance (24 h/RT)	P, +, -, F	std	P	P	P	P	P	P	P
H2O Resistance (4 d/120°F)	P, +, -, F	std	P	P	P	P	P	P	P
H2O Resistance (7 d/150°F)	P, +, -, F	std/B/Z	P/P/P	P/P/P	P/P/P	P/P/P	P/P/P	P/P/P	P/P/P
Humidity Resistance	P, +, -, F	std	P	P	P	P	P	P	P
Xe Weatherometer (500 hr)	60° Gloss	std	61.1	63.4	29.1	68.3	68.3	71.5	62.3
Xe Weatherometer (500 hr)	Delta E	std	3	3.51	3.26	1.81	3.2	5.29	3.35
23699 Oil (24 hr / 250°F)	P, +, -, F	std	P	P	P	P	P	P	P
83282 Hydraulic(24 h/150°F)	P, +, -, F	std	P	P	P	P	P	P	P
Hydrocarbon JP-5(7d/RT)	P, +, -, F	std	P	P	P	P	P	P	P
Solvent Resistance	P, +, -, F	std	P	P	P	P	P	P	P
FLEXIBILITY:									
GE Impact test)	0.5%-60%	flex	20	2	5	5	40	20	10
Mandrel Bend (-60°F)	0.125".....1"	flex	>0.25	>0.25	>0.25	>0.5	>0.25	0.125	>0.25
MISCELLANEOUS:									
60° Gloss		std	82.9	80.0	51.6	74.5	100	91.3	89.6
Color (L/a/b)		std	56/-3.1/-4.9	73/-1.3/7.5	57/-2.9/-3.6	60/1.1/2.9	55/-2.8/-5.5	67/-0.1/4.0	56.0/-3.1/-4.9
DFT Range (mils)			1.3 - 2.5	2.7 - 5.2	1.6 - 3.2	1.3 - 3.2	1.7 - 3.9	1.4 - 3.4	1.0 - 3.3

Note: std = 2024 T3 with CCC, alclad = 2024 T3 Alcad with CCC, flex = 2024 T0 with CAA
BG-St = 1010 Steel Bare Ground On One Side, ZPG-St = 1010 Steel with Zinc Phosphate Ground On One Side
For corrosion tests: Overall Rating [# of samples if other than the normal 2]
P = pass, + = borderline pass, - = borderline fail, F = fail
Single diagonal scribe (positive slope) for corrosion test on steel substrates.
DFT Range data was provided by manufacturer.

Table 46. Results of the Second Iteration of Morton Powder Coatings

ADHESION:	**Range:**		M255-92-1	M255-92-2	M255-92-3	M255-95-1	M255-95-2	M255-95-3
Dry Tape "A" Method	0 - 5 (A)	std	5A	4A	5A	5A	5A	5A
Wet Tape (24 hr / RT)	0 - 5 (A)	std	5A	5A	5A	4A	5A	5A
Wet Tape (4 day / 120°F)	0 - 5 (A)	std	5A	5A	5A	5A	5A	5A
Wet Tape (7 day / 150°F)	0 - 5 (A)	std	5A	5A	5A	4A	5A	5A
Dry Tape "A" Method	0 - 5 (A)	BG-St	5A	4A	5A	5A	5A	5A
Wet Tape (7 day / 150°F)	0 - 5 (A)	BG-St	1A	3A	5A	1A	0A	3A
Dry Tape "A" Method	0 - 5 (A)	ZPG-St	5A	4A	5A	5A	5A	5A
Wet Tape (7 day / 150°F)	0 - 5 (A)	ZPG-St	5A	3A	5A	3A	4A	5A
FLUID/CORROSION RESISTANCE:								
Salt Spray (2000 hr)	P, +, -, F	std	P	P	P	P	P	P
SO2 Spray (500 hr)	P, +, -, F	std	F	P	P/+	+/-	P/+	P/+
Filiform Corrosion	P, +, -, F	alclad	P	P	P	P	P	P
Salt Spray (500 hr)	P, +, -, F	BG-St	F	F	F	-	-	F
SO2 Spray (96 hr)	P, +, -, F	BG-St	P	F	F	P	-	P
Salt Spray (500 hr)	P, +, -, F	ZPG-St	F	-	F	-	+	+
SO2 Spray (96 hr)	P, +, -, F	ZPG-St	P	P	F	P	P	P
H2O Resistance (24 h/RT)	P, +, -, F	std	P	P	P	P	P	P
H2O Resistance (4 d/120°F)	P, +, -, F	std	P	P	P	P	P	P
H2O Resistance (7 d/150°F)	P, +, -, F	std/B/Z	P/P/P	P/P/P	P/P/P	P/P/P	P/P/P	P/P/P
Humidity Resistance	P, +, -, F	std	P	P	P	P	P	P
Xe Weatherometer (500 hr)	60° Gloss	std	1.3	1.9	0.6	74.6	73.4	57.8
Xe Weatherometer (500 hr)	Delta E	std	0.41	6.91	1.1	2.76	2.03	2.55
23699 Oil (24 hr / 250°F)	P, +, -, F	std	P	P	P	P	P	P
83282 Hydraulic(24 h/150°F)	P, +, -, F	std	P	P	P	P	P	P
Hydrocarbon JP-5(7d/RT)	P, +, -, F	std	P	P	P	P	P	P
Solvent Resistance	P, +, -, F	std	P	P	F@45	P	P	P
FLEXIBILITY:								
GE Impact test)	0.5%-60%	flex	1	1	2	20	2	1
Mandrel Bend (-60°F)	0.125".....1"	flex	0.25	>0.25	0.25	>0.5	>0.25	>0.25
MISCELLANEOUS:								
60° Gloss		std	1.2	2.1	0.6	96.2	83.9	80.9
Color (L/a/b)		std	55/-2.2/-5.3	65/-2.6/-4.6	51/-2.4/-3.5	55/-2.6/-4.9	62/0.6/9.9	56/-2.5/-3.6
DFT Range (mils)			2.1 - 4.5	1.9 - 4.3	1.6 - 5.2	1.6 - 3.7	1.3 - 3.0	0.9 - 3.3

Note: std = 2024 T3 with CCC, alclad = 2024 T3 Alcad with CCC, flex = 2024 T0 with CAA
BG-St = 1010 Steel Bare Ground On One Side, ZPG-St = 1010 Steel with Zinc Phosphate Ground On One Side
For corrosion tests: Overall Rating [# of samples if other than the normal 2]
P = pass, + = borderline pass, - = borderline fail, F = fail
Single diagonal scribe (positive slope) for corrosion test on steel substrates.
DFT Range data was provided by manufacturer.

Table 47. Total Performance Evaluation (TPE) Comparison Results for the Third Iteration of Inhibited Powder Coatings

		H096-22-1	H096-22-2	H096-22-3	H096-22-4	M281-7-1	M281-7-2	M281-7-3	STD PR/TC
FORMULATION DATA	RESIN SYS	EPOXY			EPOXY	EPOXY-PHENOLIC			EPOXY/PU
	PVC (%)	20	20	20	20	15	15	15	27 / 16
	PIGMT SYS	TiO	14L	MIX	MIX	TiO-C	14L	MIX	SrCrO / TiO
	CURE (°F)	275	275	275	300	300	300	300	75
TPE DATA	Al	91.60	89.00	79.70	88.90	93.20	93.20	90.70	88.20
	BG Steel	62.60	55.30	63.30	70.10	73.80	63.20	88.80	88.80
	ZPG Steel	78.20	92.50	83.80	86.90	96.30	85.00	92.50	96.30
	Substrate Avg	77.47	78.93	75.60	81.97	87.77	80.47	90.67	91.10

NOTE: Herberts mixture formulations consists of [13% Z14L / 7% TiO]
Morton mixture formulation consists of [10% Z14L / 5% TiO]
Std Pr/TC consists of MIL-P-85582 and MIL-C-85285
PVC values for Std Pr/TC are estimates

electrolyte has been allowed to diffuse through the coating, accumulate at the coating/substrate interface, and after chemical bonds at this interface have been disrupted. The property of adhesion was characterized by using the dry tape test and the wet (water immersion exposure) tape test. In general, the adhesion properties of all the powder coatings tested were good. Dry adhesion on all three substrate types was excellent without exception. Wet adhesion, on the other hand, displayed some variation in performance between the coating/substrate systems. Wet adhesion was excellent on aluminum without exception, generally poor on bare steel, and generally excellent on zinc phosphated steel. It is important to note that the bare steel substrate (i.e., no physical and/or chemical treatment) is not representative of actual steel substrates used in the field. For instance, most steel substrates will either receive a physical surface abrasion treatment and/or a chemical treatment. The performance of the corrosion inhibitor-containing coatings did not display a noticeable effect on adhesion versus the negative control coating formulations.

4.3.4 Corrosion. Scribed coating/substrate specimens were exposed to 5% NaCl salt fog per ASTM B117, SO_2/salt fog per ASTM G85, and filiform per ASTM D 2803. Of

Table 48. Test Results of the Third Iteration of Herberts Powder Coatings

			H096-22-1	H096-22-2	H096-22-3		H096-22-4
ADHESION:	**Range:**	**Substrate:**					
Dry Tape "A" Method	0 - 5 (A)	std	5	5	5		5
Wet Tape (24 hr / RT)	0 - 5 (A)	std	5	5	5		5
Wet Tape (4 day / 120°F)	0 - 5 (A)	std	5	5	5		5
Wet Tape (7 day / 150°F)	0 - 5 (A)	std	5	5	5		5
Dry Tape "A" Method	0 - 5 (A)	BG-St	5	5	4		5
Wet Tape (24 hr / RT)	0 - 5 (A)	BG-St	4	4	4		4
Wet Tape (4 day / 120°F)	0 - 5 (A)	BG-St	1	0	0		0
Wet Tape (7 day / 150°F)	0 - 5 (A)	BG-St	0	0	0		0
Dry Tape "A" Method	0 - 5 (A)	ZPG-St	4	5	5		4
Wet Tape (24 hr / RT)	0 - 5 (A)	ZPG-St	4	5	4		4
Wet Tape (4 day / 120°F)	0 - 5 (A)	ZPG-St	4	4	3		5
Wet Tape (7 day / 150°F)	0 - 5 (A)	ZPG-St	4/3	4	4		4
FLUID/CORROSION RESISTANCE:							
Salt Spray (2000 hr)	P, +, -, F	std	P	P	+/-		P
SO2 Spray (500 hr)	P, +, -, F	std	+/-	+	-		-
Filiform Corrosion	P, +, -, F	alclad	P	P/+	P/F		P
Salt Spray (500 hr)	P, +, -, F	BG-St	F	F	+/-		+
SO2 Spray (96 hr)	P, +, -, F	BG-St	P	-	P		P
Salt Spray (500 hr)	P, +, -, F	ZPG-St	+	P	P		+
SO2 Spray (96 hr)	P, +, -, F	ZPG-St	P	P	P		P
H2O Resis (24 h/RT)	P, +, -, F	std/B/Z	P/P/P	P/P/P	P/P/P		P/P/P
H2O Resis (4 d/120°F)	P, +, -, F	std/B/Z	P/P/P	P/P/P	P/P/P		P/P/P
H2O Resis (7 d/150°F)	P, +, -, F	std/B/Z	P/P/P	P/P/P	P/P/P		P/P/P
Humidity Resistance	P, +, -, F	std	P	P	P		P
Xe W-ometer (500 hr)	60° Gloss	std	58.2	52	30.6		37.8
Xe W-ometer (500 hr)	Delta E	std	5.17	8.97	7.26		7.86
Xe W-ometer (500 hr)	GE Impact	flex	10	5	5		5
23699 Oil (24 hr / 250°F)	P, +, -, F	std	P	P	P		P
83282 HydrFl(24h/150°F)	P, +, -, F	std	P	P	P		P
Hydrocarbon JP-5(7d/RT)	P, +, -, F	std	P	P	P		P
Solvent Resistance	P, +, -, F	std	P	P	P		P
FLEXIBILITY:							
GE Impact	0.5 - 60%	flex	20	5	5		5
Mandrel Bend (-60°F)	0.25....1"	flex	0.5	0.75	0.5		0.5
MISCELLANEOUS:							
Gloss (60°)			97.2	91.5	98.6		96.8
Color (L/a/b)			96/-1.3/1.9	67/0.5/2.0	93/-1.6/3.7		87/-1.6/0.4
81294 Removal (hrs)		std/B/Z	5/6/0.17	2/7/1	2/5/0.17		0.5/0.17/2
DFT (mean, SD) mils			2.49, 0.39	2.36, 0.25	2.60, 0.45		2.48, 0.48

Note: std = 2024 T3 with CCC, alclad = 2024 T3 Alcad with CCC, flex = 2024 T0 with CAA
BG-St = 1010 Steel Bare Ground On One Side, ZPG-St = 1010 Steel with Zinc Phosphate Ground On One Side
P = pass, + = borderline pass, - = borderline fail, F = fail
Single diagonal scribe (positive slope) for corrosion test on steel substrates.

Table 49. Test Results of the Third Iteration of Morton Powder Coatings

ADHESION:	**Range:**	**Substrate:**	M281-7-1	M281-7-2	M281-7-3		Std Pr/TC
Dry Tape "A" Method	0 - 5 (A)	std	5	5	5		5
Wet Tape (24 hr / RT)	0 - 5 (A)	std	5	5	5		5
Wet Tape (4 day / 120°F)	0 - 5 (A)	std	5	5	5		5
Wet Tape (7 day / 150°F)	0 - 5 (A)	std	5	5	5		5/4
Dry Tape "A" Method	0 - 5 (A)	BG-St	5	5	5		5
Wet Tape (24 hr / RT)	0 - 5 (A)	BG-St	5	5	5		4
Wet Tape (4 day / 120°F)	0 - 5 (A)	BG-St	4	0	5		5
Wet Tape (7 day / 150°F)	0 - 5 (A)	BG-St	0	0	5		4
Dry Tape "A" Method	0 - 5 (A)	ZPG-St	5	5	5		5
Wet Tape (24 hr / RT)	0 - 5 (A)	ZPG-St	5	5	5		5
Wet Tape (4 day / 120°F)	0 - 5 (A)	ZPG-St	5	5	4		5
Wet Tape (7 day / 150°F)	0 - 5 (A)	ZPG-St	5	1	5		5
FLUID/CORROSION RESISTANCE:							
Salt Spray (2000 hr)	P, +, -, F	std	P	P	P		P
SO2 Spray (500 hr)	P, +, -, F	std	+	+	+/-		F
Filiform Corrosion	P, +, -, F	alclad	P/F	+/F	-		P
Salt Spray (500 hr)	P, +, -, F	BG-St	F	F	F		+
SO2 Spray (96 hr)	P, +, -, F	BG-St	P	+	P		P
Salt Spray (500 hr)	P, +, -, F	ZPG-St	+	+	+		+
SO2 Spray (96 hr)	P, +, -, F	ZPG-St	P	P	P		P
H2O Resis (24 h/RT)	P, +, -, F	std/B/Z	P/P/P	P/P/P	P/P/P		P/P/P
H2O Resis (4 d/120°F)	P, +, -, F	std/B/Z	P/P/P	P/P/P	P/P/P		P/P/P
H2O Resis (7 d/150°F)	P, +, -, F	std/B/Z	P/P/P	P/P/P	P/P/P		P/P/P
Humidity Resistance	P, +, -, F	std	P	P	P		P
Xe W-ometer (500 hr)	60° Gloss	std	60.6	79.4	63.9		1.8
Xe W-ometer (500 hr)	Delta E	std	3.42	4.74	4.27		0.11
Xe W-ometer (500 hr)	GE Impact	flex	60	60	60		10
23699 Oil (24 hr / 250°F)	P, +, -, F	std	P	P	P		P
83282 HydrFl(24h/150°F)	P, +, -, F	std	P	P	P		P
Hydrocarbon JP-5(7d/RT)	P, +, -, F	std	P	P	P		P
Solvent Resistance	P, +, -, F	std	P	P	P		P
FLEXIBILITY:							
GE Impact	0.5 - 60%	flex	60	60	60		10.0
Mandrel Bend (-60°F)	0.25....1"	flex	0.25	0.25	0.25		0.5
MISCELLANEOUS:							
Gloss (60°)			103.5	95.3	96.8		1.9
Color (L/a/b)			57/-2.7/-4.5	60/1.0/6.7	57/-1.4/-4.3		58/-1.3/-2.5
81294 Removal (hrs)		std/B/Z	7/3/>8	6/0.5/4	6/3/2		1/1/1
DFT (mean, SD) mils			1.85, 0.30	2.34, 0.26	1.95, 0.27		2.60, 0.32

Note: std = 2024 T3 with CCC, alclad = 2024 T3 Alcad with CCC, flex = 2024 T0 with CAA

BG-St = 1010 Steel Bare Ground On One Side, ZPG-St = 1010 Steel with Zinc Phosphate Ground On One Side

P = pass, + = borderline pass, - = borderline fail, F = fail

Single diagonal scribe (positive slope) for corrosion test on steel substrates.

Table 50. Corrosion TPE Results for the Second Iteration of Powder Coatings

		H070-70-1	H073-63-2	H073-63-3	H089-18-1	H089-18-2	H073-72-4	M255-89-1	M255-89-2	M255-89-3	M255-89-4	M255-90-1	M255-90-2	M255-90-3	M255-92-1	M255-92-2	M255-92-3	M255-95-1	M255-95-2	M255-95-3
FORMULATION DATA	RESIN SYS	EPOXY			ACRYLIC			EPOXY			EPOXY	EPOXY-PHENOLIC			ACRYLIC			LOW TEMP EPOXY		
	PVC (%)	25	30	25	15	15	15	23	22	30	28	23	22	30	23	22	30	23	22	30
	PIGMT SYS	Z14L	MIX	TiO	Z14L	MIX	TiO	TiO-C	Z14L	MIX	SZP391	TiO-C	Z14L	MIX	TiO-C	Z14L	MIX	TiO-C	Z14L	MIX
	CURE (°F)	250	250	250	275	275	275	300	300	300	300	300	300	300	300	300	300	300	300	300
CORROSION TPE DATA	Al	77.20	68.10	55.90	77.20	77.20	37.30	77.20	84.40	100.00	65.40	77.20	90.20	82.80	70.70	100.00	93.50	77.20	93.50	93.50
	BG Steel	10.00	42.70	100.00	10.00	30.00	30.00	61.90	80.00	61.90	19.10	83.70	19.10	61.90	51.00	10.00	10.00	61.90	30.00	51.00
	ZPG Steel	100.00	100.00	100.00	83.70	83.70	83.70	83.70	89.10	83.70	70.00	83.70	83.70	89.10	51.00	61.90	10.00	61.90	83.70	83.70

NOTE: Herberts epoxy mixture formulation consists of [25% Z14L / 5% TiO]
Herberts acrylic mixture formulation consists of[10% Z14L / 5% TiO]
Morton mixture formulations consist of [20% Z14L / 10% TiO]

Table 51. Corrosion TPE Results for the Third Iteration of Powder Coatings

		H096-22-1	H096-22-2	H096-22-3	H096-22-4	M281-7-1	M281-7-2	M281-7-3	STD PR/TC
FORMULATION DATA	RESIN SYS	EPOXY			EPOXY	EPOXY-PHENOLIC			EPOXY/PU
	PVC (%)	20	20	20	20	15	15	15	27 / 16
	PIGMT SYS	TiO	Z14L	MIX	MIX	TiO-C	Z14L	MIX	SrCrO / TiO
	CURE (°F)	275	275	275	300	300	300	300	75
CORROSION TPE DATA	Al	77.20	84.10	30.00	77.20	69.00	69.00	55.90	70.70
	BG Steel	51.00	19.10	61.90	83.70	51.00	37.30	51.00	83.70
	ZPG Steel	83.70	100.00	100.00	83.70	83.70	83.70	83.70	83.70

NOTE: Herberts mixture formulations consists of [13% Z14L / 7% TiO]
Morton mixture formulation consists of [10% Z14L / 5% TiO]
Std Pr/TC consists of MIL-P-85582 and MIL-C-85285
PVC values for Std Pr/TC are estimates

the three substrates types, the powder coatings provided the lowest level of protection to the bare steel substrate. This was expected since this grade of steel (SAE 1010) is very susceptible to corrosion and did not contain a pre-paint treatment. As indicated in the corrosion performance data in Tables 44 to 46, and in the corrosion TPE data in Tables 50 and 51, the corrosion inhibited pigment systems provided a positive effect on the overall corrosion resistance on aluminum surfaces. The opposite was true on bare steel where the corrosion inhibited pigment systems provided a negative effect. Although the performance of the coatings on zinc phosphated steel was vastly superior to that on the bare steel substrate, the effect of the inhibitors does not impart a definite positive influence on zinc-phosphated steel substrates.

4.3.5 Overall Coating Performance. Using a single-tailed, paired Student's t analysis of the coating TPE data for the individual substrate types, the effect of the pigment systems containing corrosion inhibitors compared to the non-corrosion inhibited pigment system on the overall coating performance was obtained. At a 83.4% confidence level, the inhibitors provided a positive effect on overall coating performance on aluminum. Typical engineering confidence levels are 95% or greater. Nonetheless, a confidence level of 83.4% is still considered scientifically interesting. It should be noted that the second coating formulation iteration alone yielded a confidence level of 99.2% that the inhibitive pigment system provided a positive effect on aluminum. For the third coating formulation iteration on aluminum, the uninhibited pigment system performed better than the inhibited pigment based on a 93.6%

confidence level. This difference in TPE data is attributed to the reduction in PVC and thus a reduction in the concentration of corrosion inhibitive pigments in the third iteration. This was reflected in the corrosion resistance data and thus the overall performance on aluminum via TPE analysis was adversely affected in the formulations used in the third iteration.

At a 98.6% confidence level, the uninhibited formulations outperformed the inhibited formulations on bare steel. The contribution to corrosion resistance provided by the barrier properties of the titanium dioxide based pigment system is the apparent reason for this effect.

At a 57.1% confidence level, the inhibited coatings were superior to the uninhibited coatings on zinc phosphated steel. From a practical standpoint, this indicates that the inhibited and the uninhibited pigment systems provide essentially equivalent effects in these powder coatings on zinc phosphated steel.

4.3.6 HMSC-Tucson Powder Coating Test Results. The test results for powder coatings tested at HMSC-Tucson are shown in Tables 52 and 53. Table 52 shows the results of the first iteration of coatings and Table 53 contains the results from the second iteration of coatings.

4.3.6.1 Cure Time and Temperature. In general, materials were cured in accordance with the manufacturer's recommendations. Cure was verified by rubbing the coating surface lightly with a lint-free tissue wetted with methyl ethyl ketone (MEK); removal of the coating indicated undercured powder. Cure temperatures and times for the Morton powders were 149°C (300°F) for 30 minutes. Herberts provided two low-cure powders -- one which cured at 135°C (275°F) and the other which cured at 121°C (250°F). These two low-cure materials exhibited marginal physical properties, especially with respect to wet tape adhesion. After retesting the 121°C (250°F) powder at a higher cure temperature (149°C [300°F]) adhesion properties significantly improved.

One possible reason for the decreased performance at low cure temperatures is that the material might have been slightly undercured (inadequately crosslinked). However, no evidence of significant undercuring was seen in the MEK wipe or solvent exposure tests. Other factors may also have contributed to the improvement with a higher cure temperature. For example, experience at Hughes has indicated that higher cure temperatures tend to improve adhesion by driving organics and adsorbed water at the substrate surface into the coating, where they are bound in the crosslinking. When this surface contamination is slight little or no degradation of the cured coating is seen.

4.3.6.2 Material Type. A variety of materials were tested, including various epoxies, acrylics, and blends (epoxy phenolics). The only significant difference noted was that acrylics, as a class, tended to have lower flexibility than the epoxies and the blends.

4.3.6.3 Adhesion (Wet Tape). All the baseline epoxies and epoxy blends passed the 24 hour soak/wet tape test (5A rating) except for one very hard formulation provided by Morton and the low-cure temperature version manufactured by Herberts. Re-curing the low-cure material at 300 F improved the adhesion value (to 5A). The low-cure acrylic also exhibited marginal adhesion, with a 3A. Similarly, all the baseline materials performed well after a 96 hour soak, except as noted above. After 168 hours two additional powders showed a slight decrease in performance (falling to 4A). These were a second hard epoxy and an epoxy formulation, both provided by Morton.

The inhibited powders had good adhesion to aluminum under all test conditions, but exhibited marginal performance on steel (3A to 4A). This may indicate a problem with the surface preparation of the steel rather than a deficiency in the powder.

Table 52. First Iteration Test Results for Powder Coatings Sprayed and Tested at HMSC-Tucson

	M003	M005	M006	M007	MOO8	M009	M010	M011	M012	M013
Cure Temperature, F	300	300	300	300	300	300	300	300	300	300
Cure Time, Min.	30	30	30	30	30	30	30	30	30	30
Material Type	Hard Epoxy	Acrylic	Epoxy	Epxy/Phnlic	Epxy/Phnlic	Hybrid	Hard Epoxy	Epoxy	Epoxy	Acrylic
Color	Grey	Grey	Grey	Grey	Grey	Grey	Grey	Grey	Grey	Grey
Tape Test, 24 Hr. Water Soak	5A	5A	5A	5A	5A	5A	3A	5A	5A	5A
Tape Test, 96 Hr. Water Soak	5A	5A	5A	5A	5A	5A	3A	5A	5A	5A
Tape Test, 168 Hr. Water Soak	4A	5A	4A	5A	5A	5A	3A	5A	5A	5A
JP4 Fluid Resistance	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Salt Fog, 500 Hr.	(P)ASS	(P)ASS	(P)ASS	(P)ASS	(P)ASS	(P)ASS	(P)ASS	(P)ASS	(P)ASS	(P)ASS
Salt Fog, 2000 Hr,	NO TEST	4/4 (P)ASS	4/4 (P)ASS	4/4 (P)ASS	4/4 (P)ASS	4/4 (P)ASS	3 (F)AIL	4/4 (P)ASS	3 (PASS)	4/4 (F)AIL
Flexibility, 42 Inch, %	>60 PASS	20	>60 PASS	>60 PASS	>60 PASS	>60 PASS	>60 PASS	>60 PASS	>60 PASS	>60 PASS

	HOO1	H002	H003
Cure Temperature, F	250	275	300
Cure Time, Min.	35	35	35
Material Type	Epoxy	Acrylic	Epoxy
Color	White	White	White
Tape Test, 24 Hr. Water Soak	3A	3A	5A
Tape Test, 96 Hr. Water Soak	3A	3A	PASS
Tape Test, 168 Hr. Water Soak	3A	3A	PASS
JP4 Fluid Resistance	PASS	PASS	PASS
Salt Fog, 500 Hr.	-	(P)ASS	(P)ASS
Salt Fog, 2000 Hr.	(F)AIL	(P)ASS	(P)ASS
Flexibility, 42 Inch, %	>60 PASS	5	>40/<60

KEY: MFR/DESIG			
M003	Morton/233-59-1	M008	Morton/233-67-1
M005	Morton/233-58-1	M009	Morton/233-63-1
M006	Morton/233-82-1	M010	Morton/233-59-1
M007	Morton/233-67-2	M011	Morton/233-55-1
M012	Morton/233-57-1	H003	Herberts/068-14-8
M013	Morton/233-67-3		
H001	Herberts/068-14-8		
H002	Herberts/068-15-4		

Table 53. Second Iteration Test Results to Date for Powder Coatings Sprayed at HMSCTucson

	H004	H004(ST)	H005	H005(ST)
Cure Temperature, F	275	275	275	275
Cure Time, Min.	35	35	35	35
Material Type	Epoxy	Epoxy	Epoxy	Epoxy
Color	Clear	Clear	Clear	Clear
Tape Test, 24 Hr. Water Soak	5A	3A	5A	3A
Tape Test, 96 Hr. Water Soak	5A	4A	5A	4A
Tape Test, 168 Hr. Water Soak	5A	3A	5A	3A
JP4 Fluid Resistance	PASS	PASS	PASS	PASS
Salt Fog, 500 Hr.	(P)ASS	-	(F)AIL	(F)AIL
Salt Fog, 2000 Hr,	-	(F)AIL	(F)AIL	(F)AIL
Flexibility, 42 Inch, %	<5 FAIL	N/A	<20 FAIL	N/A

4.3.6.4 JP4 Fluid Resistance. All the materials tested, both baseline and inhibited, passed the JP4 (jet fuel) fluid resistance test (168 hours at 77°F, with no signs of softening, lifting, blistering, or other defects).

4.3.6.5 Salt Fog (500 and 2000 Hour). All baseline formulations passed the 500 hour ASTM B 177 salt fog test except one low-cure epoxy from Herberts, which exhibited marginal performance with slight corrosion seen. Likewise, all baseline powders passed 2000 hours of ASTM B 117 salt fog except the low-cure powder noted, which failed with significant corrosion and pitting of the aluminum substrate.

One inhibited powder passed 500 hours salt fog on aluminum, while the other failed with significant corrosion of the substrate. Both inhibited powders failed 2000 hours salt fog on aluminum. Similarly, the inhibited powders were marginal or failed both 500 and 2000 hour salt fog when applied to steel.

4.4 Powder Coatings Applications Development

4.4.1 Coating of Non-conductive Substrates

4.4.1.1 Materials and Methods. A polyetherimide thermoplastic (Ultem1000®) from Polypenco Polymer Corporation, tetrafunction epoxy laminate (FR406) and polyimide laminate (G-30) from AlliedSignal Advanced Materials were chosen as representative non-conductive substrates. Glass microslides from VWR Scientific (cat. no. 48300-025) were also used to represent non-conductive substrates. Ultem 1000 has a glass transition temperature of 217°C. The glass transition temperatures for FR406 and G-30 laminates are 170°C and 240°C, respectively. The epoxy powder used for powder painting was obtained from Morton (Corvel® #10-7317). The recommended cure schedule for this epoxy powder is 171°C for 35 minutes.

To enhance the surface conductivity of the substrate, an aerosol antistat, a topical antistat and conductive primer were used. The aerosol antistat contained dimethyl ditallow ammonium chloride. The chloride free topical antistat diluted with water (39:1) contained stearamidopropyldimethyl-b-hydroxyethyl ammonium nitrate. The conductive primer contained (by wt%) 20.9% nickel, 6.3% 2-butoxyethanol, 5-10% iron phosphide (Fe_2P), 5.2% Ca, Sr, Zn phosphosilicate, 1-5% iron silicide, 1-5% carbon, 1-5% iron phosphide (FeP) and 1.8% sec-butanol, and conductive primer was mixed 1 part primer concentrate and 4 parts water.

All powder painting experiments were carried out at the Hughes Missiles Systems site in Tucson, Arizona. The powder painting equipment, which included a spraybooth, gun, hopper and a powder pump, was made by Nordson. Since the experiments used flat panels, the charging voltage was set between 75 and 90 kV. In a typical experiment, a non-conductive panel was first treated with the antistat. The treated non-conductive panel was hung vertically in the spray booth using a metal clip that was attached to the grounded powder booth. It took roughly 2 to 3 seconds to powder paint a substrate. After painting, the painted panel was transferred to a rack until it was time to cure the epoxy coatings. The curing of the powder was done in a convection furnace at 171°C for 35 minutes.

One of the desired properties of an antistat treated non-conductive substrates was its transparency to radio frequency energy. Tests were performed on a bare FR406 epoxy laminate (3 x 3 in), an FR406 epoxy laminate (3 x 3 in) treated with the conductive primer, a FR406 epoxy laminate (3 x 3 in) treated with the topical antistat, and a FR406 epoxy laminate (3 x 3 in) treated with the aerosol antistat using setup shown schematically shown in Figure 34. The test samples were tested for transparency to radio frequency energy in the 10 to 20 gigahertz region with a setup that consist of a Hewlett Packard Sweep Generator (model HP8350), a Hewlett Packard Scalar Analyzer (model HP8757A), a Hewlett Packard Analyzer Detector or RF Detector (model HP11669E), and a Narda Standard Horns (antennas 10-20 Ghz).

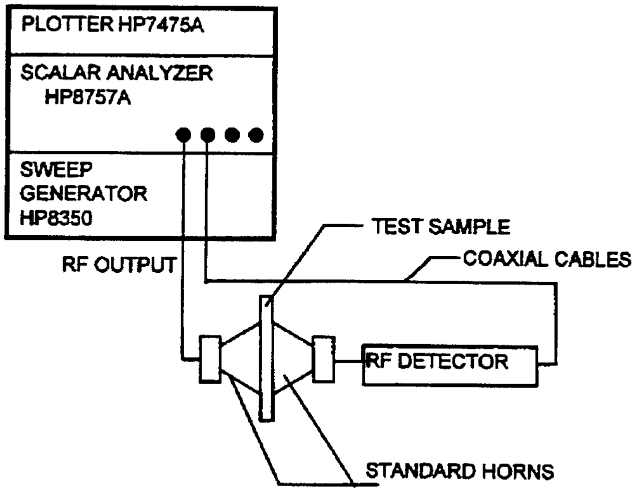


Figure 34
Radio Frequency Attenuation Test Setup

A Perkin-Elmer Thermogravimetric Analyzer (model TGA 7) was used to measure the weight loss of the substrates and antistats during various heat treatments. The TGA was also used to characterize the powder paint. In order to further characterize the antistats and powder paint, the Perkin-Elmer Differential Scanning Calorimeter (model DSC 7) was used. A Hewlett Packard Gas Chromatograph/Mass Spectrometer (model HP 5995) with Alltech Econo-Cap SE-54 (5% Phenyl 95% Methylpolysiloxane) resins in the GC column was used to characterize the antistats and the out-gassing products from the non-conductive substrates during the curing process.

Whether a antistat treated substrate can be painted depended on the surface conductivity of the substrate. A Keithly Instruments resistivity adapter (model 6105) and Keithley Instruments electrometer/source (model 617) were used to measure surface resistivity of samples. However, the combination of the Keithly Instruments resistivity adapter and the Keithly Instruments electrometer could not measure the surface resistivity of aluminum and a non-conductive substrate primed with the conductive primer since their surface resistivity was much lower (6 to 10 orders in magnitude less) compared to antistat treated glass slides. In order to measure the surface resistivity of aluminum slides (1 x 3 inches and 59 mils thick) and epoxy laminate (FR406) primed with conductive primer (1 x 3 inches), the sample is mounted in a test assembly shown schematically in Figure 35. The clips attached to the aluminum tape on both ends of the sample were connected to a Schulumberger Solartron (model 7081) Precision Voltmeter. The Schulumberger Solartron voltmeter was capable in measuring resistance in the milliohm range.

The morphology and the microstructure of the cross sections of the cured epoxy powder coating were characterized using a Hitachi Scanning Electron Microscope (model 2460N) and a Cambridge Instrument Stereoscan 360 Electron Microscope. All samples were sputtered with Au-Pd.

The coatings were characterized for their adhesion and solvent resistance using standard military specification methods. For adhesion measurements (used by Hughes Missile Systems Company and approved by the United States Air Force), a modified ASTM adhesion tape test (ASTM D 3359, method A) was used. For the adhesion tests, the painted substrates were immersed in distilled water for 24 hours at 23°C. After immersion, two parallel scribes, 3/4

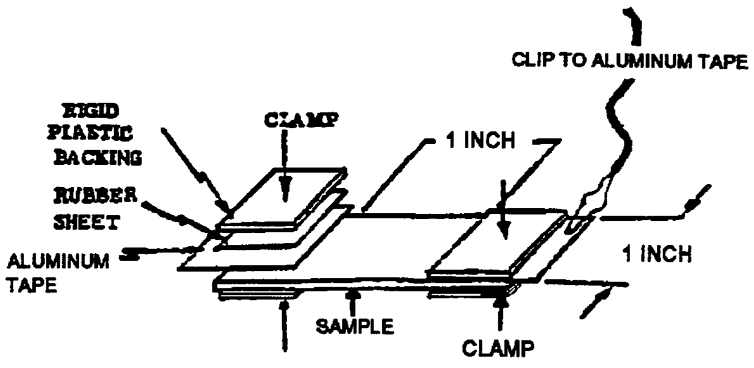


Figure 35
Test Assembly for Resistivity Measurement

inch apart, were cut through the coating and into the substrate, and an "X" was subsequently scribed through the coating between the two initial scribes. A 1 inch wide strip of 3M 250 masking tape was then applied firmly to the coating surface either perpendicular to or along the scribe lines and immediately removed with a quick motion. After peeling the tape, the adhesion was rated as shown in Table 54.

The chemical (fluid) resistance test was intended to analyze the ability of the coating to resist common fluids used in aircraft. A coated non-conductive substrate would fail the fluid resistance test if panels displayed blistering or discoloration after being immersed in a specified solvent at a given time and temperature. Separate powder painted Ultem 1000, FR406 epoxy and G-30 polyimide substrates were immersed in lubricating oil (MIL-L-23699) for 24 hours at 121°C, hydraulic fluid (MIL-H-83282) for 24 hours at 65°C and a hydrocarbon solvent (JP-4) for 168 hours at 25°C. Following immersion, the samples were taken out and optically inspected for blistering or discoloration.

The epoxy coating paint thickness and diameter of defects were measured by cutting into an epoxy coated substrate and mounting the cross section of the epoxy coated substrate in a polymeric resin. The mounts containing the samples were typically 1 1/4 inch in diameter. The mounted samples were then placed on an inverted stage Lasico Neomet Microscope equipped with a movable filar. The filar lays across the field of view and could be rotated in the field of view by 90 degrees (either clockwise or counter clockwise) in order to measure horizontal distances, vertical distances or distances at a slope. The filar was moved by rotating a knob located on the microscope, and the distance the filar travels was recorded digitally in inches with accuracy in the thousandth of micron. The length of the epoxy coating on the cross sectioned substrate mounted in the polymeric resin was measured in inches with accuracy in the hundredth of micron by using the Nikon Measurescope 20.

A Polymer Laboratories DMTA (Dynamic Mechanical Thermal Analysis -- model Mark II) was used to measure the shear loss modulus and shear storage as a function of time under isothermal heating. Figure 36 illustrates the test schematic for the powder paint in the DMTA. In Figure 36, the shear studs (Figure 36B) and the shear plate (Figure 36C) were powder painted. The powder painted shear studs made contact on both sides of the powder painted shear plate as shown schematically in Figure 36C. The numbers (# 1-6) shown in Figure 36C represented schematically where the threaded pin (#1-6) in Figure 36A would fit. The shear plate was connected to the 'T' bar (Figure 36A) and oscillated at 10 Hz. A tube furnace fitted around the entire tests assembly. Since the test assembly for measuring stored and loss shear modulus for the epoxy powder was unusual, there was reasonable doubt in the instrumentation's ability to accurately measure the shear modulus of the epoxy coating. The purpose of the DMTA spectra was to record gelation time of the powder paint under a given heat treatment.

Table 54. ASTM D3359 Adhesion Ratings

Rating	Description
5A	No Peeling or removal
4A	Trace peeling or removal along incisions
3A	Jagged removal along incisions up to 1/16 in. (1.6 mm) on either side
2A	Jagged removal along most of incisions up to 1/8 in. (3.2 mm) on either side
1A	Removal from most of the area of the "X" under the tape
0A	Removal beyond the area of the "X"

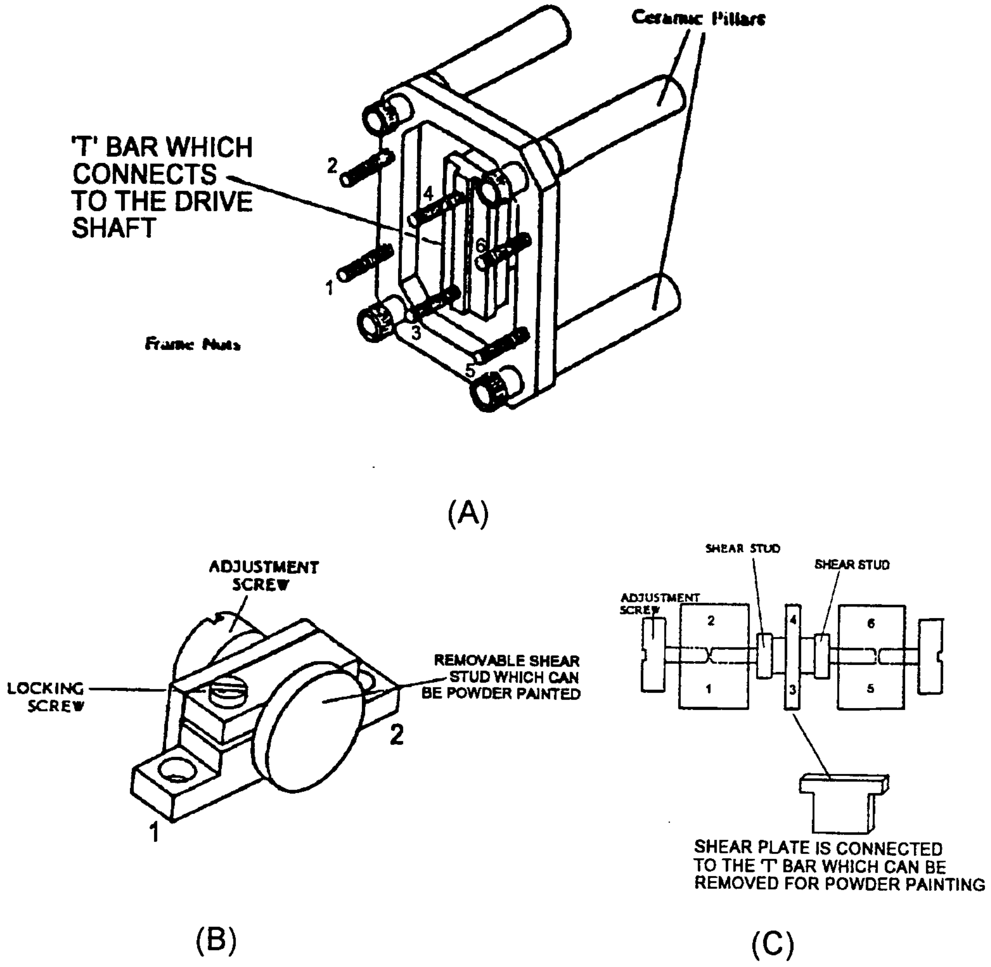


Figure 36
Test Assembly For DMTA

4.4.1.2 Characterization of Powder Paint. Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA) and Dynamic Mechanical Thermal Analysis (DMTA) were used to characterize the epoxy powder. The cure schedule for the epoxy powder was 171°C for 35 minutes. The DSC with a ramp rate of 20°C per minute obtained the following data for the epoxy powder as shown in Figure 37. As seen in this, the onset of exothermic reaction occurred at 173°C. The first peak at 64°C (t_g) the flow of the epoxy powder. The cure temperature for the epoxy powder was set at the onset of exothermic reaction in the DSC spectrum. The exothermic reaction corresponded to the crosslinking of the polymers within the epoxy paint.

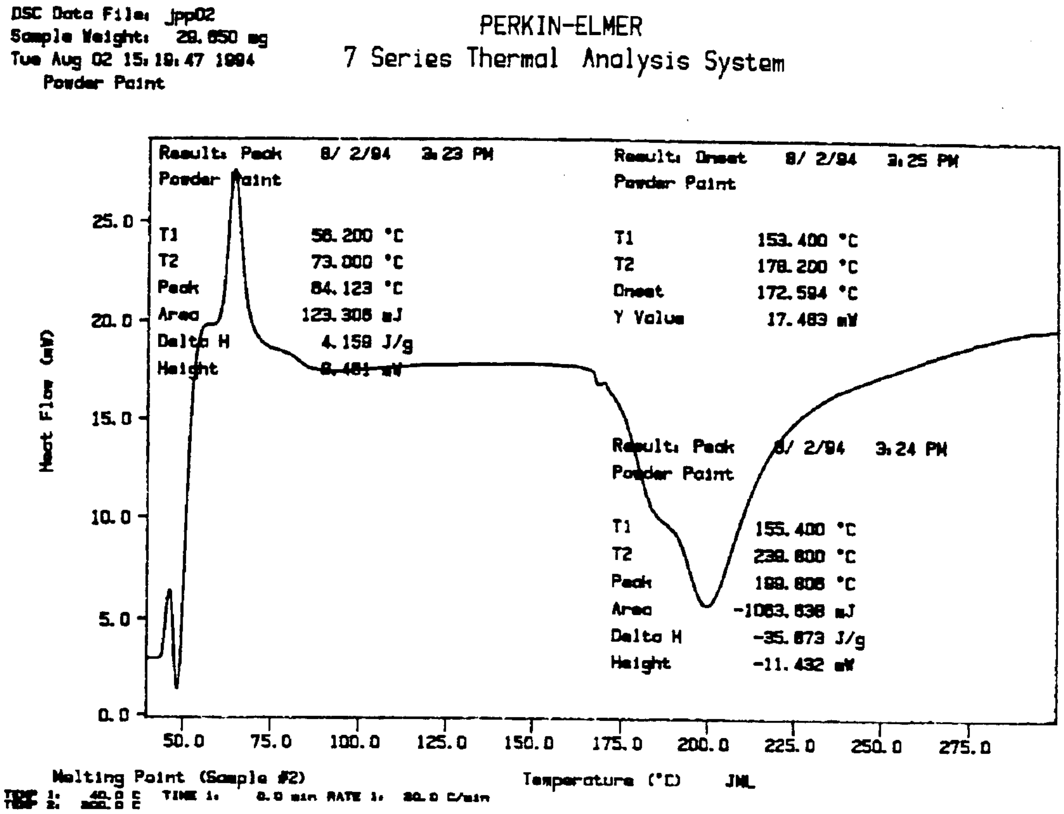


Figure 37
DSC spectrum of uncured epoxy powder.

Thermogravimetric analysis was performed (ramp rate of 30°C per minute from 30°C to 600°C) to characterize the uncured epoxy powder as shown in Figure 38. The onset for weight loss for the cured epoxy was 395°C as shown in Figure 38. The weight of the epoxy powder appeared to remain constant (Figure 38) from 30°C to 395°C.

Next, the DMTA was used to find the gelation time of the epoxy powder. The point on the DMTA spectrum where shear stored modulus crossed over the shear loss modulus was the location of the gelation point of the epoxy powder. In the DMTA analysis, it had taken approximately 12 minutes and 5 seconds to raise the temperature within the DMTA chamber from 25°C to 171°C. When reaching the target temperature at 171°C, the DMTA spectrum was recorded as shown in Figure 39. As seen in DMTA spectrum (Figure 39), the epoxy powder reached the gelation point just below five minutes. In another words, it has taken 17 minutes to turn the epoxy powder paint into a solid epoxy coating.

4.4.1.3 Characterization of Selected Non-conductive Substrates. The characterization of the selected non-conductive substrates under the curing temperature of the epoxy powder was conducted using thermogravimetric analysis. The temperature was ramped at 100C/min to 171°C and held at this temperature for 120 minutes. The ramp rate was self adjusting and decreased as the target temperature approached to prevent temperature oscillation around the target temperature. Note that the powder painted substrates were approximately 1 x 2 inch, and the thickness of the Ultem 1000 substrate, FR406 Tetrafunctional Epoxy substrate and G-30

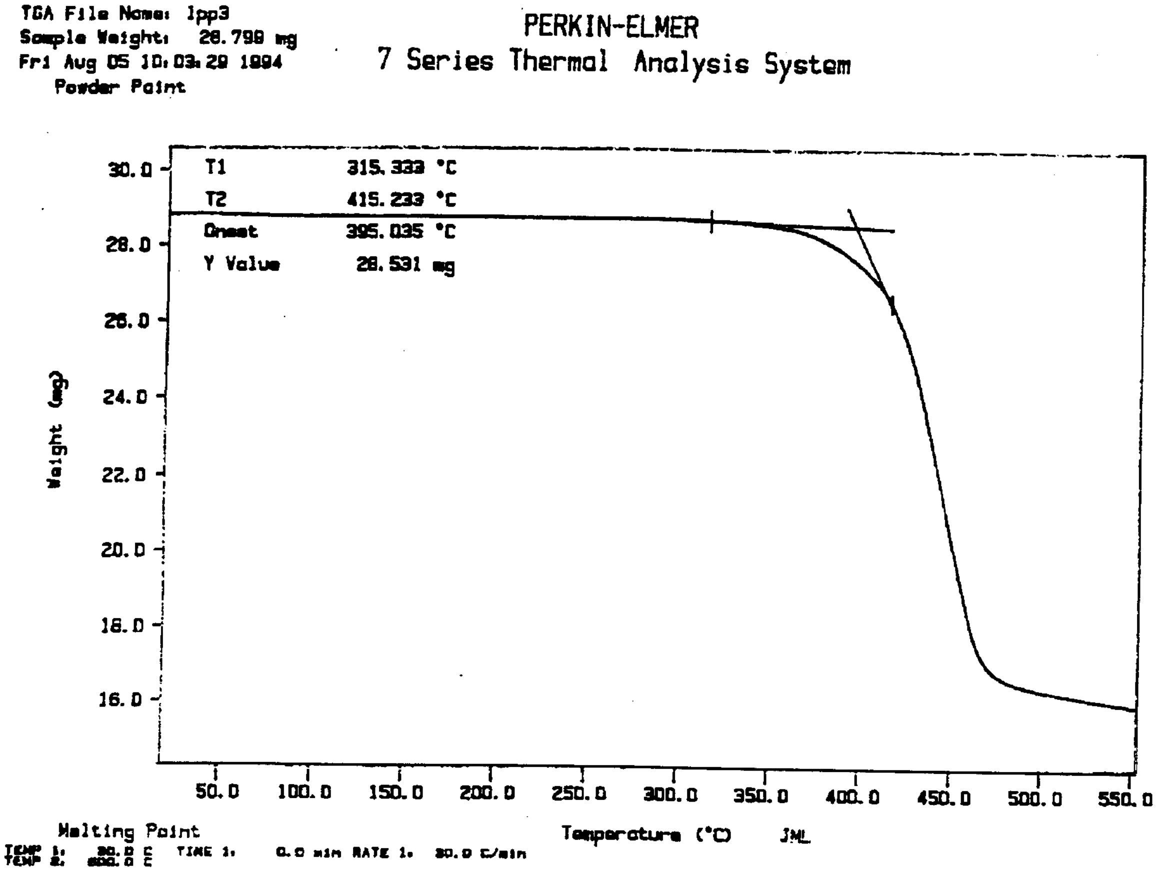


Figure 38
TGA spectrum of Epoxy Powder.

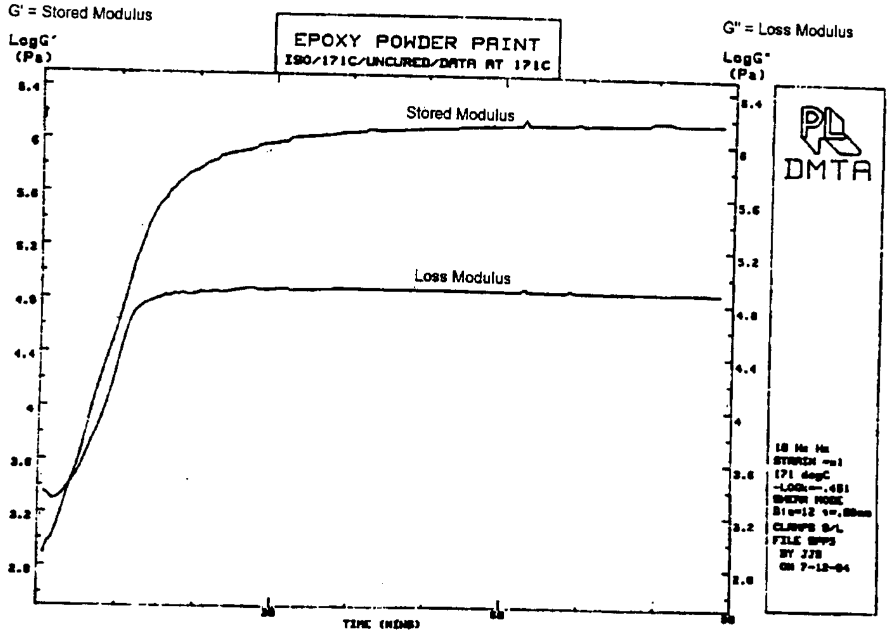


Figure 39
DMTA spectrum of the Epoxy Powder under isothermal heating at 171°C

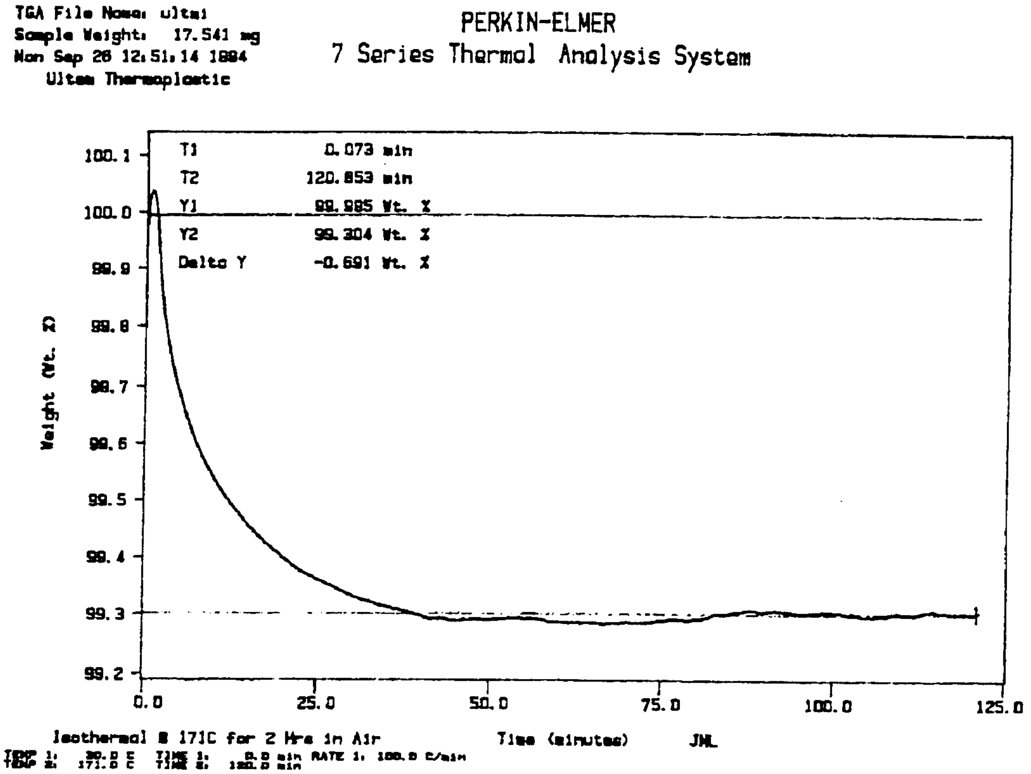


Figure 40
TGA spectrum of Ultem 1000 at 171°C for 2 hours

Polyimide substrate were 5842mm, 1422mm and 305mm, respectively. The weight of powder painted substrates were approximately 10.3 grams, 3.8 grams and 0.8 grams for Ultem 1000, FR406 Tetrafunctional Epoxy and G-30 Polyimide, respectively. The TGA spectra (Figures 40, 41, and 42) for Ultem 1000 substrate, FR406 tetrafunctional epoxy substrate, and G-30 Polyimide substrate indicated a weight loss of 0.691%, 0.232%, and 0.633% in 120 minutes, respectively.

A Gas Chromatograph/Mass Spectrometer (GC/MS) was used to identify the volatile species from the selected non-conductive substrates. As shown in the spectra for the selected non-conductive substrates (Figures 43, 44, and 45), the GC/MS identified the volatile species as water vapor. The nitrogen peak in the spectrum was due to the carrier gas used in the experiments. The peaks that appeared after 30 minutes in all GC/MS spectra represented the analysis of the resins within the GC column.

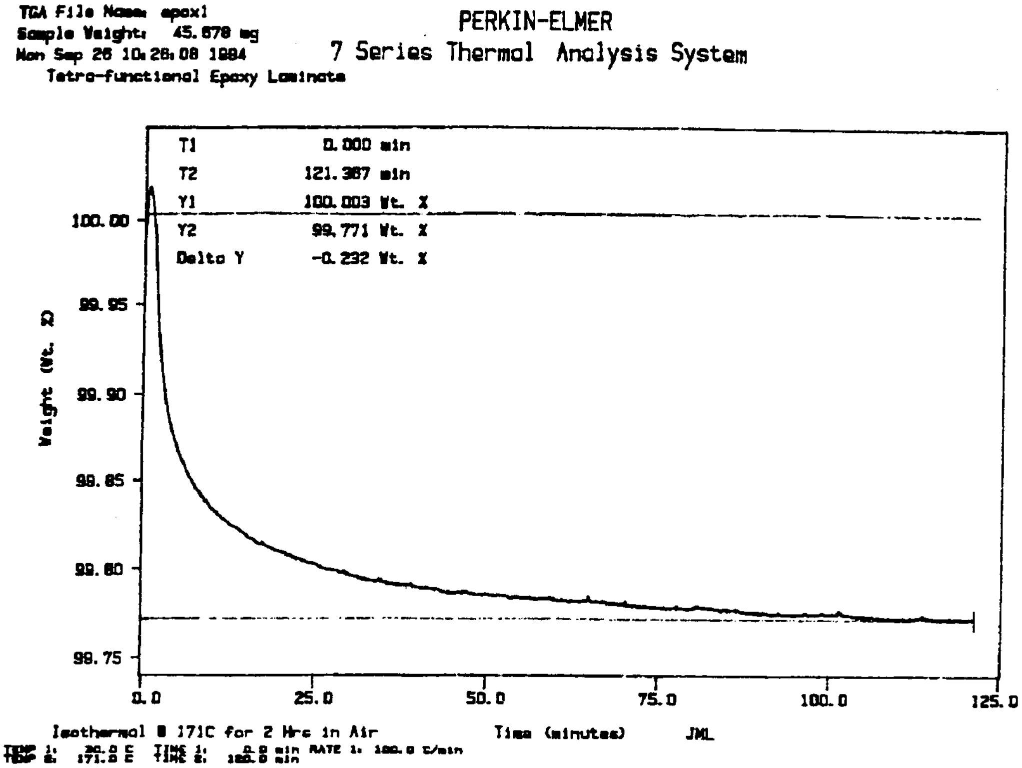


Figure 41
TGA spectrum of FR406 Epoxy at 171°C for 2 hours

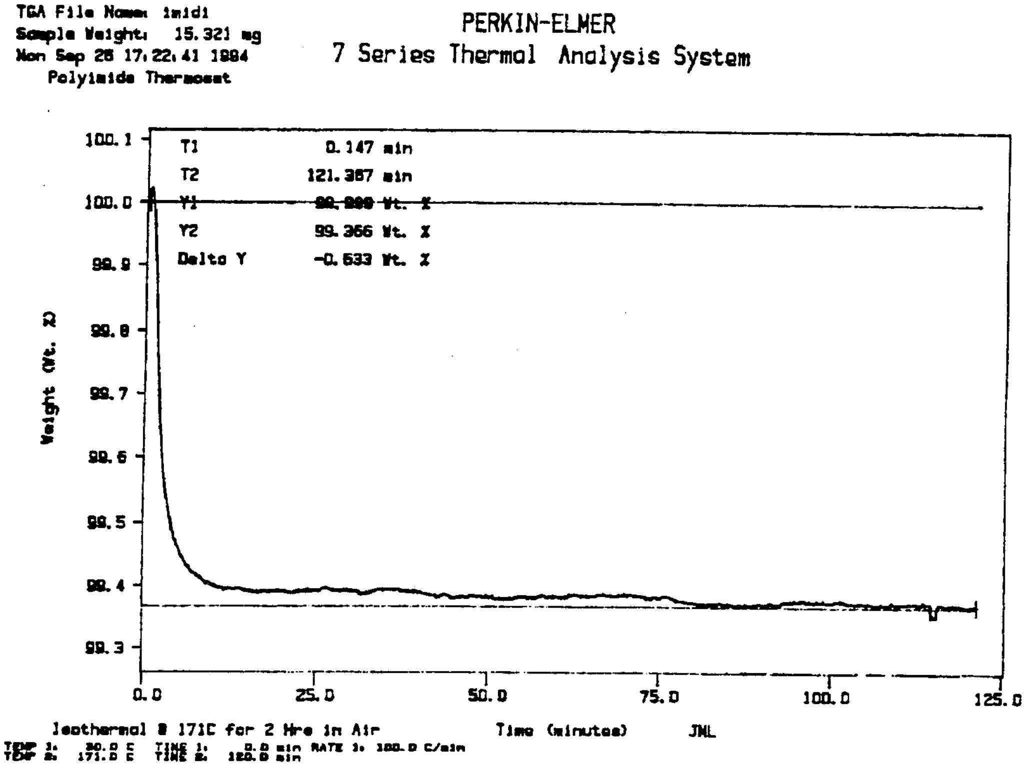


Figure 42
TGA spectrum of G-30 polyimide at 171°C for 2 hours

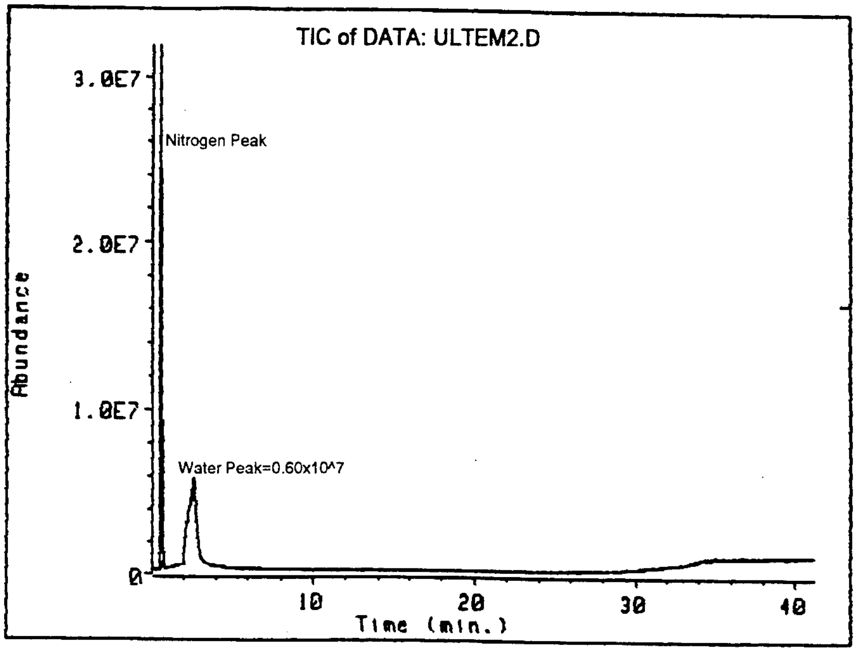


Figure 43
GC/MS spectrum of Ultem 1000

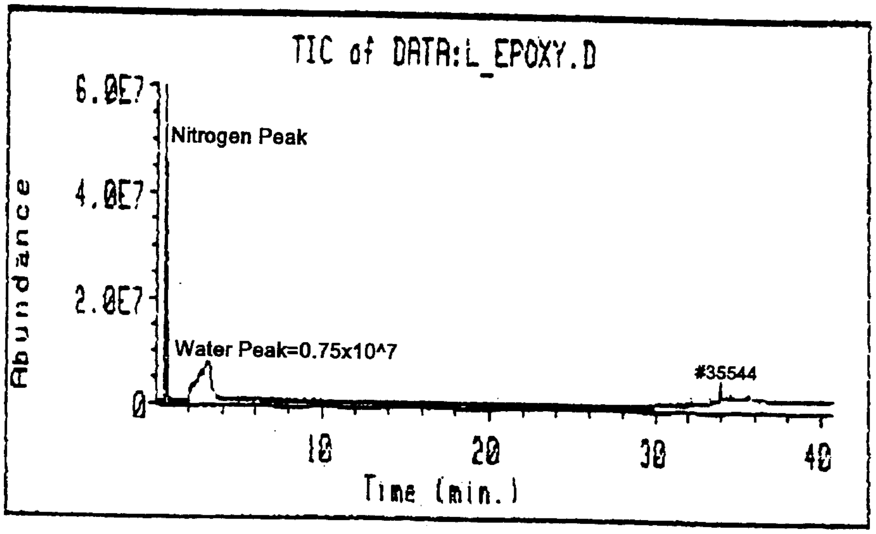


Figure 44
GC/MS graph of FR406 epoxy

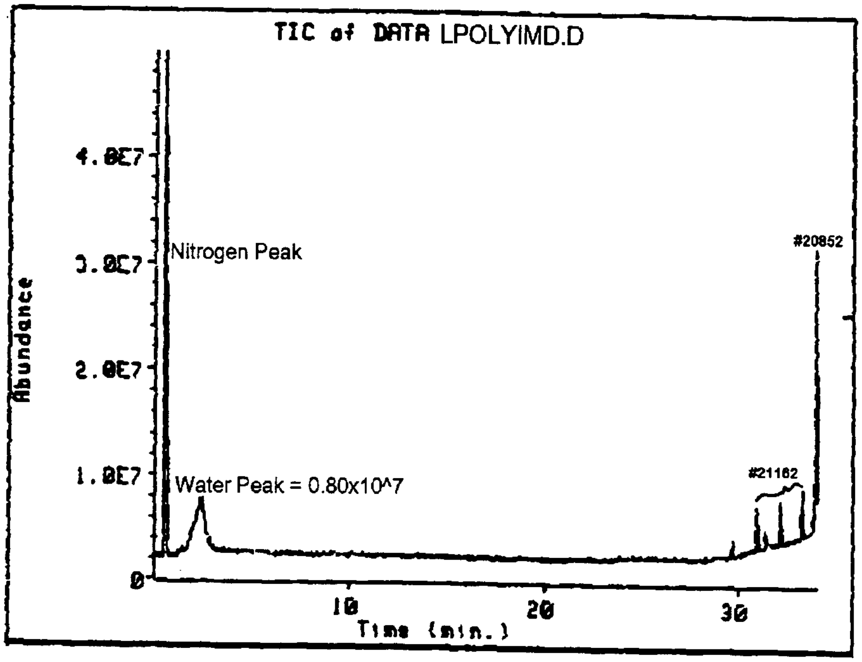


Figure 45
GC/MS graph

4.4.1.4 Characterization of Antistats. The aerosol antistat coating and topical antistat coating measured (9.29+/-1.83)x10^{-3} g/cm^2 and (13.33+/-1.33)x10^{-3} g/cm^2 when freshly applied, respectively. After air drying from 7 to 8 minutes, the aerosol antistat coating measured (1.0+/-0.4)x10^{-4} g/cm^2 due to evaporation of propellant. After air drying from 53 minutes to 1 hour and 20 minutes, the topical antistat coating measure (1.3+/-0.5)x10^{-4} g/cm^2 due to evaporation of water.

Since the aerosol antistat and the topical antistat are commercial products, an attempt was made to identify the ingredients in both antistats. The analysis was carried out using GC/MS and the results are shown for the aerosol antistat in Figure 46. The five peaks in Figure 46 may be identified as follows: peak #1 is isobutane (C_4H_{10}), peak #2 is ethanol (C_2H_5OH), peak #3 is tert-butyl alcohol ($C_4H_{10}O$), peak #4 is 4-Penten-2-ol ($C_5H_{10}O$) and peak #5 may be ascribed to 2-propanoic acid, 2-methyl-, and butyl ester. Ethanol is most likely the carrier solvent, and isobutane is most likely the propellant for the commercial aerosol antistat. Another analysis was carried out using GC/MS and the results for the topical antistat are shown in Figure 47.

The five peaks in Figure 47 may be identified as follows: peak #1 is 2-Pentanone and 5-(acetyloxy)- ($C_7H_{12}O_3$), peak #2 is 2-Propanol (C_3H_8O), peak #3 is Ethanol and 2-(1-methylethoxy)- ($C_5H_{12}O_2$), and peak #4 is 2-Propenoic acid, 2-methyl-, and butyl ester ($C_8H_{14}O_2$). The GC/MS was set to identify species with molecular weight greater than 18 g/mol (H_2O).

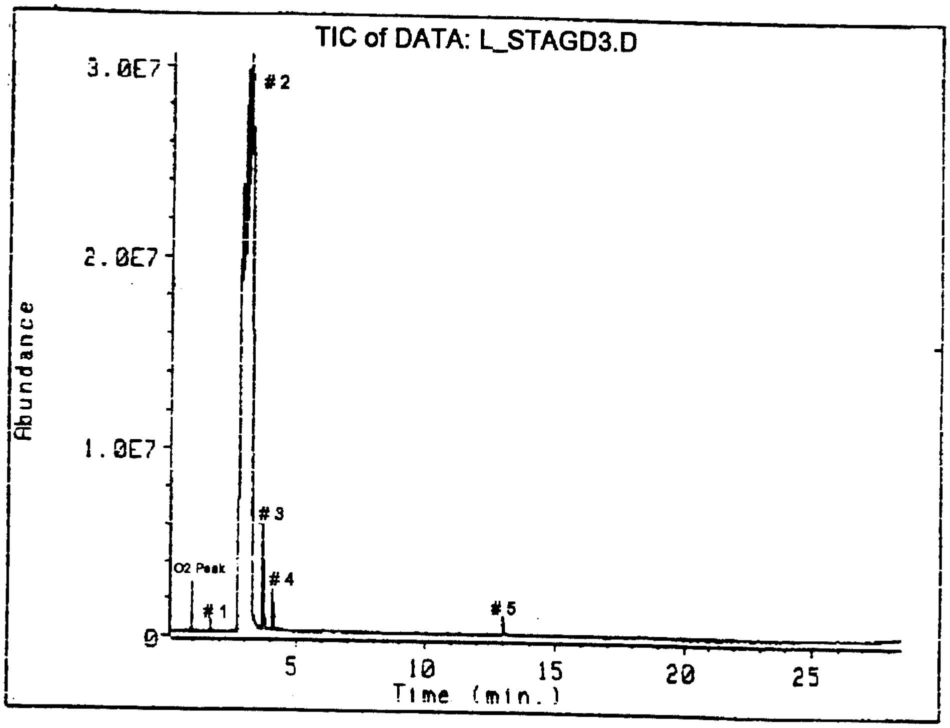


Figure 46
GC/MS spectrum of aerosol antistat.

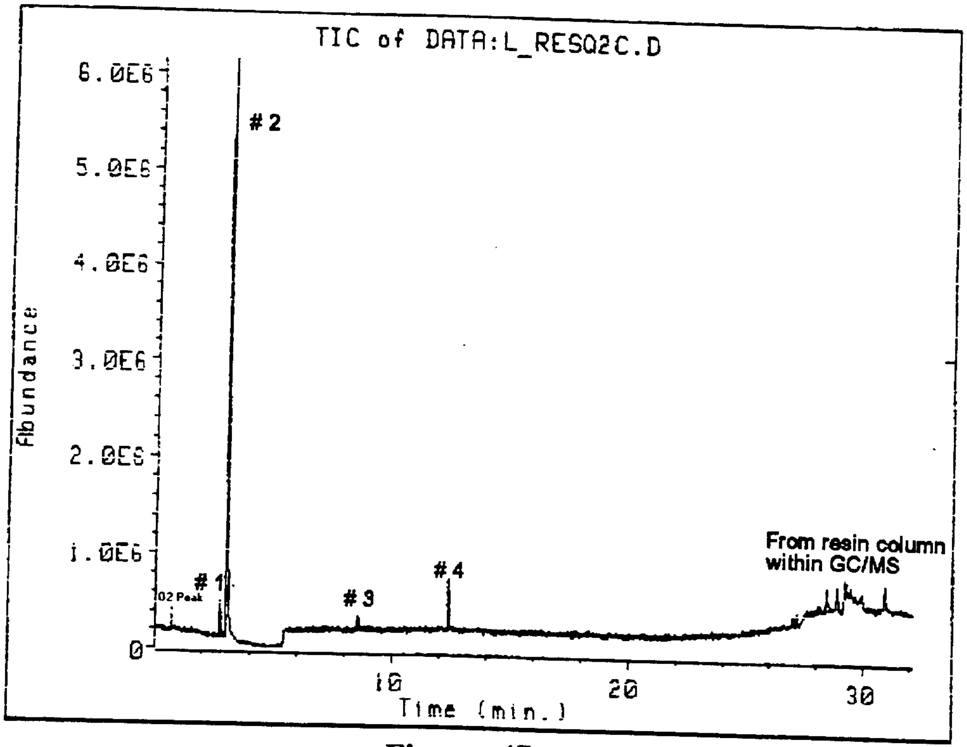


Figure 47
GC/MS spectrum of topical antistat.

Differential Scanning Calorimetry and Thermogravimetric analysis were performed to characterize the antistats during heating. For the DSC and TGA analysis of the antistats, it was decided to analyze the solids of the antistats. For the TGA analysis, the antistats were first sprayed into the TGA pan, heated to 100°C and held for 30 minutes under dry nitrogen. At 30 minutes, both antistats had dropped to a constant weight. At the end of this holding period the samples were cooled to 30°C. The antistats were then ramped to 500°C at 10°C per minute. For the DSC analysis, the antistats were sprayed into an aluminum dish and were placed in an air-circulating oven at 52°C for 4 hours. The ramp rate for the DSC analysis was also 10°C per minute. Figures 48 and 49 shows the data collected by the DSC and TGA on antistats during heating.

In the TGA spectrum of the aerosol antistat, the onset for weight loss was around 187°C (Figure 48a) and ended at 336°C. The first endothermic peak in Figure 48b, from 125°C to 160°C, was possibly an endothermic chemical reaction(s) since the aerosol antistat did not lose weight between 125°C and 160°C in the TGA spectrum. As shown in Figure 48b, the second endothermic peak (from 180°C to 201°C) and third endothermic peak (from 201°C to 271°C) corresponded to the weight loss in the TGA spectrum from 187°C to 271°C. The weight loss from 271°C to 336°C in the TGA spectrum corresponded to the last endothermic peak in the DSC spectrum from 271°C to 338°C. The endothermic peaks with corresponding weight loss suggested sublimation of several different species while the aerosol antistat was heated.

For the topical antistat, the TGA spectrum (Figure 49a) showed that the onset for weight loss of the topical antistat at 233°C and ended at 285°C. The DSC spectrum (Figure 49b) of the topical antistat displayed two exothermic reaction. The first exothermic reaction from 166°C to 205°C did not have a corresponding weight loss in the TGA spectrum (Figure 49a). The second exothermic reaction from 235°C to 287°C appeared to be responsible for the weight loss of the topical antistat.

The TGA analysis in Figures 48 and 49 had given weight loss at a given ramp rate and not weight loss during isothermal heating. Thermogravimetric analysis were performed to measure weight loss of the antistats at the curing temperature - 171°C. The antistats were sprayed into an aluminum dish and were placed in an air-circulating oven at 49°C overnight in order to expel the hydrocarbons (in the propellant) from the aerosol antistat and water from the topical antistat. After drying the sample in the oven, the antistats were placed in the TGA chamber which was purged with dry air. The temperature was ramped at 100C/min to 171°C and held at this temperature for 120 minutes. The ramp rate was self adjusting and decreased as the target temperature approached to prevent temperature oscillation around the target temperature. As shown in Figure 50, the aerosol antistat lost 22.3 wt% of its initial dried weight after 2 hours. Figure 51 shows that the topical antistat lost 6.3 wt% of its initial dried weight after 2 hours.

<u>4.4.1.5 Feasibility of Using Antistats to Powder Paint.</u> Applying antistats on non-conductive substrates made it possible to electrostatically powder paint these substrates. Several issues needed to be addressed. The first issue centered on whether these epoxy coatings formed on antistat treated non-conductive substrates could pass the military specifications test for adhesion and fluid resistance tests. The second issue addressed on whether the thickness of the coatings formed on antistat treated non-conductive substrates would be comparable to the thickness of the coating form on metal surfaces. Since the antistats lost weight during the curing schedule (Figures 50 and 51), the last issue addressed whether there would be defects in the form of voids within the cured epoxy coating.

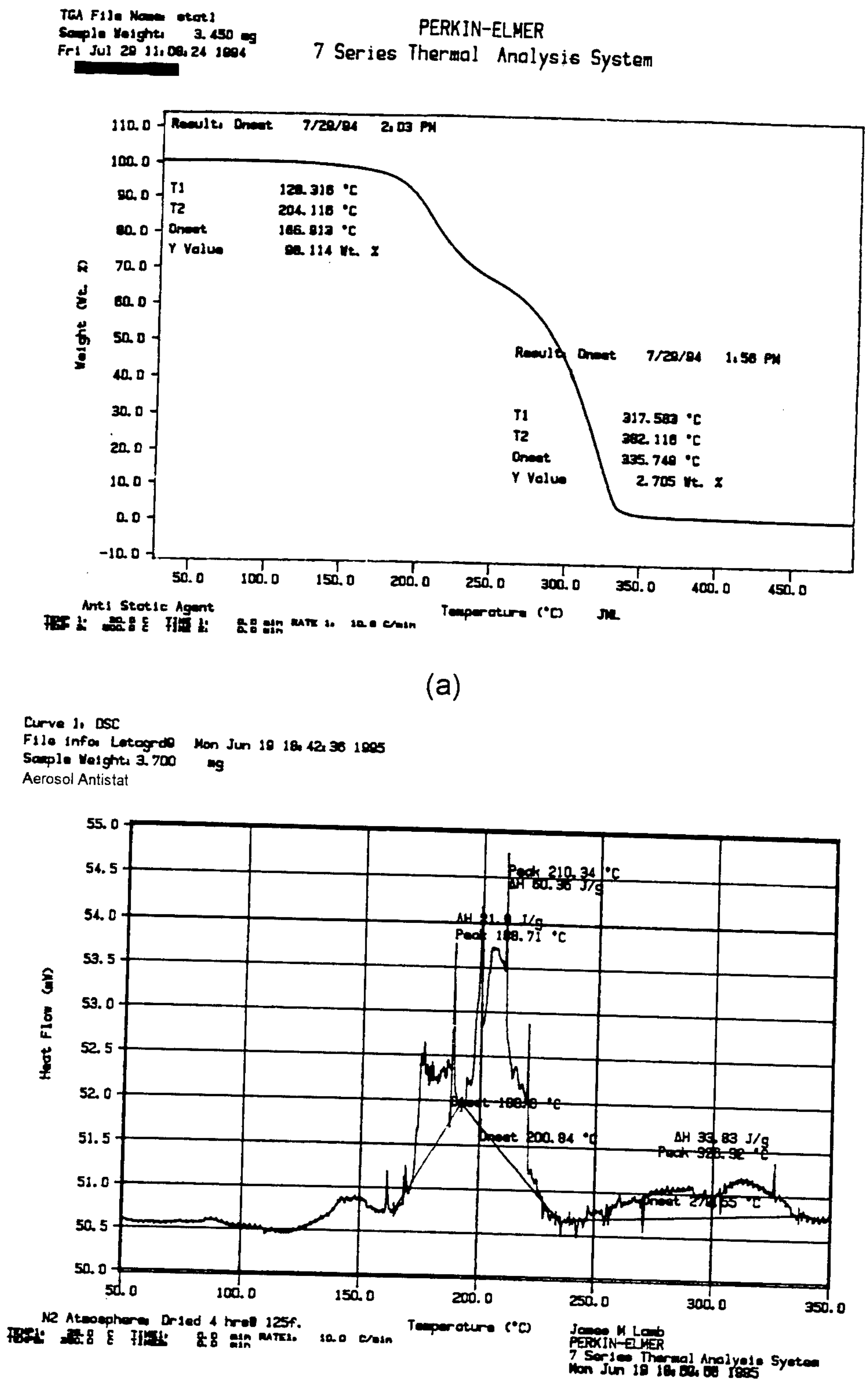


Figure 48
Aerosol antistat: (a) TGA spectrum with a ramp rate of 10°C/min, and (b) DSC spectrum with a ramp rate of 10°C/min.

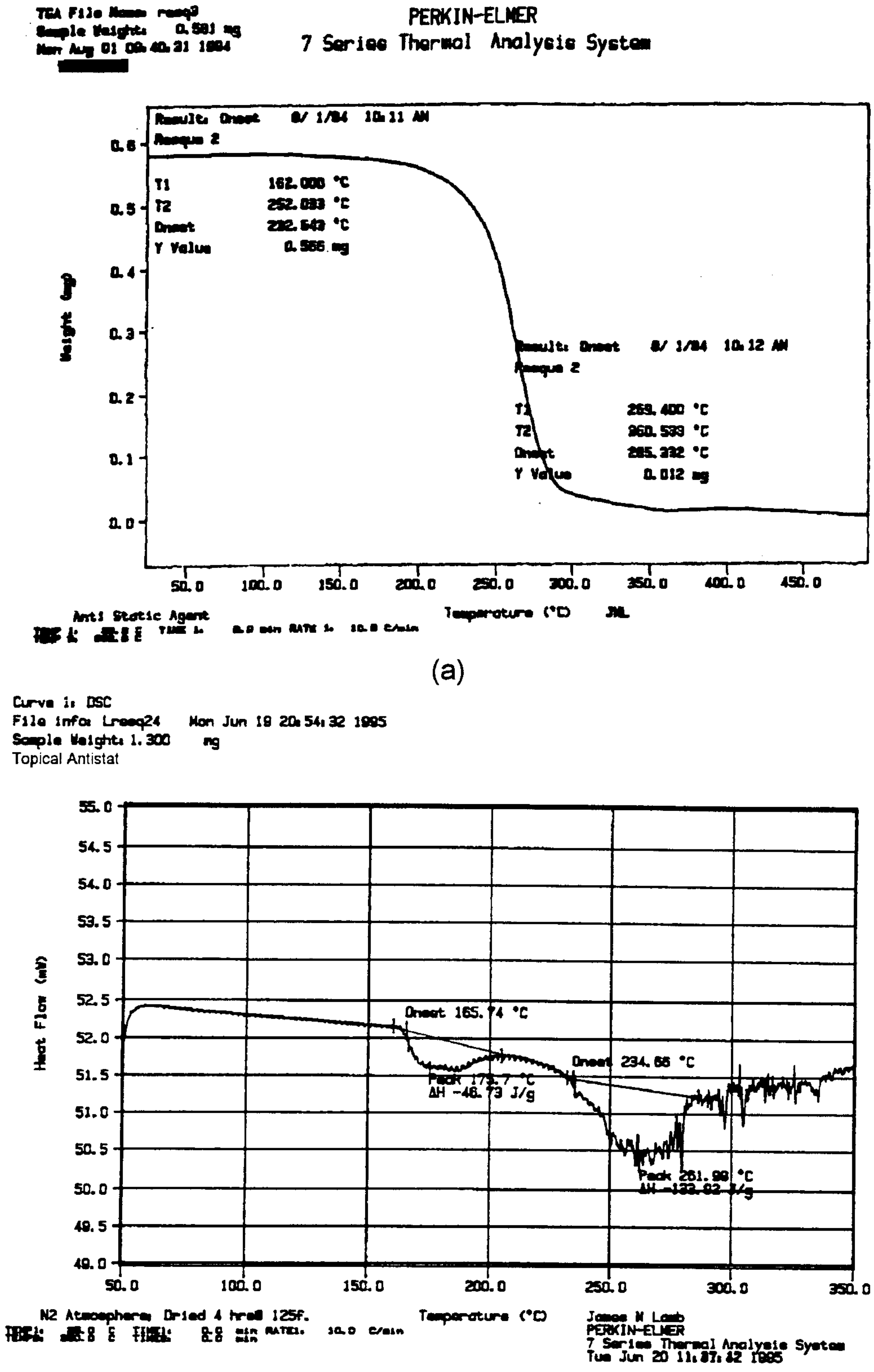


Figure 49
Topical antistat: (a) TGA spectrum with a ramp rate of 10°C/min, and (b) DSC spectrum with a ramp rate of 10°C/min

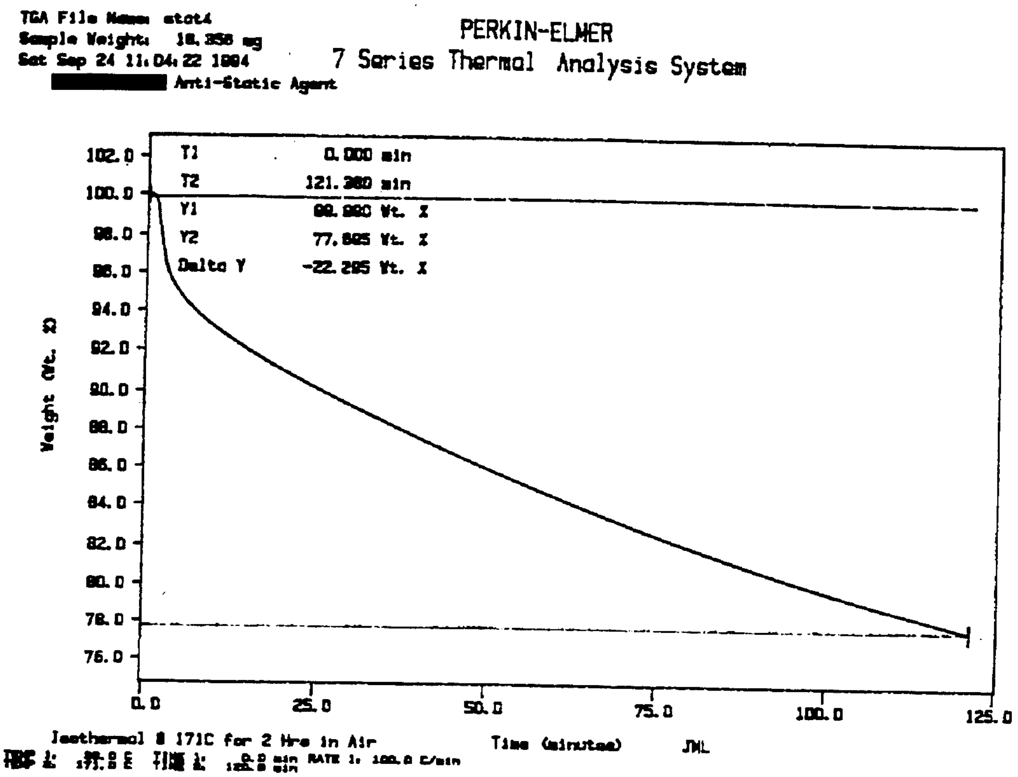


Figure 50
Weight loss suffered by aerosol antistat at 171°C for 2 hours.

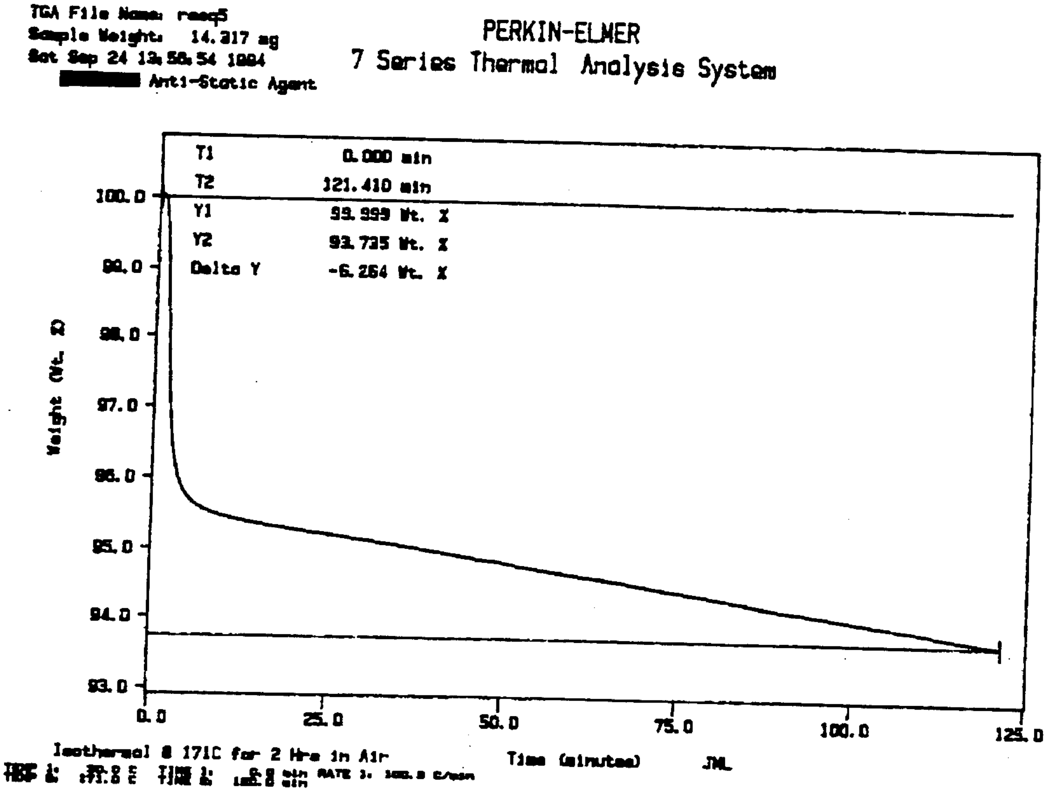


Figure 51
Weight loss suffered by topical antistat at 171°C for 2 hours.

Table 55 Results of Physical Performance Tests

SUBSTRATE TYPE AND ANTISTAT USED	WET TAPE ADHESION TEST	LUBRICATION OIL	HYDRAULIC FLUID	HYDROCARBON SOLVENT
Tetrafunction epoxy (FR406) substrate treated with aerosol antistat	5A	PASS	PASS	PASS
Polyimide (G-30) substrate treated with aerosol antistat	5A	PASS	PASS	PASS
Ultem 1000 substrate treated with aerosol antistat	5A	PASS	PASS	PASS
Tetrafunction epoxy (FR406) substrate treated with topical spray antistat	5A	PASS	PASS	PASS
Polyimide (G-30) substrate treated with topical spray antistat	5A	PASS	PASS	PASS
Ultem 1000 substrate treated with topical spray antistat	5A	PASS	PASS	PASS

Epoxy coatings on the antistat treated non-conductive substrates were subjected to adhesion and fluid resistance tests. As shown in Table 55, the coatings passed the military specifications tests.

A series experiments dealt with the issue on whether the coating thickness formed on an antistat treated non-conductive substrate would be comparable to the coating thickness formed on metal surfaces. The experimental setup for comparing relative thickness is schematically shown in Figure 52. The choice for non-conductive substrate was glass microslides (1x3 in.), and the choice for metal substrate was 2024 aluminum slides (1x3 in.). The voltage for the powder booth was set at 75 kV.

In Figure 52, all clamps that were attached to the slides were equal in size. A set in the experiment contained one aluminum slide, one aerosol antistat treated glass slide and one topical antistat treated glass slides. There were a total of five sets and in each set the position of the antistat treated glass slides and the aluminum slide were placed randomly. By randomizing the position of the slides in each set prior to powder painting, it would be possible to minimize the difference in mean powder paint thickness between the aluminum slides, the aerosol antistat treated glass sides, and the topical antistat treated glass slides due to powder painting technique. The surface resistivity of all antistat treated glass sides was measured prior to powder painting. Each slide was cut and mounted as shown in Figure 53, and there were a total of 30 powder paint thickness measurements for each section (in some case more) or a total of 90 measurements per slide. After the experiment, all of the measurements from the five sets were used to calculate the mean powder paint thickness on aluminum slides, aerosol antistat treated glass slides and topical antistat treated glass slides.

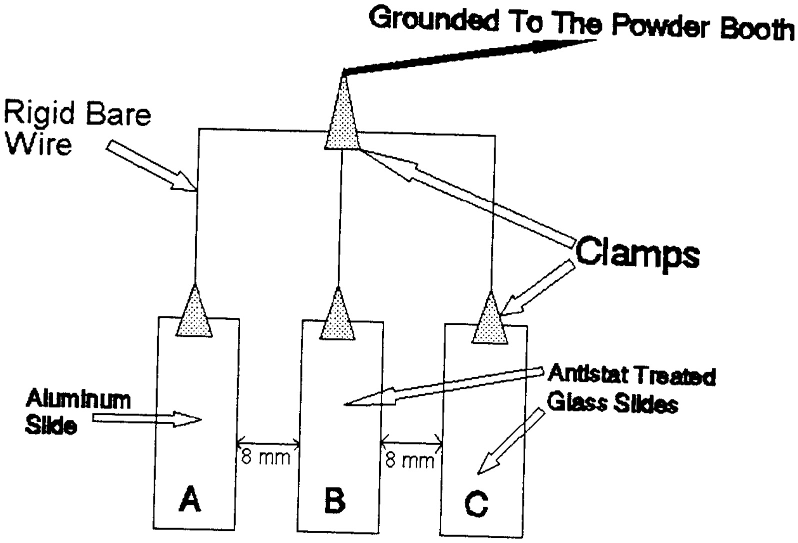


Figure 52
Experimental schematic for testing relative paint thickness on substrates with large difference in surface resistivity.

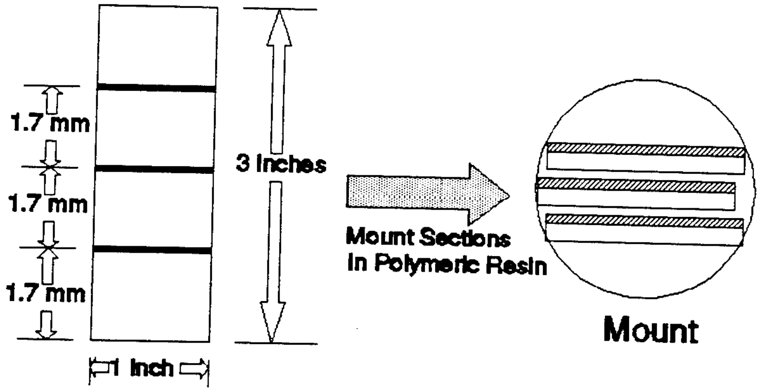


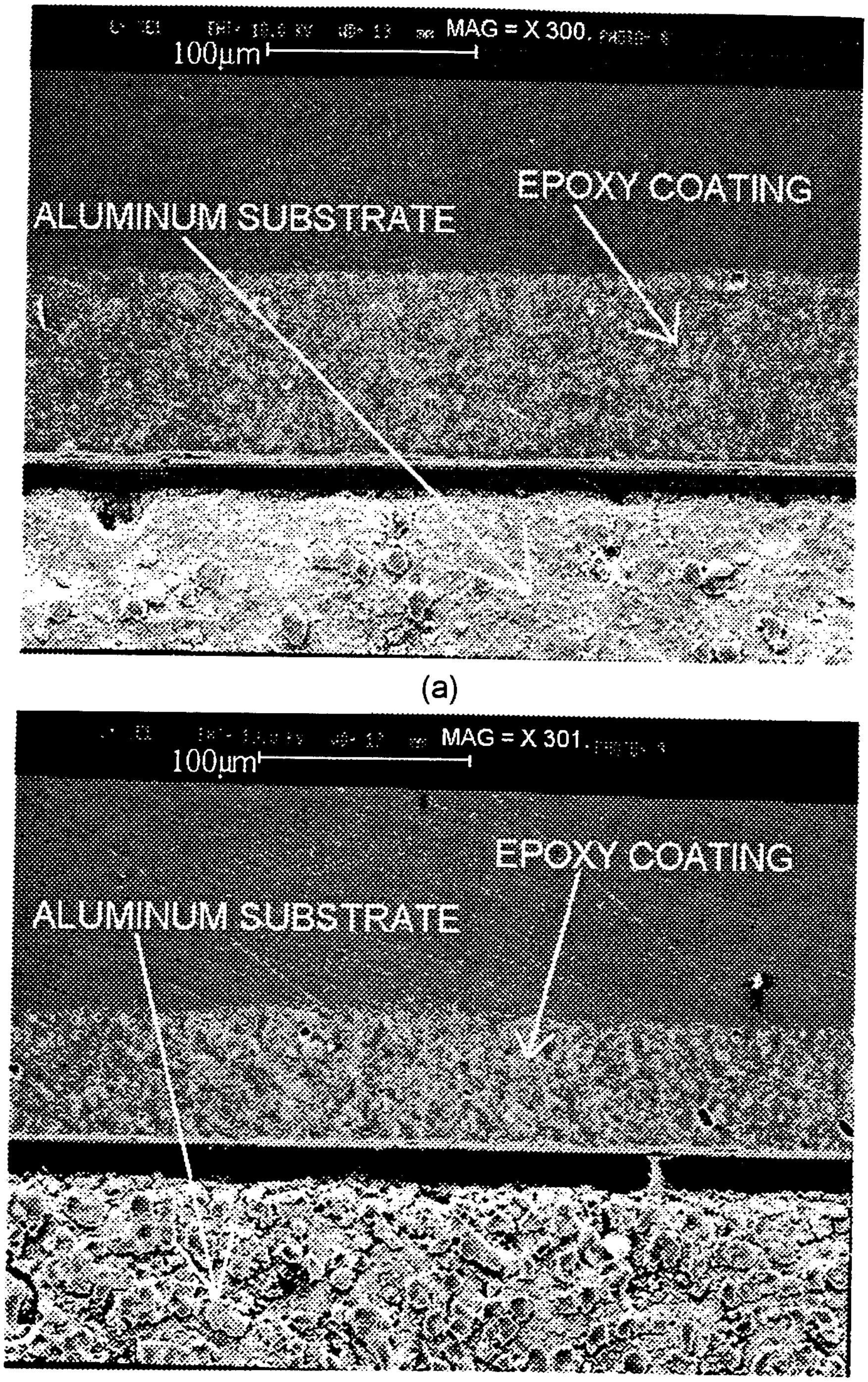
Figure 53
Schematic for sectioning and mounting of slide.

The surface resistivity for the aerosol antistat treated glass slides was (3.62 +/- 0.65)x10^8 ohms per square, and the surface resistivity for the topical antistat treated glass slides was (1.23 +/- 0.47)x10^9 ohms per square. Aluminum slides had a typical surface resistivity value of 3.9x10^{-2} ohms per square. There were a total of 459 paint thickness measurements for aluminum slides, 450 measurements for aerosol antistat treated glass slides and 450 measurements for topical antistat treated glass slides. The mean powder paint thickness on aluminum glass slide was (3.129 +/- 0.395) mils. The mean powder paint thickness on aerosol antistat treated glass slide was (3.270 +/0 0.493) mils, and the mean powder paint thickness on topical antistat treated glass slide was (3.222 +/- 0.753) mils. A statistical analysis (t-test) conducted, at a level of confidence of 95%, indicated that the mean powder paint thickness on aluminum did not match the mean powder paint thickness on either the topical antistat treated glass slide or the aerosol antistat treated glass slides. However, the t-test indicated that the mean powder paint thickness between the topical antistat treated glass slide and the aerosol antistat treated glass slide did match. The difference between the mean powder paint thickness on aluminum slides and the combined mean powder paint thickness on antistat treated glass slides was 3.60%. The difference between the mean powder paint thickness on antistat treated glass slides and metals slides could be minimized by increasing the number of sets within the experiment. This experiment suggested that the thickness of the epoxy coating on antistat treated non-conductive substrate would be would be comparable to the powder paint thickness on metal surfaces.

The last issue that needed to be addressed was whether the weight loss of the antistat during isothermal heating at 171°C (Figures 50 and 51) created voids within the cured epoxy coating. Four 2024 aluminum panels were powder coated. Two of the aluminum panels were control panels. The control panels were powder painted bare aluminum panels. The third aluminum panel was treated with the topical antistat (roughly 0.13 mg/cm^2) and the fourth panel was treated with the aerosol antistat (roughly 0.10 mg/cm^2). The antistat treated aluminum panels were allowed to dry in ambient air and then powder painted. In Figure 54a, the SEM micrograph shows the cross section of control panel 1. The SEM micrograph shown in Figure 54b shows a cross section of control panel 2. The surface resistivity of the epoxy coatings on control panel 1 and control panel 2 were 9.1x10^{13} ohms per square, and 1.1x10^{14} ohms per square, respectively.

In Figure 55a, the SEM micrograph showed the cross section of a topical antistat treated aluminum panel. The SEM micrograph shown in Figure 55b shows a cross section of an aerosol antistat treated aluminum panel. The surface resistivity of the epoxy coatings on the topical antistat treated aluminum panel and the aerosol antistat treated panel were 9.6x10^{13} ohms per square, and 8.0x10^{13} ohms per square, respectively.

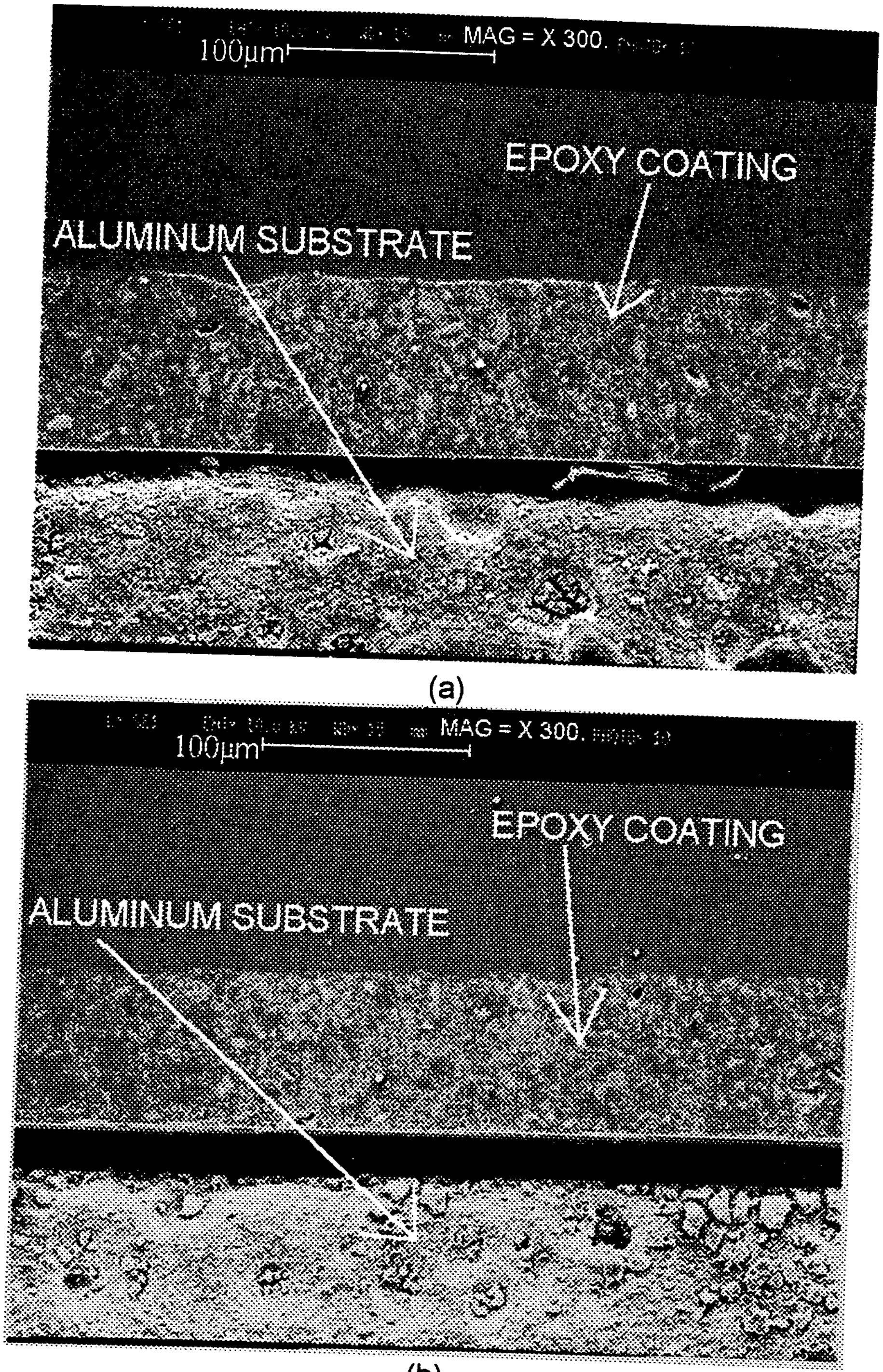
A metric was needed to quantify the number of voids within the epoxy coating. The metric chosen was percent porosity. Percent porosity is the average size of void times the number of voids divided by the total cross section area of the epoxy coating and rounding to the nearest percent. The analysis for percent porosity of epoxy coating was conducted by cutting three one inch cross sections (similar in schematic as shown in Figure 53) from a panel and mounting the cross sections in a polymeric mount, one was chosen for detailed analysis -- the three substrate were visually identical in porosity. The detailed analysis includes counting and measuring the diameter of every voids (large or small) within the epoxy coating. The percent porosity of epoxy coatings on aluminum substrates (Figure 54 and 55) were 0% for both control panels and the antistat treated panels. The weight loss of the antistats on aluminum substrates did not create voids within the cured epoxy coating.



(a)

(b)

Figure 54
SEM micrograph: (a) control panel 1, and (b) control panel 2



(a)

(b)

Figure 55
SEM micrograph: (a) topical antistat treated aluminum panel, and (b) aerosol antistat treated control panel 2

4.4.1.6 Control of Surface Conductivity on Antistat Treated Substrate. The weight loss of the antistat during heating could affect the antistats ability to enhance the surface conductivity of non-conductive substrates for electrostatic powder painting. To determine the effect of the antistat weight loss during heating, glass slides (25x75x1 mm) were sprayed with either the aerosol antistat or the topical antistat and dried in an oven at a specified temperature for a predetermined time and then were powder coated. The aerosol antistat coating on glass slide measured an average of 0.10 mg/cm^2. The topical antistat coating on glass slide measured an average of 0.13 mg/cm^2. The results of the powder coating were qualitatively evaluated after curing and ranked on a scale of 1 (bad) to 10 (good). A ranking of 10 indicates that coating was uniform and covered the glass slide entirely with no bare spots. A ranking of less than 10 indicates incomplete powder painting where the coating was non-uniform and had bare spots. The drying temperature was used as a variable to determine whether the antistat would cease to function as a conductivity enhancing agent above a certain temperature. The relative humidity in the laboratory during the experiment was low (roughly 30%).

The results of these tests for the aerosol antistat displayed in Figure 56 showed that at lower drying temperatures coating was possible even at long drying times. At higher temperatures, depending on the drying time, the coatings exhibited incomplete coverage. For example at 171°C, if the drying was done for 30 minutes or longer, the ranking of the coating was 7 or less. The same experiment was conducted for the topical antistat and the results were all 10's -- from 156°C to 176°C. The TGA spectra (Figure 50 and 51) for the aerosol antistat and the topical antistat under isothermal heating at 171°C showed that the aerosol antistat lost around 10 wt% in 25 minutes and more than 10 wt% in 30 minutes while the topical antistat only lost 6 wt% in 120 minutes. These tests indicated that a 10% or more loss in weight for the antistats could effect the antistats ability to enhance the surface conductivity of non-conductive substrates for electrostatic powder painting.

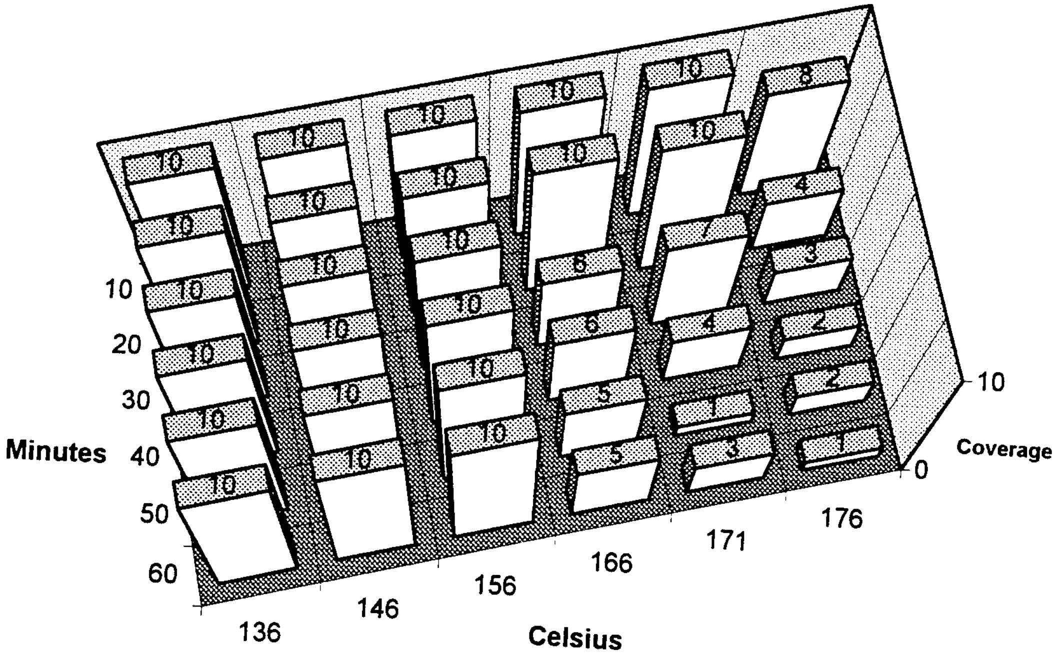


Figure 56
Time-temperature-coverage graph for the powder painting of glass slides treated with aerosol antistat.

Since the surface resistivity of the antistat treated glass slides were not measured before and after heat treatment, the next experiment included measuring the surface resistivity before and after heat treatment (prior to powder painting) and rating the coating (10 or less than 10) on the samples after curing the epoxy coating. The surface resistivity of the glass slides treated with the aerosol antistat before and after heating in an oven is shown in Figures 57a and 57b. The units for surface resistivity are ohms per square. In Figure 57, the coating on glass slides were rated less than 10 (non-uniform coverage including bare spots) when the surface conductivity was greater than 10^{10} ohms per square. The same experiment was conducted for the topical antistat and the results are given in Figure 58. The surface resistivity for all of the topical antistat treated glass slides were below 10^{10} ohms per square (Figure 58), and the coatings on all topical antistat treated glass slides were complete and uniform -- a rating of 10.

4.4.1.7 Conductive Primer Versus Antistats. The conductive primer could be easily applied to flat horizontal surfaces. However, on vertical surfaces (3-D objects), the nickel particles tended to slide off of these surfaces due to gravity rendering the vertical surfaces non-conductive making the conductive primer difficult to use.

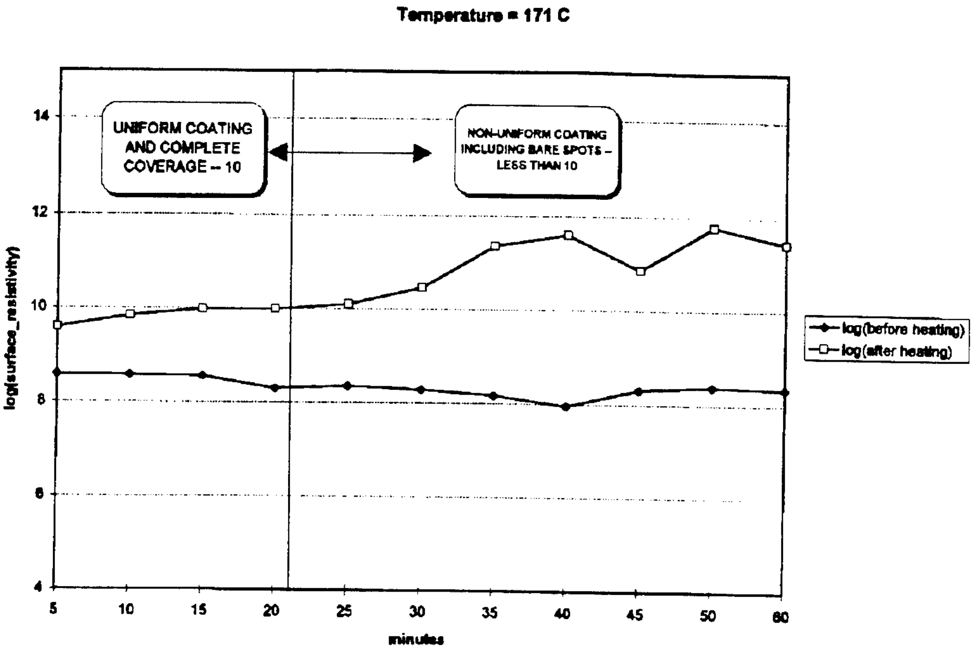
A couple of issues in certain aerospace applications needed to be addressed. First, it is desirable in the aerospace industry to add the least amount of weight onto a non-conductive surface when it comes to enhancing the surface conductivity of a non-conductive surface. Second, conductive primers often resulted in the attenuation of RF signals at unacceptable levels due to their high surface conductivity.

The average mass added onto a substrate with the topical antistat, aerosol antistat and conductive primer is $(1.3 +/- 0.5)x10^{-4}$ gram/cm^2, $(1.0 +/- 0.4)x10^{-4}$ gram/cm^2 and $(6.30 +/- 0.33)x10^{-3}$ grams/cm^2, respectively. By comparing the mean mass added onto a substrate with the antistats and the mean mass added onto a substrate with the conductive primer, the mean mass of the antistats was only 1.8% of the mean mass of the conducive primer.

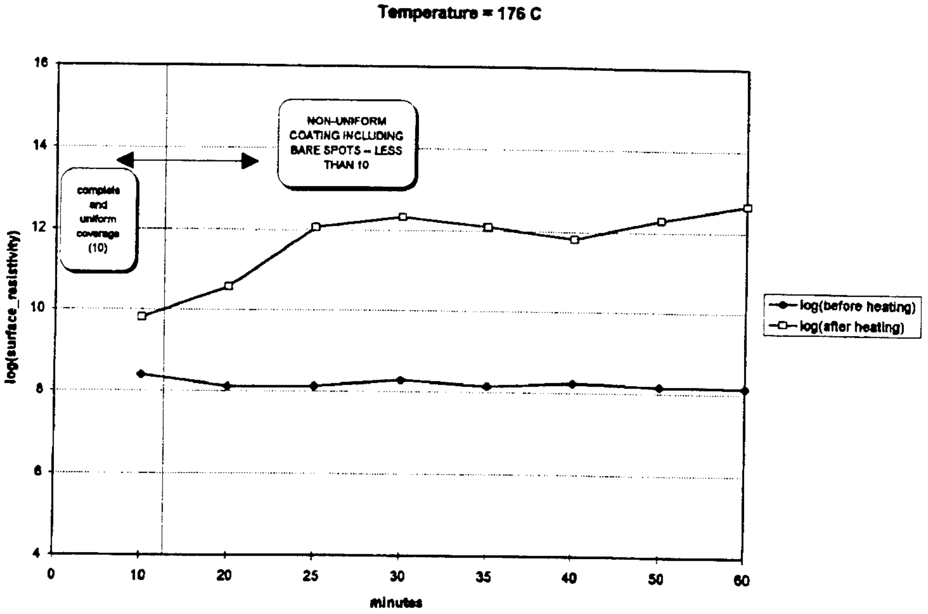
The following test was to determine the effect of the film transparency (antistats and conductive primer) to radio frequency energy in the 10 to 20 Gigahertz region. The test substrates were 3 X 3 inches tetrafunctional epoxy (FR406) substrates. The thickness of the FR406 epoxy substrates were 1422mm. The mass added onto the test substrates and its surface conductivity are shown in Table 56. Note that all of the FR406 epoxy substrates were treated 24 hours prior to testing. After RF testing, the primed epoxy substrate was cut into 1x3 in strip for surface resistivity measurements. In Figure 59, the bare FR406 epoxy substrate was used to calibrate the instrumentation by subtracting its contribution to radio frequency energy absorption. In Figures 60, 61, and 62, the attenuation characteristics of treated FR406 epoxy substrates were measured.

Table 56. Information on Test Substrates Prior to RF Testing

Surface Conductivity Enhancing Agent	Mass Added To Test Substrate -- grams/cm^2	Surface Resistivity Of Treated Substrate -- ohms per square
None	N/A	$1.55x10^{14}$
Aerosol Antistat	$1.21x10^{-4}$	$6.14x10^{9}$
Topical Antistat	$1.72x10^{-4}$	$2.83x10^{9}$
Conductive Primer	$6.92x10^{-3}$	$1.17x10^{2}$

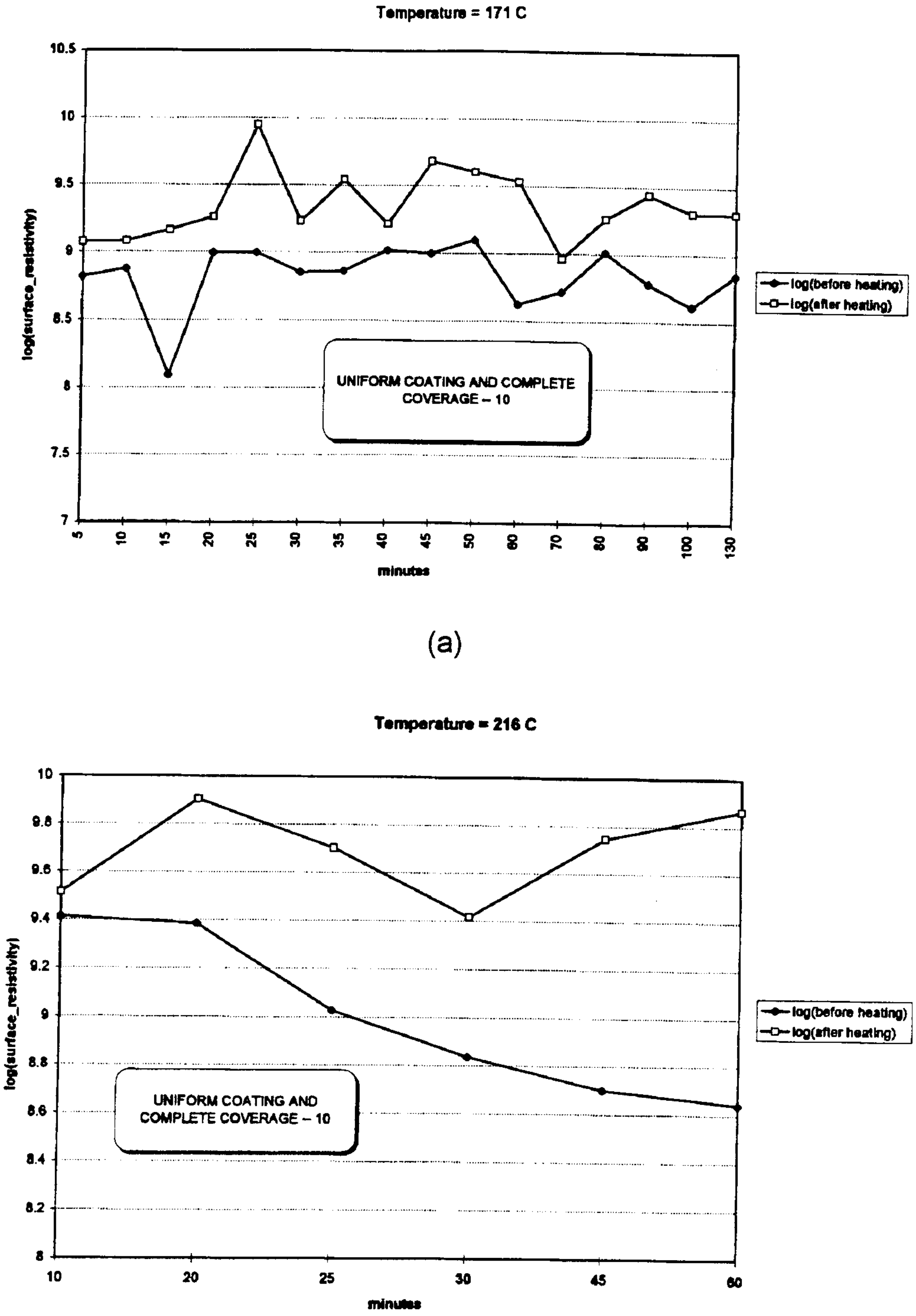


(a)



(b)

Figure 57
Log(ohms/square) vs. time for aerosol antistat: (a) temperature at 171° C, and (b) temperature at 176° C.



(a)

(b)

Figure 58
Log(ohms/square) vs. time for topical antistat: (a) temperature at 171° C, and (b) temperature at 216° C.

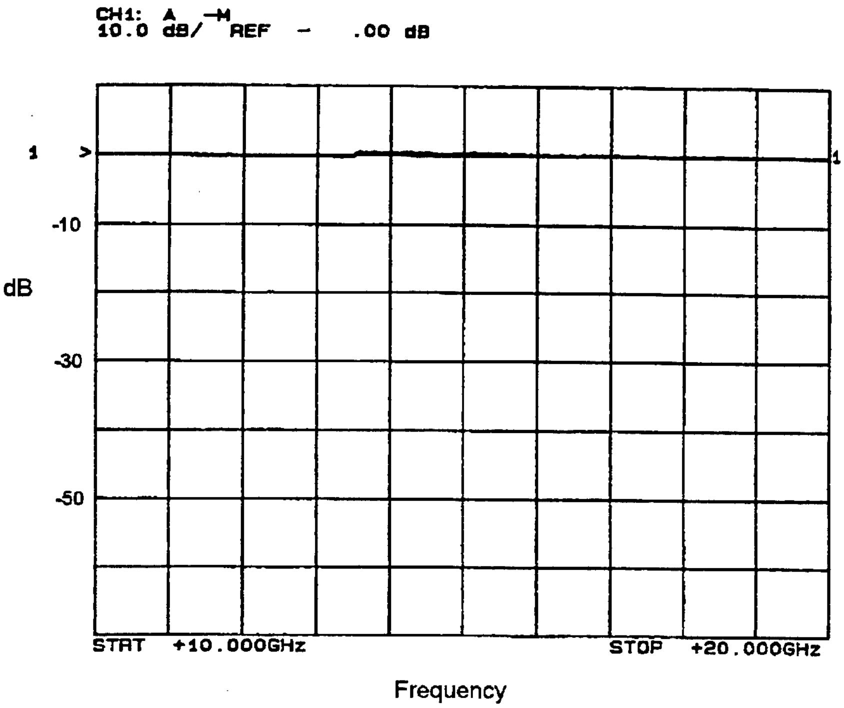


Figure 59
Bare Epoxy Substrate Calibration Characteristic

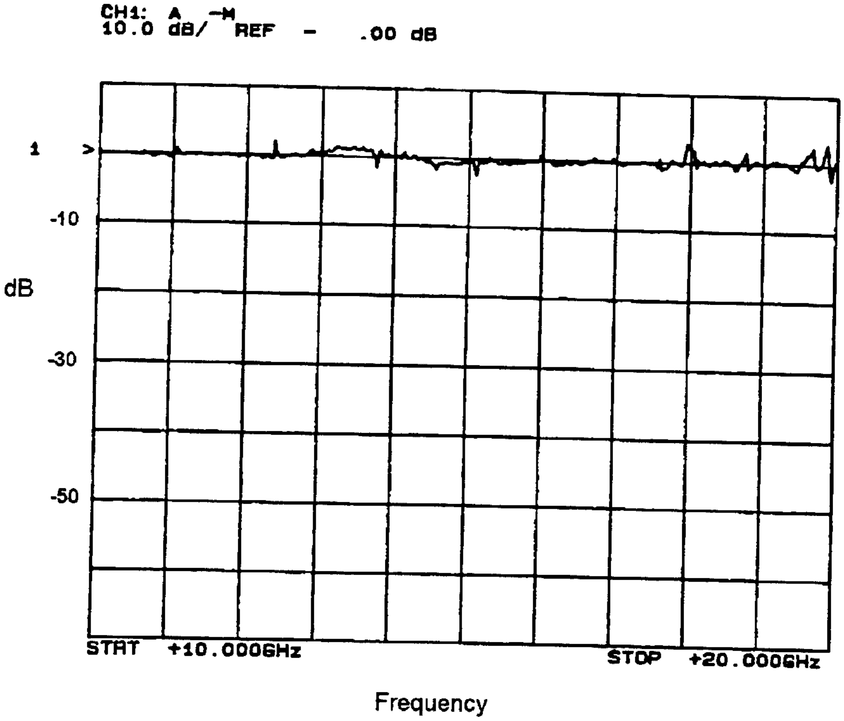


Figure 60
Attenuation Characteristics Of Topical Antistat Treated Epoxy Substrate

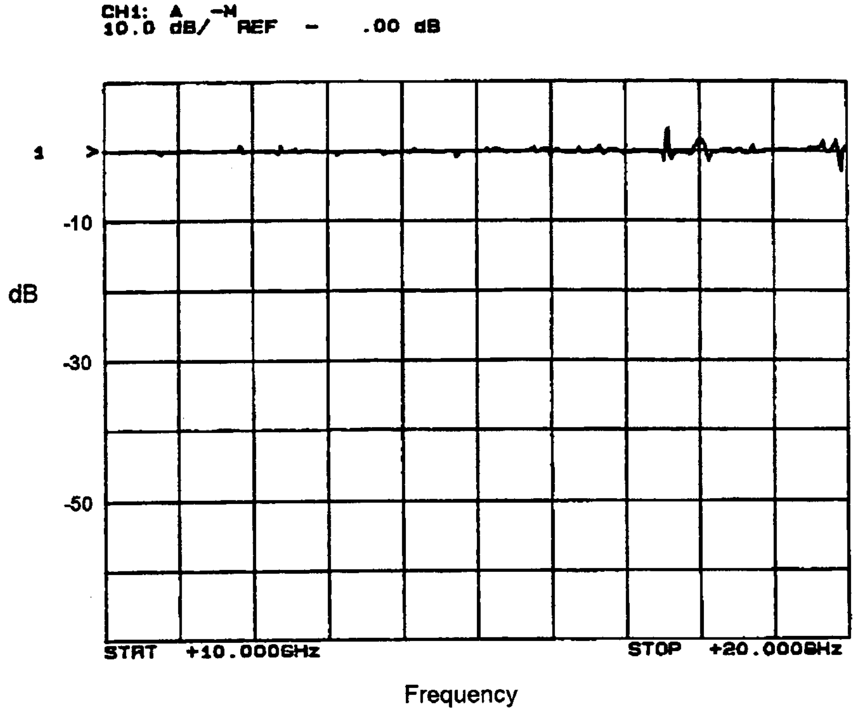


Figure 61
Attenuation Characteristics Of Topical Antistat Treated Epoxy Substrate

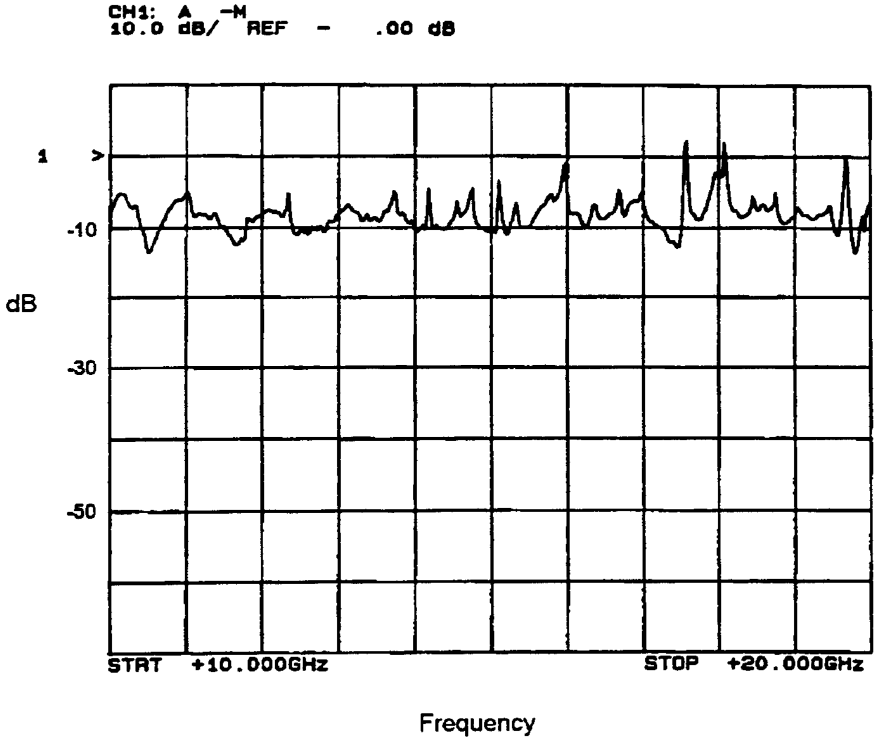
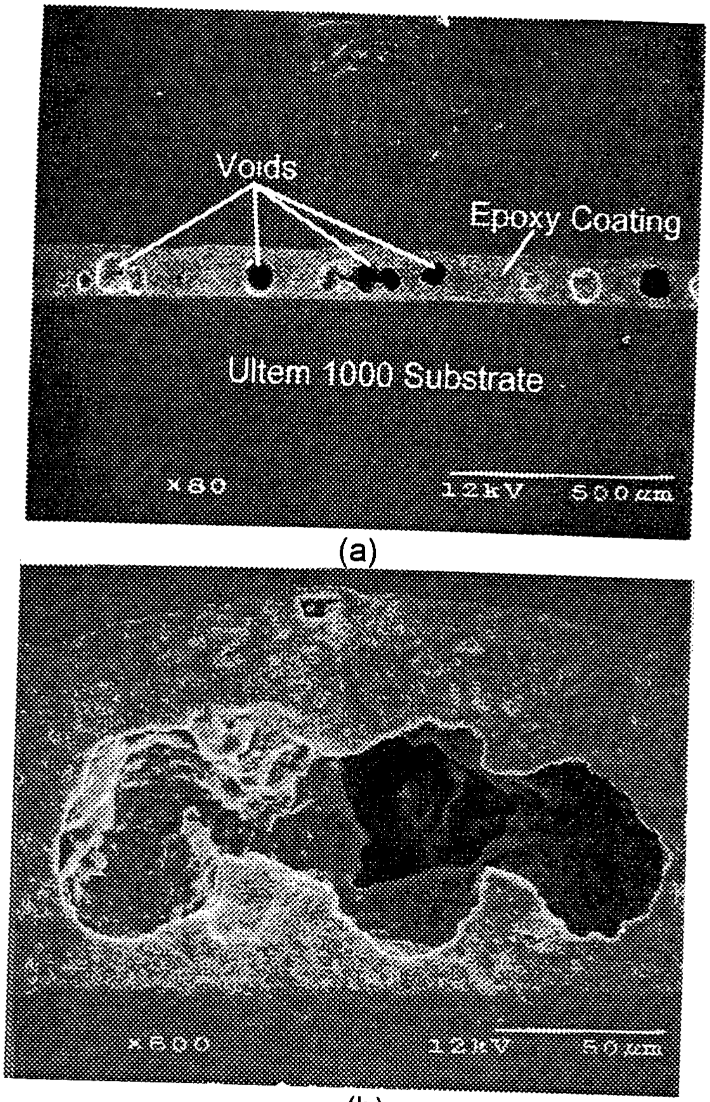


Figure 62
Attenuation characteristics of epoxy substrate coated with conductive primer.



(a)

(b)

Figure 63
SEM micrograph of polymeric coating on Ultem substrate: (a) Magnification 80X, and (b) Magnification 600X.

The data from RF testing indicated that the conductive primer attenuated at approximately 10 dB from 10 to 20 Gigahertz relative to the bare epoxy substrate which was unacceptable in certain aerospace applications. The antistats did not provide any attenuation relative to the bare epoxy substrate from 10 to 20 Gigahertz and would be acceptable in aerospace applications. The variation in the attenuation for the treated test samples could be caused by the lack of uniform distribution of the antistat film and coating on the test substrates.

<u>4.4.1.8 Void Formation.</u> The characterization of epoxy coating and selected non-conductive substrates indicated that under similar heating conditions, the non-conductive substrates acted as sources of water vapor up to and beyond the gelation time for the epoxy powder. It was very conceivable that there could be void formation within the cured epoxy coating due to water vapor expulsion from the non-conductive substrates. An Ultem substrate was treated with an aerosol antistat and then powder painted and cured. After powder painting, the Ultem substrate was cut normal to its surface to expose the internal morphology and microstructure of the polymeric coating. As shown in Figure 63a and Figure 63b, the water vapor phase was trapped within the polymeric coating creating voids. The void shown in Figure 63b is over 150 mm in length.

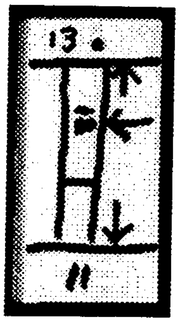


Figure 64
Sectioning of Ultem substrate. Cross sections were numbered 11, 12, and 13.

It needed to be determined whether the cross section displayed in Figure 63 was atypical or typical morphology of the epoxy coating. Figure 64 displays an actual image of a separate Ultem substrate that was powder painted and later sectioned. Three cross sections were separated from the 1 X 2 inch substrate (#11, #12, and #13) where each cross section is approximately one inch in length. The arrows shown in Figure 64 pointed to the cross section that would be exposed and characterized under the SEM after it has been separated from the substrate and mounted in a polymeric resin.

The morphology and microstructure of cross section #13 (Figure 65) represented a typical morphology and microstructure as seen in cross sections #11 and #12. Figure 66 displayed the morphology and microstructure of cross sections numbered 13, 12, and 11. As seen in Figure 66, the voids were internally spread throughout the epoxy coating homogeneously.

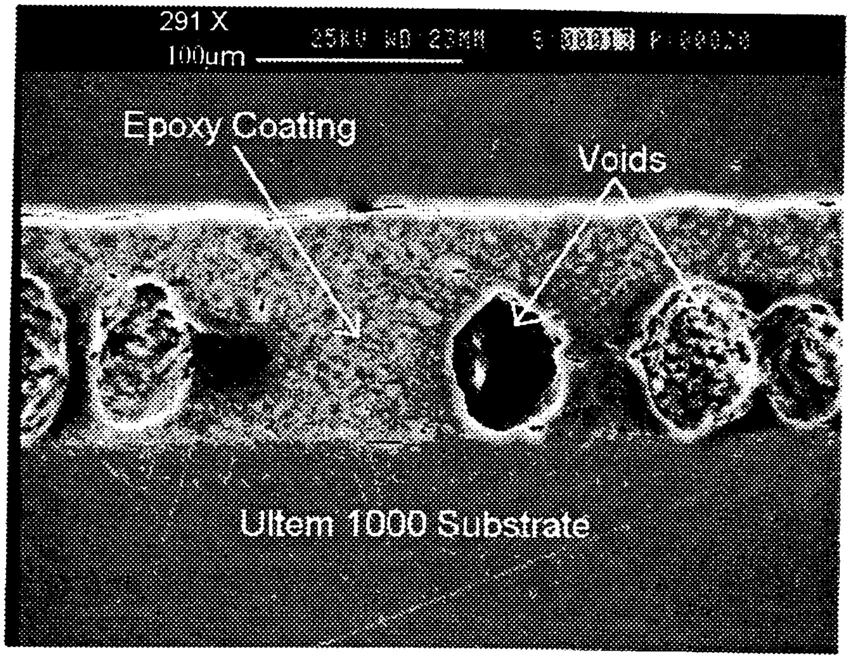


Figure 65
SEM micrograph of epoxy coating on cross section #13 .

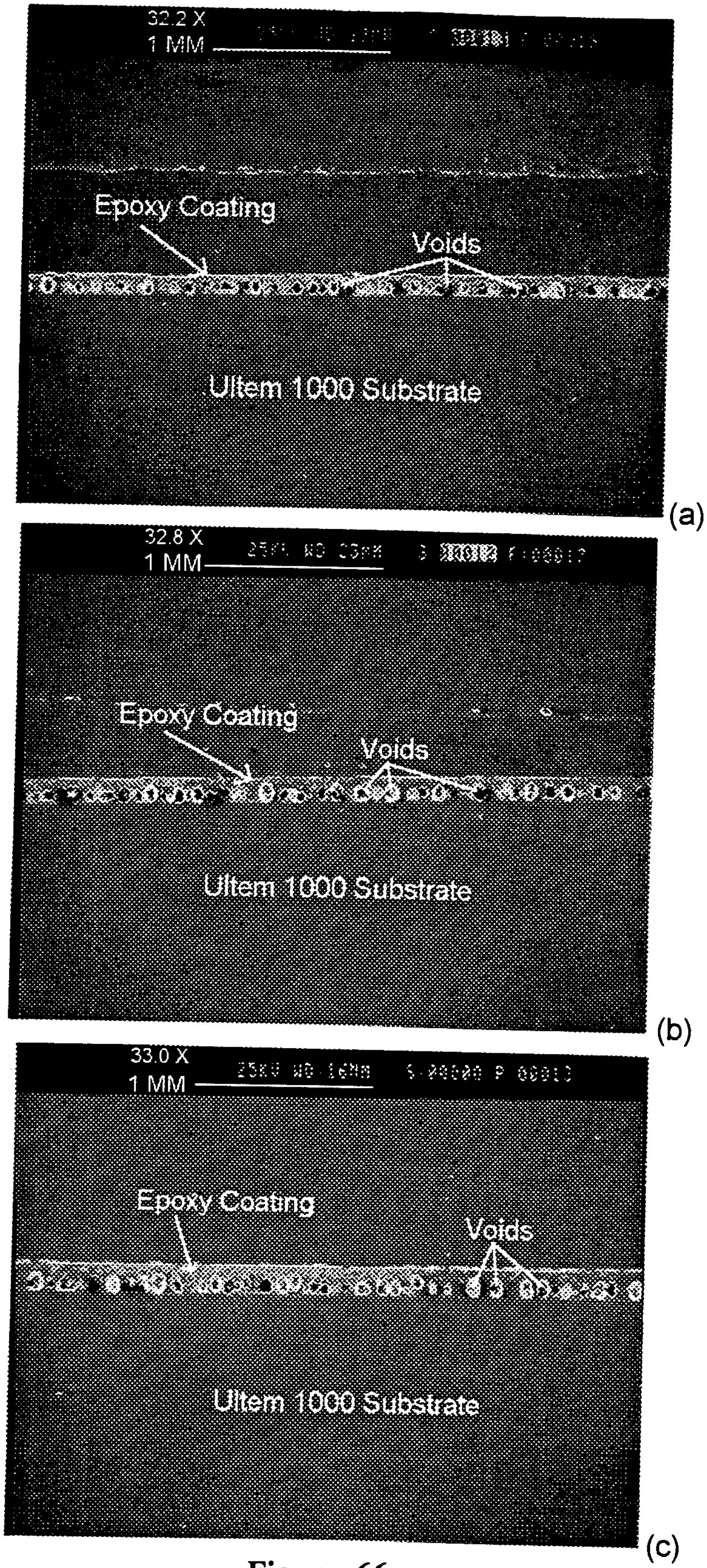


Figure 66
SEM micrograph of cross section of polymeric coating on Ultem substrate pictured in Figure 64: (a) cross section # 13, (b) cross section #12, and (c) cross section # 11.

Table 57 - Data for Percent Porosity of Epoxy Coating on Non-Conductive Substrates

Type Of Substrate	Treated with Topical Antistat	Treated with Aerosol Antistat
FR406 Tetrafunction Epoxy	7%	4%
G-30 Polyimide	24%	20%
Ultem 1000	26%	18%

Table 57 shows the data for percent porosity of epoxy coating on selected non-conductive substrates treated either with topical antistat or aerosol antistat. The powder painted substrates were approximately 1 x 2 inch, and the thickness of the Ultem 1000 substrate, FR406 Tetrafunctional Epoxy substrate and G-30 Polyimide substrate were 5842mm, 1422mm and 305mm, respectively. The weight of powder painted substrates were approximately 10.3 grams, 3.8 grams and 0.8 grams for Ultem 1000, FR406 Tetrafunctional Epoxy and G-30 Polyimide, respectively. The percent porosity for topical antistat treated substrates were higher than the percent porosity for aerosol antistat treated substrates. The topical antistat solution was 39 parts water and 1 part antistat concentrate. While treating the non-conductive substrates with the topical antistat, the substrates were saturated with water which would explain the higher figures for percent porosity of epoxy coating since the selected substrates could absorb water.

4.4.1.9 Eliminating Voids Within Epoxy Coatings. Two approaches were taken to reduce the porosity of the epoxy coating on non-conductive substrates. The first approach taken was to preheat the antistat treated substrate and to powder paint the substrate after it had cooled to room temperature. The second approach taken was to see if the conductive primer trapped the volatiles within the substrate and prevented the volatiles from reaching the epoxy coating during curing.

The first experiment dealt with preheating the antistat treated substrate. A set of non-conductive substrates were treated with the aerosol antistat and the topical antistat and were preheated to 165°C for 20 minutes. In Table 58, the data for percent porosity is shown for preheated and non-preheated substrates.

As seen in Table 58, the porosity decreased when the substrates were preheated with the exception of the tetrafunctional epoxy treated with the aerosol antistat. The problem associated with preheating the substrate was that it might be a part of an assembly in which preheating an entire assembly could damage components within the assembly.

The second attempt to reduce porosity was to trap the volatiles within the substrate by applying the conductive primer onto non-conductive substrates. The amount of conductive primer added to Tetrafunction Epoxy, Polyimide and Ultem substrates are 5.988×10^{-3} gram/cm^2, 6.549×10^{-3} grams/cm^2 and 6.421×10^{-3} grams/cm^2, respectively. Figure 67 shows the morphology and microstructure of the epoxy coating on Ultem 1000 substrate treated with the conductive primer as compared to Figure 65. The micrograph in Figure 67 did not clearly show the nickel particles in the conductive primer. In Figure 68, the microstructure of the epoxy coating on tetrafunctional epoxy treated with the conductive primer did clearly show the nickel particles. The epoxy powder seemed to flow into the conductive primer during curing which could be seen in both Figure 67 and Figure 68.

Table 59 showed the percent porosity between aerosol treated substrates and substrates treated

Table 58 - Comparison of Percent Porosity Between Preheated and Non Preheated Substrates.

SUBSTRATE TYPE AND ANTISTAT USED	PERCENT POROSITY WITHOUT PREHEATING	PERCENT POROSITY WITH PREHEATING AT 165°C FOR 20 MINUTES	CHANGE IN POROSITY
Tetrafunctional epoxy (FR406) substrate treated with aerosol antistat	4%	4%	No Change 0%
Polyimide (G-30) substrate treated with aerosol antistat	20%	7%	Decreased by 65%
Ultem 1000 substrate treated with aerosol antistat	18%	11%	Decreased by 39%
Tetrafunctional epoxy (FR406) substrate treated with topical antistat	7%	3%	Decreased by 57%
Polyimide (G-30) substrate treated with topical antistat	24%	10%	Decreased by 58%
Ultem 1000 substrate treated with topical antistat	26%	15%	Decreased by 42%

with the conductive primer. Note that volatiles have penetrated through the conductive primer on the polyimide substrate. As noted earlier, the conductive primer was difficult to apply onto 3-D objects. What was needed is a water based primer that could be easily applied to 3-D objects which could trap volatiles within the substrate during curing of the epoxy powder. After applying the primer, the antistat could be used to enhance the surface conductivity of the primer making it possible to powder paint the substrate. This combination of water based primer sealant and antistats used to powder paint non-conductive substrates is currently being evaluated by Hughes Missile Systems Company in Tucson, Arizona.

Table 59. Comparison of Percent Porosity Between Aerosol Treated Substrates and Substrates Treated with Primer.

Substrate	Percent Porosity Of Epoxy Coating On Aerosol Antistat Treated Substrate	Percent Porosity Of Epoxy Coating On Substrate Treated With Conductive Primer	Change In Porosity
FR406 Tetrafunctional Epoxy	4%	0%	DECREASED BY 100%
G-30 Polyimide	20%	5%	DECREASED BY 75%
Ultem 1000	18%	0%	DECREASED BY 100%

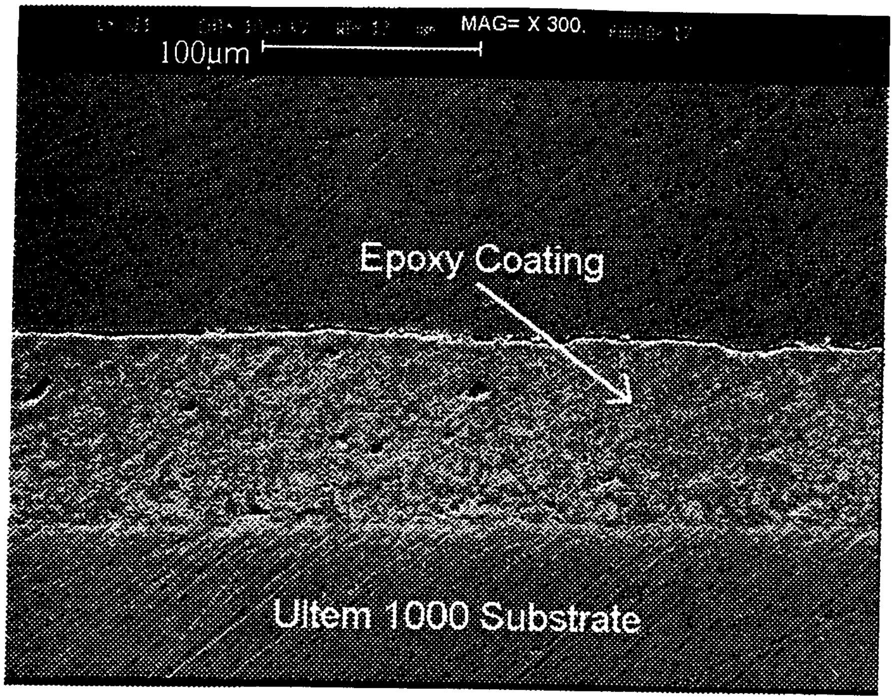


Figure 67
SEM micrograph of epoxy coating on Ultem substrate treated with conductive primer.

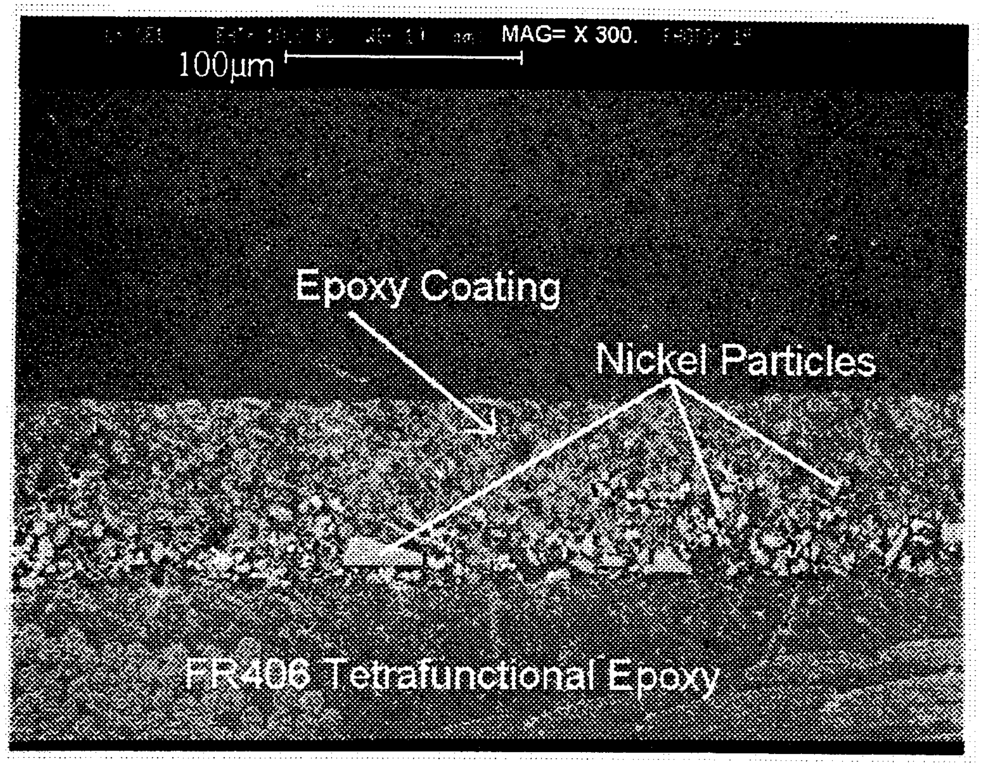


Figure 68
SEM micrograph of epoxy coating on tetrafunctional epoxy substrate treated with conductive primer.

4.4.2 IR Curing

4.4.2.1 IR Curing Equipment Survey. HMSC conducted a literature search to identify manufacturers and users of IR curing equipment. The survey included supplier literature and data available through HMSC Procurement. In general, very little mention of IR curing of powder coatings was discovered. Most IR curing in commercial industry is aimed at high-rate production of consumer items and finishing of certain commodities for the construction and architectural industries. In the majority of cases wet (solvent-based) finishing systems were used.

HMSC personnel made two trips to the Southern California area to survey IR equipment types and to conduct preliminary testing. The Southern California Edison (SCE) Customer Technology Applications Center (CTAC) was identified as a user of IR curing equipment. SCE CTAC is a utility sponsored technology center which assists large industrial consumers of electricity in identifying and developing energy-efficient manufacturing methods. SCE CTAC owns and uses a wide variety of IR curing equipment, and has experimented with IR curing of powders (primarily clear-coats).

Infratech Inc. was also visited as a supplier of IR curing apparatuses. Infratech offers a number of off-the-shelf IR models, and also manufactures custom designed units. They offer an in-house design service and have produced IR curing equipment for a wide variety of industries. They also use IR curing in their manufacturing operations and have successfully IR cured powders as a standard finish.

A summary of equipment related findings are as follows:

- Mediumwave IR was found to be best for curing powders. Shortwave IR is also used in industry, but tends to overheat the epoxy used in the HMSC tests. Longwave IR was generally limited to preheating substrates and coated assemblies.

- Most IR equipment is conveyorized. This is the result of the industry focus on high-rate, large volume coating and finishing. Batch units are available but are normally limited to laboratory and research and development applications.

- Temperature control is important as IR can easily overheat the object to be cured. There are two approaches to temperature control. The first always runs the elements at full power, and cycles them on and off to control temperature. These on/off cycles normally range from a few seconds to a minute or two "on" followed by an "off" period which also ranges from a few seconds to minutes. A time slice percentage controller is provided to control the cycles (for example, 60% "on" and 40% "off"). With this approach the exposure to IR energy is kept short enough to eliminate the possibility of overheating.

With the second form of temperature control the IR elements are always powered but at a reduced intensity. For example, the elements might be operating at 85% of full rated power. A potentiometer or silicon controlled rectifier (SCR) is provided to control the elements at reduced power. There is some disagreement in the industry as to the effect of operating IR elements at reduced power; Infratech indicated that doing so may reduce element life, but had no data to correlate their belief. Observations indicated that the variable intensity approach has limited range since the IR elements must be powered above a threshold level to generate appreciable IR energy. Generally, levels above about 80% are most efficient, and below about 60% there is not sufficient IR energy to cure powders.

4.4.2.2 Preliminary IR Cure Powder Testing. Preliminary testing was performed with IR curing equipment during on-site visits to SCE CTAC and Infratech, Inc.. The purpose of the testing was to qualitatively assess the performance of IR cured powder finishes and to define operating parameters of interest. The powder used was the standard HMSC gray epoxy powder paint. Test substrates were various sizes and thicknesses of aluminum sheet. A solvent wipe with methyl ethyl ketone (MEK) was used as a "quick-look" indicator of extent of cure. Table 60 shows the results obtained at SCE and Table 61 shows the results obtained at Infratech.

Essential findings of the preliminary testing included:

- Mediumwave IR was found to produce the best test results. Shortwave IR tended to overheat the panels resulting in browning and scorching. No tests were done with longwave (see 4.4.2.1)

- To achieve full cure of the epoxy, panels must achieve and be held at a temperature of at least 170°C for a period of several minutes. For the powder used in the tests 170°C essentially corresponds to the manufacturer's recommended cure temperature. A total cure time of 600 seconds (10 minutes) was found to give the best results. Increasingly shorter cure times led to incomplete cure (even if the film appeared to have fused and hardened) and poor physical properties.

- Fusion (melting or flow) occurs very rapidly in the IR systems, generally within 20 seconds, with polymerization following.

- A correlation between high IR power levels/high temperature/fast cure times (less than 3 or 4 minutes) and high gloss was found. This is consistent with HMSC production experience with the powder being tested.

- Physical properties (adhesion, flexibility, etc.) tended to improve with longer cure times and relatively low temperatures (close to the manufacturer's recommendation). All samples passed corrosion resistance testing regardless of cure time and temperature.

4.4.2.3 IR Curing of Powder Versus Convection Curing. The initial development using the IR oven procured as part of this project and located at HMSC-Tucson required profiling to determine the required equipment settings. The IR oven was profiled to determine the required settings to obtain the substrate surface temperatures needed to obtain a full coating cure. Steel panels were instrumented with thermal couples and processed through the IR oven to obtain thermal profiles of the substrate surface. The instrumented panels were then powder coated and processed through the oven since the emissivity of the coated panels would be slightly different than the bare steel panels. The profile was then complete and the required IR oven settings determined. An MEK wipe was used to determine the extent of cure on the coated substrates to insure a full cure was obtained.

Figures 69 and 70 contain the results of oven calibration and paint cure versus IR oven settings obtained during profiling of the IR oven. From these results, the desired surface temperature can be achieved to insure a full cure of the powder coating. These results were used to process substrates to test the coating properties when cured with IR.

A Herberts white epoxy powder paint was used to evaluate the effects of IR curing on the properties of the powder coating. Aluminum test panels were painted and cured with the IR oven and the physical properties were tested and compared to panels cured in a convection oven. Table 62 shows the results of both the IR cured and convection cured aluminum panels. Unfortunately, the extended salt fog testing on the IR cured panels was not completed due to

Table 60. IR Cured Powder Coat Test Results Sprayed and Cured at SCE

Sample	Power, %	Range	Time, s	Peak Temp, C	Gloss, 60 Degree	Thickness, mm	MEK Wipe	Adhesion	Corrosion	Bend, mm
1	--	H	--	--	4.2	0.043	F	F	P	75+
2	30	H	60	221	4.2	0.067	F	F	P	75+
3	20	H	60	216	4.6	0.048	F	F	P	75+
4	10	H	60	210	5.1	0.040	F	F	P	75+
5	5	L	60	210	4.5	0.041	F	F	P	75+
6	100	L	240	177	8.1	0.032	F	F	P	41
7	100	L	90	179	11.4	0.042	F	F	P	75+
8	80	L	180	177	5.7	0.032	F	F	P	26
9	70	L	300	175	4.6	0.040	P	P	P	75+
10	60	L	300	182	5.1	0.035	P	F	P	0
11	60	L	600	184	4.7	0.059	P	P	P	0
12	70	L	600	171	5.1	0.025	P	F	P	0
13	80	L	600	189	4.4	0.045	P	P	P	75+
14*	--	--	--	204	3.5	0.036	P	P	P	75+
15*	--	--	--	171	4.1	0.047	P	P	P	75+
16*	--	--	--	177	3.7	0.040	P	P	P	0
17	90	L	600	181	5.8	0.034	P	P	P	6
18	100	L	600	183	5.0	0.014	P	P	P	0
19	80	L	600	--	4.5	0.092	P	F	P	75+
20	80	L	600	--	4.5	0.066	F	P	P	6

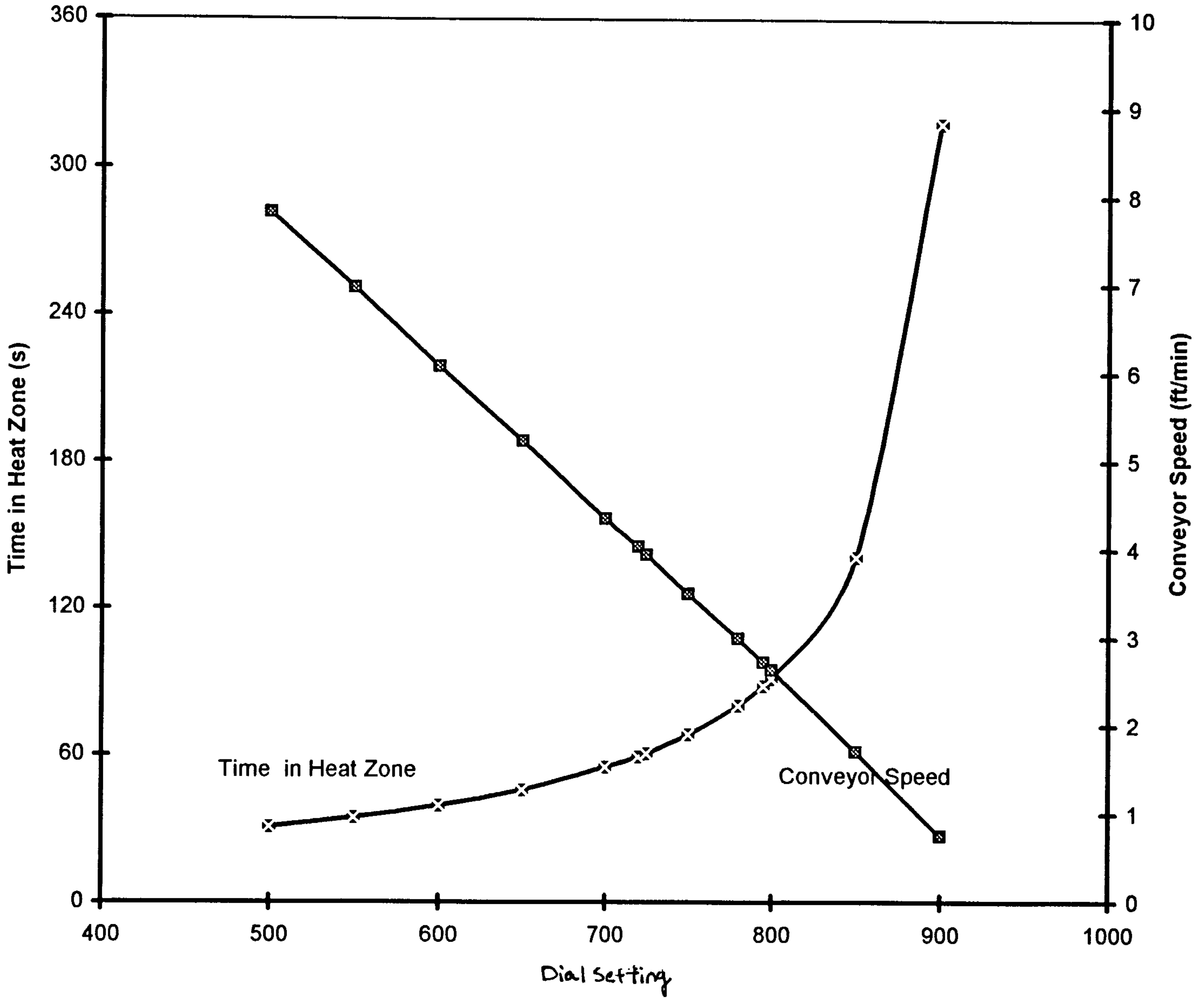
Notes:
1. Ambient temperature = 84 F
2. Powder was Courtaulds 801500-103 (grey) expiring July 31, 1994
3. Range: "H" = high = shortwave IR, "L" = low = mediumwave IR
4. '--' in Peak temperature column indicates measurement not taken
5. For test methods see text
6. Specimens 14, 15, and 16 were cured in a conveyorized dual-side chamber and are considered "No Tests" since they were overheated and badly discolored (see text).
7. "P" = Pass, "F" = Fail

Table 61. IR Cured Powder Coat Test Results Sprayed and Cured at Infratech, Inc.

Sample	Power, %	Speed (Setting)	Speed (Seconds)	Position		MEK Wipe	Adhesion (Wet Tape)	Color	Gloss	Comments
1	100	2	245	+		P	P	Brown	Low	
2	100	5	34	+		F	P	OK	Low	Edges Bubbled
3	75	2	155	+		P	P	OK	Low	Edges Bubbled
4	30	2	168	+		F	F	OK	High	
5	100	10	20	+		F	F	OK	High	
6	30	* --	600	+		F	F	OK	High	
7	30	* --	600	/ /		F	F	OK	Mod.	
8	80	4	61	+		F	F	OK	Mod.	
9	60	4	60	+		F	F	OK	High	Edges Bubbled
10	35	* --	600	+		P	NT	OK	Low	

Notes:
1. Powder was Courtaulds 801500-103 (low-gloss grey) expiring July 31, 1994.
2. Speed in seconds is residence time in curing zone.
3. Speed settings indicated "* --" were run into curing zone, stopped, then run out to achieve long dwell.
4. Position:
   "+" indicates sample perpendicular to heating elements
   "//" indicates sample parallel to heating elements
5. For test methods see text.
6. "P" = Pass, "F" = Fail, "NT" = No Test
7. Color: "Brown" indicates evidence of scorching, "OK" indicates normal grey color.
8. Gloss is subjective.

Figure 69
IR Oven Conveyor Calibration



Oven Dwell (s)	Hold Time (s)	Peak Temperature (F)	Solvent Resistance
30	0	415	poor
90	0	411-425	fair(loss of gloss)
-	90	410	good
-	180	425	good but yellowing

Figure 70 Paint Cure Versus IR Oven Setting and Peak Temperature

problems with the salt fog chamber and completion of this ARPA contract. From the existing data, however, it can be seen that the faster cure time associated with IR curing does not effect the physical properties of the epoxy powder paint. Although limited salt fog testing was performed on the IR cured panels, the salt fog results of IR cured panels are not expected to vary from those results obtained from convection cured powder paints.

4.4.2.4 IR Curing of Non-Conventional Shapes. In order to evaluate the impact of substrate configuration on the ability to IR cure powder paint, a graphite polyimide composite substrate was used. This testing was focused at determining if the internal portion of the substrate could be kept to a minimum while achieving the desired surface temperatures required to cure the powder paint. In addition, the thermal temperature gradient across the surface of the

Table 62. Powder Paint Properties of IR Cured Versus Convection Cured Samples

	Test#1	2	3	4	5	6	7	8
Paint Code (Whites)	24 Hour Water	96 Hour Water	168 Hour Water	JP4 Fuels	Lubricating Fluid	Hydraulic Fluid	2,000 Hour Salt Fog	42 Inch Flex
Convection Cured	5A	5A	5A	PASS	PASS	PASS	3/4 Pass	PASS
IR Cured	5A	5A	5A	PASS	PASS	PASS	4/4 PASS*	PASS

Notes:

1. Key to tests #1 to 3 from ASTM D3359, Table 1.

Code	Description
5A	No Peeling or Removal
4A	Trace peeling of removal along incisions
3A	Jagged removal along incisions up to 1/16" on either side
2A	Jagged removal along most of the incisions up to 1/8"
1A	Removal from most of the area of the X under the tape
0A	Removal beyond the area of the X

2. The 42 Inch Flex Ratings - Knobs on impact fixture set for elongation ratings of: .5, 1, 2, 5, 10, 20, 40, 60% A statement of 40% means that the paint failed at the 40% elongation.

* Salt fog tested for 120 hours only.

part was measured to determine if temperatures could be maintained across the surface with the irregular shape of the substrate. The shape of the sample parts used and the thermocouple locations are shown in Figure 71.

The sample was prepared with shallow grooves to accommodate thermocouple wire. The thermocouples were attached to the sample with epoxy adhesive. Only a portion of the thermocouple bead was exposed at the surface prior to painting. Type K thermocouples were used for this test to monitor temperatures up to 500°F. Both the outer surface and the unpainted inner surface were instrumented to determine the gradient through the sample thickness. The numerous thermocouples along the outer surface helped to determine the thermal gradients across the surface of the sample.

Two tests were performed with different oven settings. In the initial test the paint did not exceed 400°F to achieve cure. Therefore, the second test was performed to cure the paint by exceeding 400°F for a minimum of 90 seconds. During the second test, most of the sample did not exceed 400°F. However, the peak temperature on the sample was greater the 450°F. The temperatures could not go much higher without discoloring the white paint.

The test data showed that the response of the sample under the oven heat load was rapid. the thin outer tips of the sample heated much faster than the thicker central crotch area of the sample. The hot tips are evident when looking at the temperatures along the outer surface, that is thermocouples 0 through 5 plotted in Figures 72 and 73. Thermocouples 0,1, and 5 are nearest to the tips and are also the hottest. Thermocouples 2,3, and 4 are nearest the center and are cooler.

Figures 72 and 73 also show the difference in temperature between the upper section and the lower legs. The upper section of the sample is hotter than the lower legs. This temperature difference is probably due to heating on both sides of the upper section where the legs are only heated by radiation on one side.

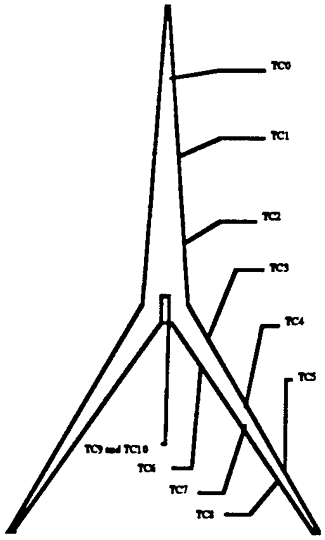


Figure 71
Composite Sample Cross-Section Showing Thermocouple Locations

Figure 72: Composite Sample Powder Paint Test #1
Outer Surface Temperatures

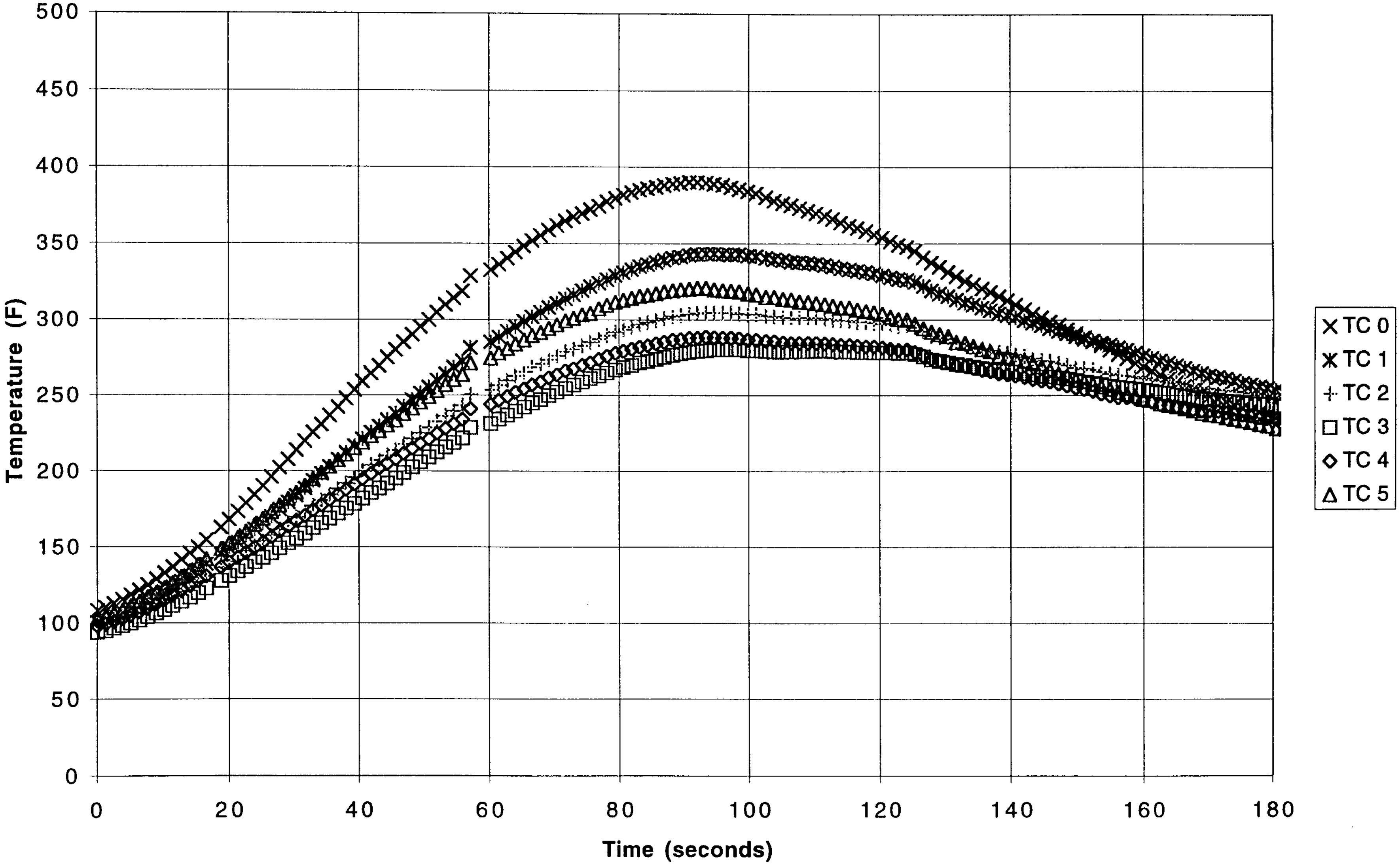


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Figure 73: Composite Sample Powder Paint Test #2
Outer Surface Temperatures

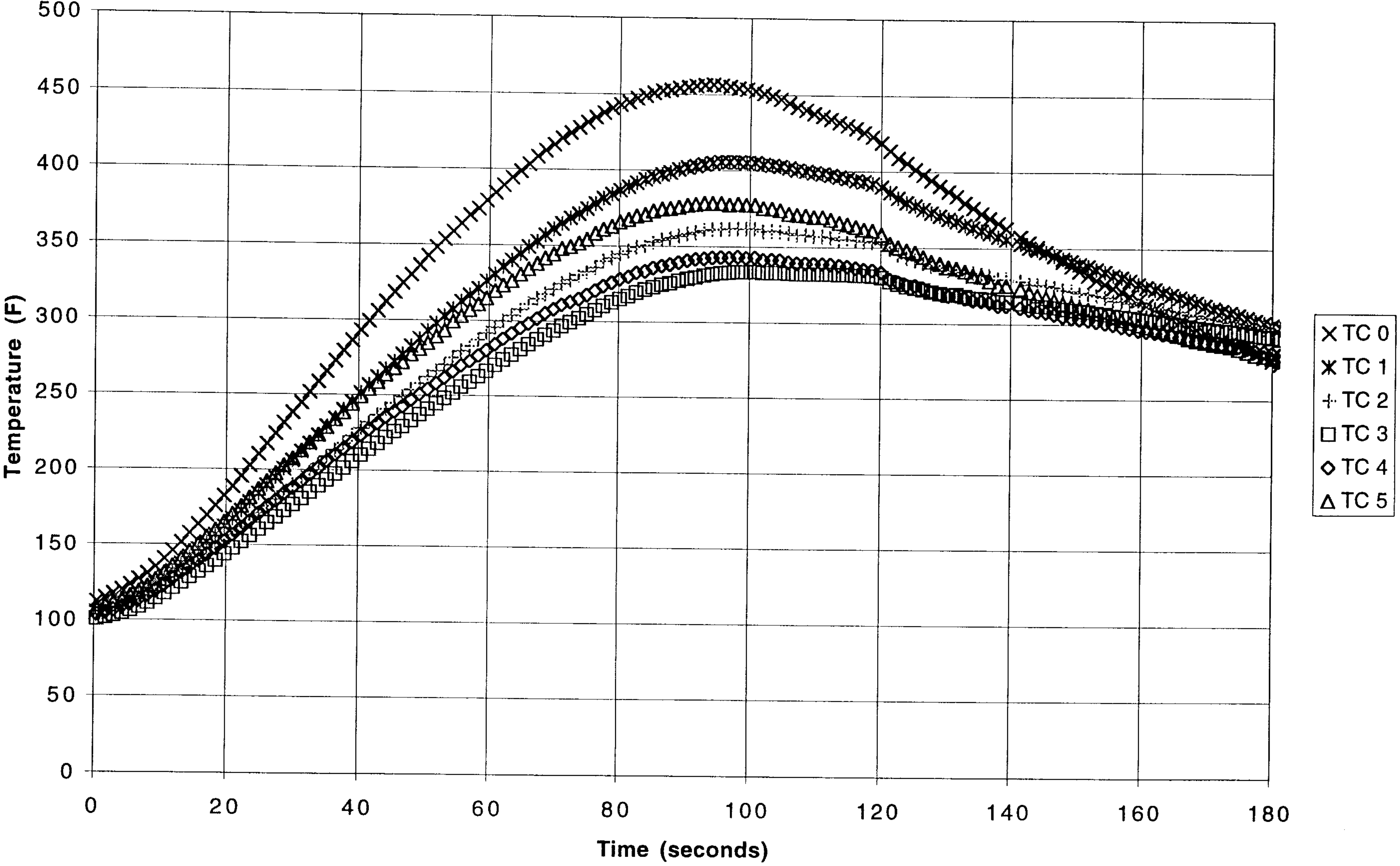


Figure 74: Composite Sample Powder Paint Test #1
Leg temperature: Inner & Outer Surfaces

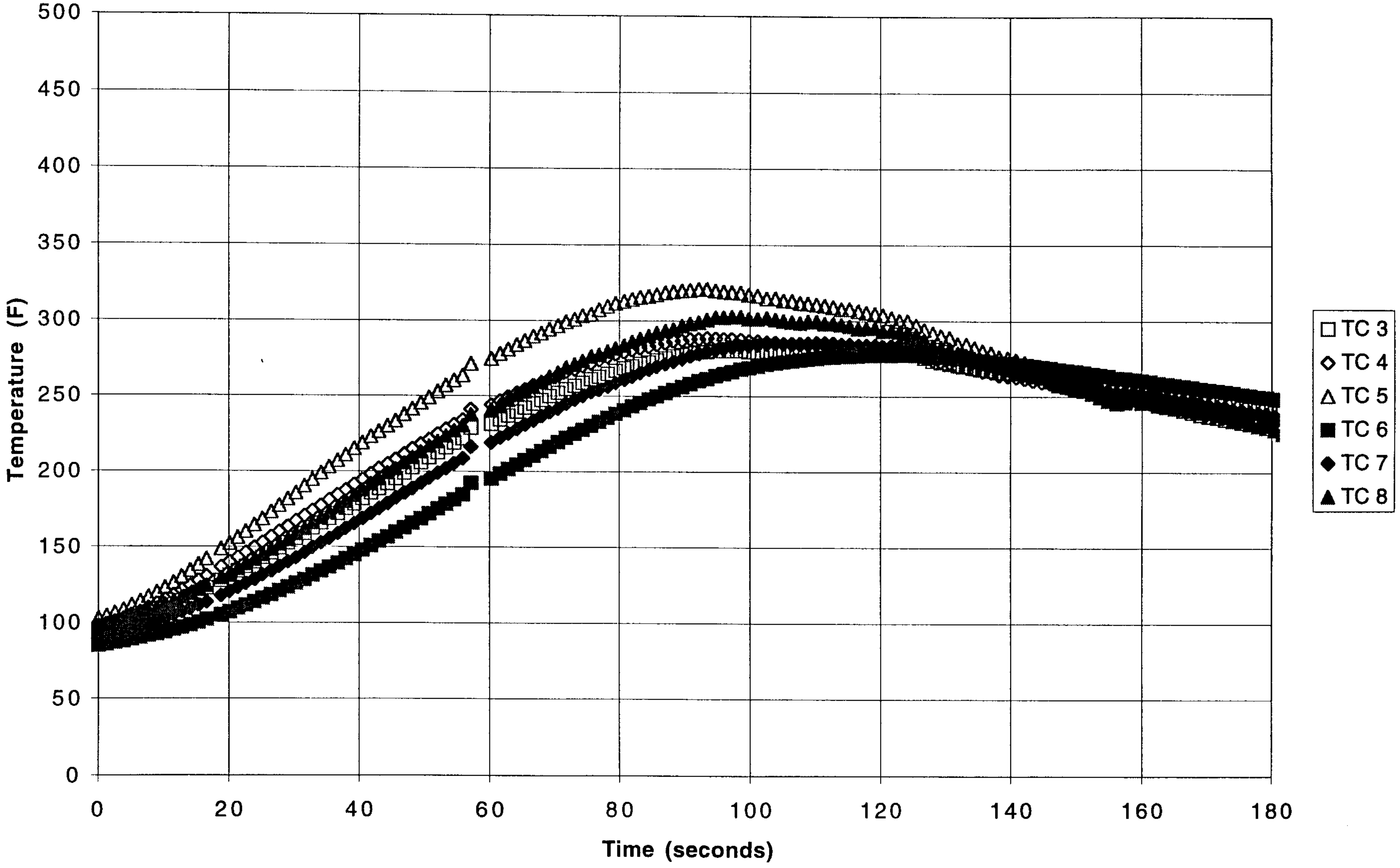
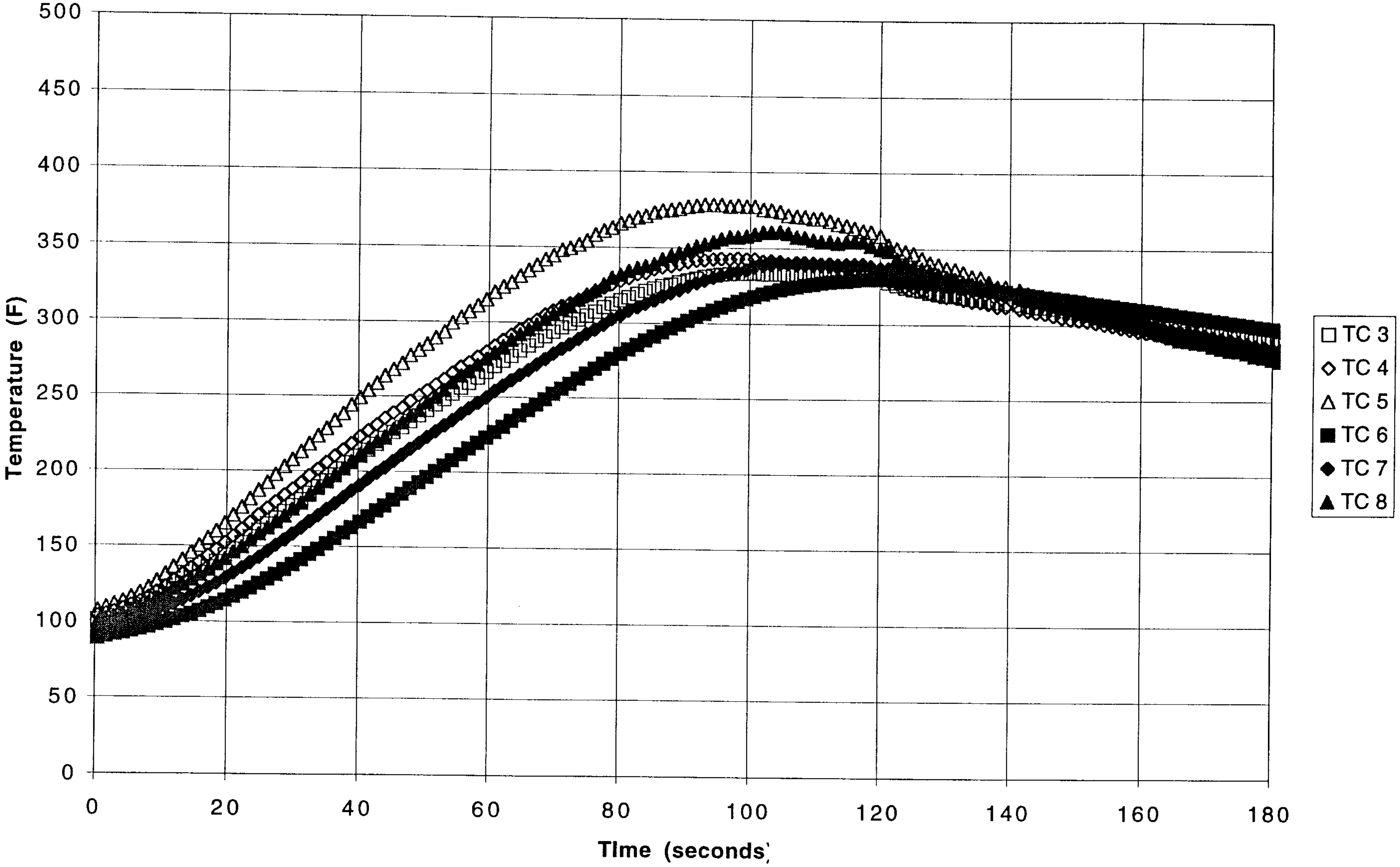


Figure 75: Composite Sample Powder Paint Test #2
Leg Temperatures: Inner & Outer Surface



The temperature gradient through the thickness is plotted in Figures 74 and 75. These plots compare thermocouples on the outer surface with the corresponding inner surface thermocouples. As shown in Figure 71 the outer thermocouples 3,4, and 5 have corresponding inner thermocouples 6, 7, and 8, respectively. Again the pattern is hottest at the tip and cooler towards the center. These plots demonstrate why the proposed cure process is not possible with this substrate configuration. The inner thermocouple, TC8, is hotter than the outer surface thermocouples TC3 and TC4.

Heating the painted outer surface while maintaining a cooler substrate temperature does not appear to be feasible because of the thin cross section of the substrate. The amount of time required to cure the paint is greater than the thermal response time of the inner surfaces of the sample, especially near the tip. The large thermal gradient on the outer surface will cause another problem. To completely cure the paint on the substrate, the coolest portion of the outer surface must exceed 400°F. The thermal gradient on the outer substrate surface is well over 100°F. This thermal gradient requires the hottest part of the substrate to exceed 500°F, while the coolest section is barely cured. Exposure to temperatures in excess of 500°F will cause discoloration and degradation of the epoxy paint.

The shape of the substrate is important in determining if IR curing can be applied. Irregular shapes such as those tested as part of this program illustrated uneven surface heating making a uniform cure difficult. A modified IR curing oven, in which the IR source is located proportionally to the shape of the part, may provide the even surface temperatures by eliminating thermal gradients across the surface. The internal temperature of the part was not minimized by the short heating cycle of the IR cure. Although only a 90 second heating cycle was required, the thermal conduction of the substrate material and the cross-sectional thickness of the substrate allowed the internal temperature to rise quickly. Based on the material, shape and thickness of the part, some substrates would exhibit cooler internal temperatures but this would be a case by case basis.

4.5 Inhibitor Characterization and Analysis. The technical results in this section are organized into 7 subsections which describe the various techniques used to determine corrosion inhibitor mechanisms in protective coatings.

4.5.1 Electrochemical Impedance Spectroscopy Results. The selection of EIS as a tool for the inhibitor mechanism study was based on observations [50] that an increase in low frequency impedance implies an increase in polarization resistance of the specimen and indicates greater corrosion resistance, and for these systems, implies that the inhibitor is effective. Mechanistically, it is postulated that increases in low frequency impedance are due to the incorporation of the inhibitor species in the oxide film which results in a more resistive oxide and/or the formation of a resistive barrier on the oxide surface.

EIS measurements were made on epoxy coated aluminum panels. Two impedance systems were used: (1) an EG&G Princeton Applied Research Corporation Model 173/179 potentiostat with a computer-controlled Schlumberger Solartron 1250 frequency response analyzer (Figure 76), and (2) a Gamry Instruments CMS300 Electrochemical Impedance Software and a Stanford Research Systems model SR810DSP Lock-in Amplifier. The impedance spectra were generated using a frequency range of 10^5 - 0.003 Hz. The amplitude of the AC signal was 5 mV for coatings with defects and porous coatings, and 50 mV for non-porous coatings. A three-electrode setup was used where the working electrode was the aluminum substrate, the reference electrode was Ag/AgCl, and the counter electrode was a graphite rod. The electrochemical cell (Figure 76) consisted of a glass cylinder fitted with an O-ring sealed to the sample surface. The area of exposure was 8.8 cm^2. All impedance spectra were obtained at room temperature (23 ± 2 degrees C).

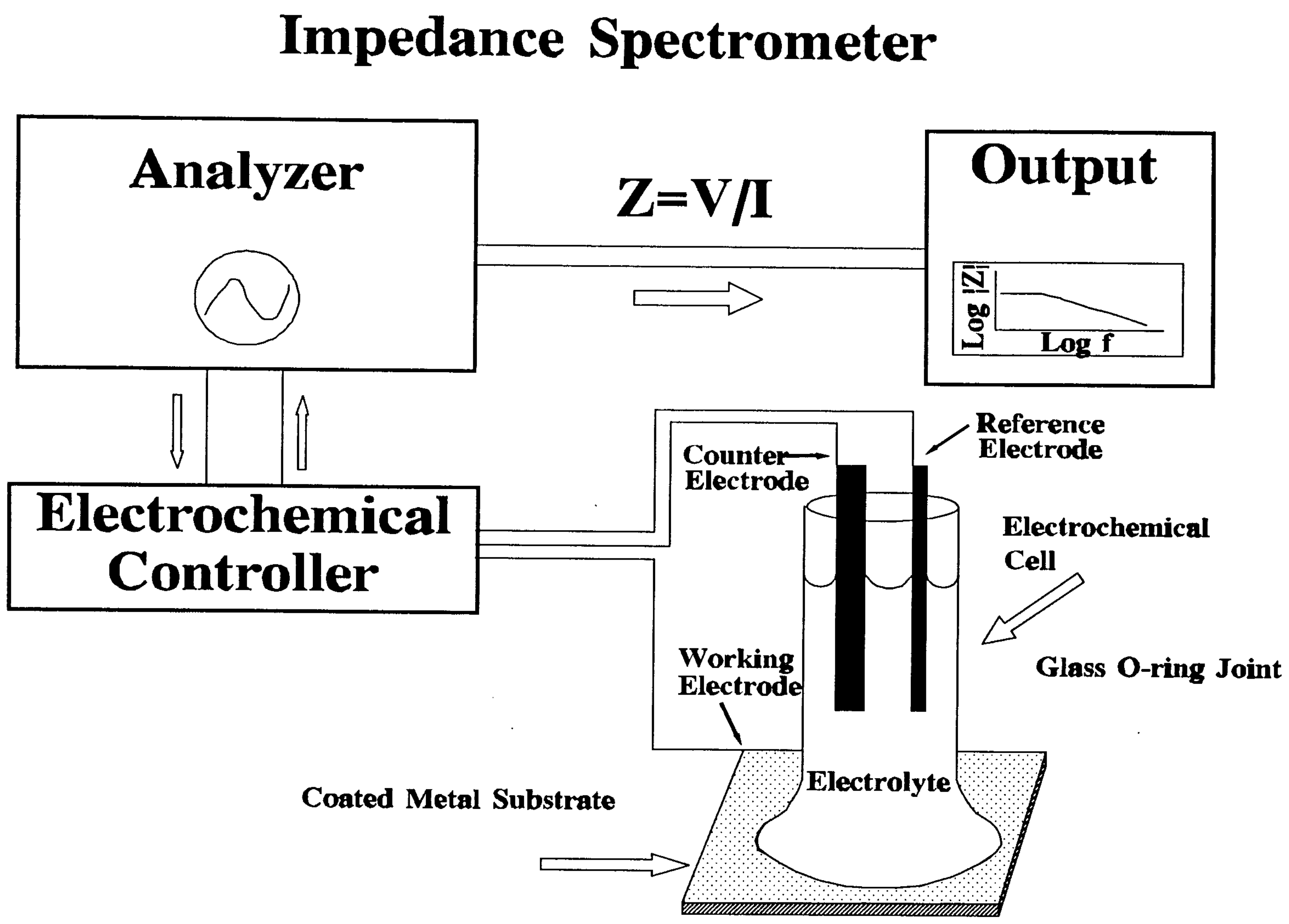


Figure 76. Schematic of electrochemical impedance spectroscopy setup.

Table 63. Epoxy Coating Compositions

Coating	Coating Composition
Epoxy 1	Biosphenol A Epichlorohydrin cured with Polyamide
Epoxy 2	Biosphenol A + Polyglycol Diepoxide (1:1) cured with Polyamide
Epoxy 3	Polyglycol Diepoxide cured with Polyamide

4.5.1.1 Epoxy 1 on Chromium Conversion Coated Aluminum. The initial EIS measurements were made on the following system as a function of time for 3 months: Bisphenol A epichlorohydrin resin cured with a polyamide resin obtained from the Shell Co. (Epoxy 1, see Table 63 for coating identification) at room temperature for 7 days, without filters and with 0.2 micron and 5.0 micron pore diameter polycarbonate filters (Millipore), on chromium conversion coated (CCC) (meets criteria for MIL-C-81706A and MIL-C-5541D) 2024 T3 aluminum panels (See Table 64 for elemental composition). CCC 2024 T3 aluminum panels (7.6 cm x 7.6 cm) were used to duplicate material used in aluminum aircraft structures. The coated substrates were prepared by spin coating the resin mixture at various speeds and times to obtain uniform film thicknesses. The film thickness of this system ranged between 46 - 71 microns. The purpose of the filters was to provide another interface for the resin to wet to create a defect-free coating. The electrolyte consisted of 0.01 M potassium sulfate (initially 0.1 M was used, but was decreased by a factor of ten due to concentration effects on the osmotic pressure through the film) saturated with 10 selected inhibitors (Table 5). These saturated electrolyte/inhibitor solutions were prepared in distilled water and allowed to stand with occasional mixing for a period of 1 week at ambient temperature. The supernatant liquid was used to prepare 0.01 M potassium sulfate. In the case of the BaBor inhibitor, the supernatant liquid was cloudy indicating a substantial amount of undissolved inhibitor material.

The impedance spectra of the Epoxy 1 systems cured at room temperature on CCC aluminum are given in Appendix G (Figures 77 - 111). The impedance spectra show that these systems behave as perfect capacitors, where the impedance increases linearly with frequency and the phase angle (not shown for clarity) remains constant at 90 degrees. There were no discernible effects on the impedance behavior due to the passage of time (up to 3 months), the inhibitors in the electrolyte, or the filters. The low frequency (3 mHz) impedance values were above 10^{10} ohm cm^2 indicating that little or no electrolyte penetrated these coatings to the coating-metal interface. Thus, these results demonstrated that (1) Epoxy 1 cured at room temperature for 1 week is an excellent barrier to water and ions, (2) defect free coatings can be achieved without the use of filters (thus, the use of filters was discontinued), and (3) impedance changes due to inhibitor action at the coating-metal interface were not observed because water and inhibitor were unable to penetrate the coating and reach the coating-metal interface.

4.5.1.2 Epoxy 1 with Defect on CCC Aluminum. Since no changes in impedance were observed with the Epoxy 1 system up to 3 months, it was decided to achieve rapid failure (water and ions at the coating metal interface) by placing a defect in the Epoxy 1 coating. This was done by drilling an 800 micron diameter hole, with a conical point bit, through the resin film to the aluminum substrate. Besides the addition of a defect, the effect of cure temperature was also investigated by curing the Epoxy 1 system at 100 degrees C for 2 hours. Defects were made in these systems as well. The impedance of both these systems was measured in

Table 64. Aluminum Alloy Elemental Composition* (%)

Alloy	Cr	Cu	Mg	Mn	Si
2024 T3	0.1	3.8-4.9	1.2-1.8	0.3-0.9	0.5

* Fe (SEM and XPS) and Pb (SEM) also found.

inhibitor saturated 0.01 M potassium sulfate solutions. Since the low frequency impedance values of defect-free Epoxy 1 films were extremely high, the electrolyte exposure area used was 5.02×10^{-3} cm^2 (area of the defect), instead of 8.8 cm^2.

The impedance spectra of the Epoxy 1 system on CCC aluminum panels cured at room temperature and 100 degrees C with defects are shown in Figures 112 - 122 and Figures 123 - 133, respectively, in Appendix G. Changes in the low frequency impedance were dependent on time, type of inhibitor, and cure temperature. Unlike the defect-free Epoxy 1 coatings, changes in impedance were evident after 24 hours of exposure. Since low frequency impedance changes were observed relative to the non-inhibited electrolyte (control) in both room temperature and 100 degree C cured Epoxy 1 systems, the following criteria were established to rank the inhibitors' effectiveness. After 720 hours, the low frequency impedance values of the control increased due to the passivation of the aluminum surface in the defect. Therefore, the impedance data at 168 hours were used to rank the inhibitors' effectiveness. These low frequency values were calculated by analyzing the impedance data with the nonlinear least-squares program of Boukamp [51]. The circuit model and example analysis are given in Figure 134. The elements in the circuit model represent the electrolyte resistance (R_2), and the electrolyte-metal interfacial resistance (R_1) and capacitance (C_1). The value of R_1 was used to calculate an inhibitor rank value by

$$\text{Rank} = (\text{Log } R_{inh} - \text{Log } R_{contr})/\text{Log } R_{contr}$$

where the subscripts inh and contr refer to the inhibitor and the control, respectively. The resistance values and rankings for each inhibitor are given in Table 65.

The rankings of the inhibitors in the room temperature cured Epoxy 1 system show that all but 2 inhibitors (ZnAlP and ZnoN) have resistance values above those of the control, indicating that 8 of the 10 selected inhibitors cause an increase in resistance of the electrolyte-metal interface. This increase in resistance was ascribed to increased corrosion resistance. The rankings of the inhibitors in the 100 degree C cured Epoxy 1 system show that 9 out of the 10 selected inhibitors caused an increase in the electrolyte-metal interfacial resistance. The differences in the rankings between the 100 degree C and room temperature Epoxy 1 systems

Table 65. Electrolyte-Metal Resistance Values and Inhibitor Rankings

Inhibitor	Epoxy 1 cured 7 d at Room T			Epoxy 1 cured 2 h at 100°C		
	R_1 (168h)	log R	Rank	R_1 (168h)	log R	Rank
Control	3.0E2	2.5	---	7.7E2	2.9	---
MPSi	1.4E7	7.1	1.8	2.2E4	4.3	0.48
BaBor*	3.4E6	6.5	1.6	2.9E6	6.5	1.2
ZnMoP	9.1E5	5.9	1.4	4.9E4	4.7	0.62
CaSi	1.0E6	6.0	1.4	7.6E3	3.9	0.34
M1PSi	1.2E5	5.1	1.0	9.5E3	4.0	0.38
MoZnP	3.2E4	4.5	0.80	3.6E4	4.6	0.59
CaPSi	7.2E3	3.9	0.56	2.2E4	4.3	0.52
ZnCin	2.4E3	3.4	0.36	5.1E2	2.7	-0.07
ZnA1P	2.2E2	2.3	-0.08	1.8E4	4.3	0.48
ZnoN	7.7E1	1.0	-0.24	1.0E4	4.0	0.38

* 48th impedance data

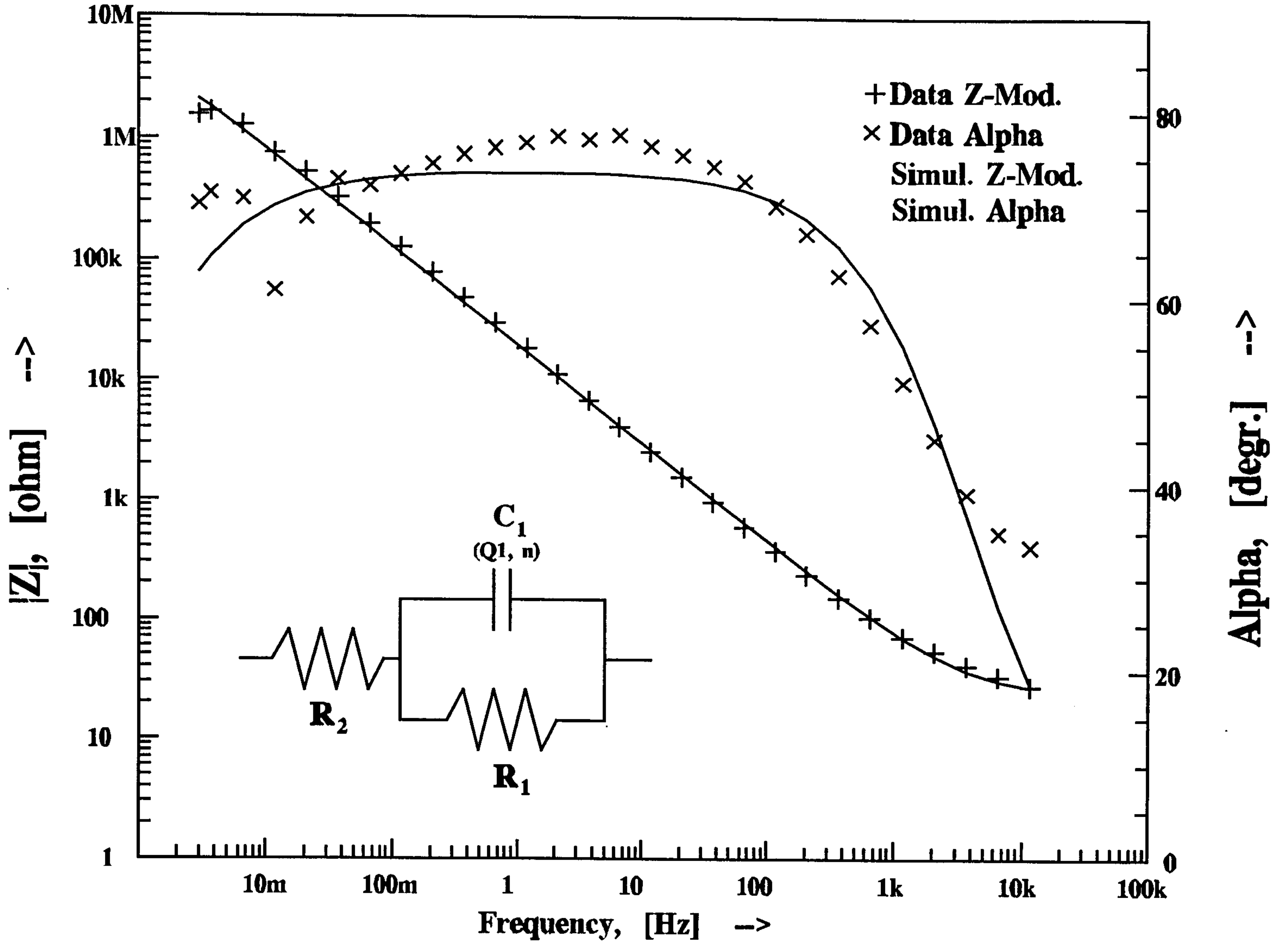


Figure 134. Equivalent circuit analysis showing circuit model, data, and simulated data.

suggests that the cure temperature affects the corrosion inhibitor's effectiveness by changing the electrolyte-metal interfacial resistance in the defect. Therefore, a corrosion inhibitor's effectiveness depends on the epoxy coating's physical properties, even though a defect is present.

4.5.1.3 Epoxy 2 on CCC Aluminum. The preceding experiments have shown that inhibitors saturated in an electrolyte solution cause an increase in the electrolyte-metal interfacial resistance in a coating with a defect, which relates to the first mode of coating failure described in section 3.5. In an effort to understand the mechanisms of corrosion inhibition in an intact coating (second mode of coating failure as described in Section 3.5) in a short period of time (168 hours), it was decided to select a resin system that would be more permeable to water than the Epoxy 1 system. This system consisted of a 1:1 weight ratio of a bisphenol A epoxide resin and a polyglycol diepoxide resin (obtained from Dow) cured with a polyamide resin (obtained from Union Camp Co.) at 100 degrees C for 2 hours (Epoxy 2). These systems were made with selected inhibitors: (1) incorporated in the coating (0.3% by weight), (2) saturated in the electrolyte, and (3) in both the coating and the electrolyte. The inhibitors chosen were MPSi, BaBor, and ZnoN. These were selected because the first two were found to be the most effective inhibitors (Table 65), while the last one was found to be one of the least effective. The film thicknesses of these coatings ranged from 25 - 38 microns.

The impedance spectra of the Epoxy 2 systems are given in Figures 136 - 143 in Appendix G. With the exception of the initial curves, the impedance spectra of the Epoxy 2 systems did not vary with time, type of inhibitor, or location of inhibitor. All the curves showed impedance spectra consisting of two time constants. The first time constant (high frequency) was due to the coating capacitance and the second time constant (low frequency) was due to the coating-substrate interfacial capacitance. The coating resistance value of the Epoxy 2 coatings was approximately 2.8E6 ohm cm^2, which is lower than >10^{10} ohm cm^2 values of the Epoxy 1 coatings. Since the low frequency impedance values of all the Epoxy 2 coatings did not become constant with frequency (0 degree phase angle), the coating-substrate resistance cannot be determined. The coating-substrate resistance is the parameter which would be expected to be altered by the presence of a corrosion inhibitor. In order to see impedance changes due to the substrate, it was decided to create a defect in the coating in the same manner as described previously with the Epoxy 1 system.

4.5.1.4 Epoxy 2 with Defect on CCC Aluminum. The impedance spectra of the Epoxy 2 system with defects are given in Figures 144 - 152 in Appendix G. The Epoxy 2 coating was conductive when exposed to electrolyte, and therefore, the area of electrolyte exposure was 8.8 cm^2. The impedance spectra of Epoxy 2 coatings with defects, with the exception of the initial curves, did not show any significant changes with respect to time, inhibitor type, or inhibitor location. The shape of the impedance spectra of the Epoxy 2 coatings with defects was less well defined (the two time constants were not as distinct) than the defect-free Epoxy 2 coatings' impedance spectra. The effects of the inhibitor on the electrolyte-metal interfacial resistance in the defect were not observed as in the Epoxy 1 system because the area of the defect was four orders of magnitude smaller than the total area of electrolyte exposure. Therefore, any resistance changes at the defect surface due to the inhibitor were outweighed by the impedance signal from the conductive Epoxy 2 coating.

4.5.1.5 Epoxy 3 on CCC Aluminum. Since interfacial resistance changes were not detected with the defect-free Epoxy 2 coatings, it was again decided to select an even more permeable coating to water. The system selected was the polyglycol diepoxide resin cured with polyamide resin (Epoxy 3) for 2 hours at 100 degrees C (film thickness = 13 - 25 microns). The impedance spectra of the Epoxy 3 coatings were determined with: (1) both 0.01 M potassium sulfate and a mixture of 0.01 M potassium sulfate and 0.003 M potassium chloride as the electrolyte, (2) the inhibitor saturated in the electrolyte, and (3) 17% (by weight) inhibitor in the coating. The inhibitors selected were MPSi and BaBor (the most effective inhibitors from Table 65). The more aggressive electrolyte (0.01 M potassium sulfate + 0.003 M potassium chloride) was saturated with various inhibitors by adding an excess of inhibitor to the electrolyte solution and allowing this solution to stand 1 week at ambient temperature. The supernatant liquid was used as the electrolyte/inhibitor solution.

The impedance spectra of the Epoxy 3 systems on CCC aluminum panels are given in Figures 153 - 162 in Appendix G. All of the spectra show a high frequency resistive component due to the coating resistance (3.6E3 ohm cm^2) and at low frequency, a capacitive component due the capacitance of the coating-metal interface. With the specimens exposed to 0.01 M potassium sulfate, the low frequency impedance (3 mHz) values were about 10^7 ohm cm^2 and were constant with time for 168 hours. The extremely low value of the coating resistance (about 3 orders of magnitude lower than the Epoxy 2 system), indicates that water and ions penetrate the Epoxy 3 system and form conductive pathways through the coating to the coating-metal interface. Therefore, the decreases in the low frequency impedance after 720 hours in the control (Figure 154) and the 17% BaBor coating (Figure 158) specimens were due to the breakdown of the CCC in the presence of water and ions. Since a breakdown of the CCC's in the other inhibited systems [17% MPSi in film (Figures 155 and 156), and MPSi (Figure 159) and BaBor (Figure 160) saturated in the 0.01 M potassium sulfate] was not observed, the breakdown of the CCC where BaBor was present in the film was due to the fact that BaBor incorporated in the resin was not transported to the interface by the electrolyte.

With the specimens exposed to 0.01 M potassium sulfate and 0.003 M potassium chloride (Figures 161 and 162), the low frequency impedance decreased after 720 hours in the control specimen and after 24 hours in the 17% MPSi in film specimen. Therefore, the impedance behavior of the control was the same as the chloride-free control (Figure 154) and the impedance decrease in the 17% MPSi specimen was due to the immediate breakdown of the CCC in the presence of the electrolyte. The later result indicates that the MPSi incorporated in the film was not transported to the interface by the electrolyte or if present at the interface was ineffective in the presence of chloride.

4.5.1.6 Epoxy 3 on Bare Aluminum. The impedance results of Epoxy 3 on CCC aluminum with potassium sulfate electrolyte showed low frequency impedance decreases after 720 hours. However, these systems showed no changes in the impedance spectra up to 168 hours indicating that the electrolyte and the inhibitor had no affect on the coating-metal interface. This lack of impedance change showed that the CCC was protecting the aluminum from chemical interaction with the electrolyte and inhibitor. Therefore, it was decided to coat bare aluminum substrates with Epoxy 3.

Two surface treatments were employed on the bare aluminum panels: (1) as-received panels immersed for 30 - 60 seconds in hot (49 - 60 degrees C) 5% NaOH, etched 1 - 2 min in 82 degrees C 25% sulfuric acid, rinsed in distilled water for 30 - 60 s, immersed in room temperature 50% nitric acid for 60 - 90 seconds, rinsed with distilled water, washed with ethanol, allowed to air dry at room temperature, and then placed in a silica gel desicator (referred to as chemically cleaned); and (2) as-received panels stripped of polyethylene film and rinsed with acetone and wiped with lintless laboratory tissue (referred to as solvent cleaned). These panels were then coated with the Epoxy 3 and cured 2 hours at 100 degrees C. Impedance measurements on the Epoxy 3 system on bare aluminum were made with the inhibitor: (1) incorporated in the film (17% by weight), (2) saturated in the electrolyte (0.01 M potassium sulfate), and (3) in both the coating and the electrolyte.

The impedance spectra of the Epoxy 3 systems on bare aluminum are given in Figures 163 - 183 in Appendix G. These impedance spectra showed a coating resistance at high frequencies and then a capacitive component at lower frequencies which have 3 mHz values between 10^4 and 10^7 ohm cm^2. The control specimens (Figures 163, 164, 171 -173) showed decreases in low frequency impedance with time with values between 10^4 and 10^5 ohm cm^2. These impedance values were 2 to 3 orders of magnitude lower than the 3 mHz values of the Epoxy 3 system on CCC aluminum (Figure 154); therefore, it was concluded that the CCC has an impedance value between 10^6 and 10^7 ohm cm^2. Also, there were no major differences in the impedance spectra of the control specimens on chemically cleaned and solvent cleaned substrates.

The impedance spectra of the Epoxy 3 coatings with BaBor saturated electrolyte on both chemically cleaned (Figure 170) and solvent rinsed aluminum (Figures 180 and 181) substrates showed an increase in the coating resistance of approximately an order of magnitude as a function of time. The 3 mHz impedance values also increased about an order of magnitude with time and were about 2 orders of magnitude higher than the controls at 168 hours. The impedance spectra of the Epoxy 3 coating with 17% BaBor in the film on chemically (Figures 167 and 168) and solvent cleaned (Figures 176 and 177) aluminum substrates showed no increase in coating resistance with time and the 3 mHz impedance values were about the same as those of the control at 168 hours. These results show that BaBor forms a resistive film on the Epoxy 3 surface causing an increase in coating resistance and an increase in the 3 mHz impedance. When BaBor is incorporated in the coating it is unable to form this resistive film, and therefore, does not function as an inhibitor.

The impedance spectra of the Epoxy 3 coating on the chemically cleaned aluminum with 17% MPSi in the film (Figure 166) showed a 3mHz impedance value 2 orders of magnitude higher than the control at 168 hours. The impedance spectrum of the identical system (Figure 165) showed a decrease in the 3 mHz impedance values as a function of time. This result when compared to the control indicates that the MPSi was not functioning as an inhibitor. However, polarization resistance measurements were run on this specimen (See section 4.5.2) prior to impedance measurements, which may have artificially induced corrosion at the coating-metal interface, and thus, rendered the inhibitor ineffective. The impedance spectra of Epoxy 3 on solvent cleaned aluminum with MPSi in the film (Figures 174 and 175) showed a decrease in the 3 mHz impedance as a function of time and the 3 mHz values were about the same as the controls' at 168 hours. This result indicates that surface preparation affects the ability of MPSi to form a resistive film on the aluminum substrate. The impedance spectra of Epoxy 3 on both solvent (Figures 178 and 179) and chemically cleaned aluminum (Figure 169) in MPSi saturated electrolyte showed decreases in the 3 mHz impedance with time and these values at 168 hours were about the same as the controls'. Also, no change in the coating resistance was observed with time. These results indicate that MPSi migrates through the coating and forms a resistive film at the coating-metal interface.

4.5.1.7 Epoxy 1 With Defect in Chloride Solution. The last set of impedance experiments was designed to determine the effect of chloride on a coating with a defect. Epoxy 1 was coated on CCC, chemically cleaned, and solvent cleaned aluminum panels and allowed to cure 7 days at room temperature. An 800 µm diameter defect was drilled into the coatings. The inhibitors used (MPSi and BaBor) were saturated in 0.01 M potassium sulfate + 0.003 M potassium chloride. The area of electrolyte exposure was 5.02E-3 ohm cm^2.

These impedance spectra are shown in Figures 184 - 192 in Appendix G. The interpretation of the impedance spectra is the same as in section 4.5.1.2. The control specimens (Figures 184, 187, and 190) (no inhibitor) showed 3 mHz impedance values between 10^4 - 10^5 ohm cm^2. These impedance spectra were not affected by time up to 720 hours and were the same for each substrate preparation. Unlike the identical system without chloride (Figure 112), passivation was not observed after 720 hours. This result indicates that chloride prevented passivation up to 720 hours. With the MPSi inhibitor in the electrolyte on CCC (Figure 185), chemically cleaned (Figure 188), and solvent cleaned (Figure 191) aluminum substrates, the 3 mHz impedance values increased with time and at 720 hours were 1 to 2 orders of magnitude higher than the control. This result shows that the MPSi inhibitor increases the value of the electrolyte-substrate resistance in the presence of chloride. With the BaBor inhibitor in the electrolyte on CCC (Figure 186), chemically cleaned (Figure 189), and solvent cleaned (Figure 192) aluminum substrates the 3 mHz impedance values increased as a function of time and at 720 hours were 2 to 3 orders of magnitude higher than the control. This result shows that BaBor increases the resistance of the electrolyte-substrate interface, and therefore, inhibits corrosion.

4.5.2 Polarization Resistance Results. Polarization resistance measurements were made to support the impedance data, since correlations between polarization resistance measurements and inhibitor performance exist. Polarization resistance measurements were made on the Epoxy 3 systems cured 2 hours at 100 degrees C on CCC, chemically cleaned, and solvent rinsed aluminum substrates. The electrolyte used was 0.01 M potassium sulfate and 17% inhibitor (MPSi and BaBor) was incorporated in the coatings. The polarization resistance measurements were obtained with a Gamry Instruments CMS100 Portable DC Corrosion Measurement System. The polarization scans ranged from -20 mV to 10 mV relative to the open circuit potential at a scan rate of 0.05 mV/s. The cell used in these experiments was the same one used for the impedance measurements as shown in Figure 76. Polarization measurements were made as a function of time up to 48 hours. After each polarization resistance measurement an impedance measurement was made as well. The polarization resistance (R_p) was calculated by determining the slope of the polarization curve at zero current. The resistance of the coating-metal interface (R) was calculated from the impedance data in the same manner as described in Section 4.5.1.2. In theory, the polarization resistance and coating-metal interfacial resistance from the impedance measurements should be identical.

The polarization and the coating-metal interfacial resistances determined initially and after 24 hours and 48 hours are given in Table 66 and the polarization curves are given in Figures 193 - 219 in Appendix H. The R_p and R values were approximately the same (within an order of

Table 66. Polarization (R_p) and Coating-Metal Interfacial (R) Resistances (Wcm^2)

Al prep	Inhibitor 17% in coating	Initial		24 h		48 h	
		R	R_p	R	R_p	R	R_p
CCC	none	2.5E6	2.4E6	1.4E7	5.8E7	1.8E7	5.9E6
chem	none	1.9E5	4.7E5	1.5E5	2.9E5	1.2E5	1.0E5
solv	none	2.0E5	1.6E5	2.8E5	3.4E5	1.0E6	4.7E5
CCC	MPSi	1.4E7	5.9E6	2.4E7	2.0E7	2.0E7	1.0E7
chem	MPSi	4.1E6	2.9E6	6.2E5	2.0E5	2.4E5	5.0E5
solv	MPSi	1.5E6	1.0E6	2.4E6	2.8E6	2.4E6	6.1E6
CCC	BaBor	4.9E7	2.7E7	4.9E7	-5.5E8	3.1E7	-2.1E8
chem	BaBor	1.0E5	4.1E4	7.1E4	3.2E4	6.6E4	1.2E3
solv	BaBor	1.1E5	2.5E4	1.3E5	1.2E5	2.9E5	2.9E5

CCC = chromate conversion coated A1
chem = chemically cleaned A1
solv = solvent cleaned A1

magnitude). In two cases the R_p values were negative which was due to the extremely high value of R_p. This high value may be caused by the presence of a resistive film (from the BaBor inhibitor) on the epoxy surface. Since increases in R_p values have been shown to indicate that an inhibitor is effective [50] and the R values calculated from impedance measurements were nearly identical to the R_p values, it is clear that impedance measurements can be used to determine inhibitor effectiveness in coated metal systems.

4.5.3 Positron Annihilation Lifetime Spectroscopy Results. The free volume of a coating is one pathway by which water and ions migrate to the coating-metal interface [52]. Positron Annihilation Lifetime Spectroscopy (PALS) is an analytical technique for measuring the free volume characteristics of polymers and coatings [53,54]. The lifetime of the positron (τ_3) is proportional to the free volume cavity size, while the intensity of τ_3 (I_3) is proportional to the number of free volume cavities per unit volume of polymer. Therefore, the product $\tau_3 I_3$ is a measure of the free volume fraction of a polymer.

The lifetime measurements were made with a standard fast-fast coincidence system based on fast plastic scintillators, RCA photomultipliers, and EG&G Ortec electronics (Figure 135) [55]. The source of positrons was 20 microCurie sodium-22 sealed in Kapton foil. The lifetimes and intensities were extracted from the raw data using the POSITRONFIT computer program [56].

PALS measurements were obtained on 2 - 4 mm thick wafers of Epoxy 3 cured for 2 hours at 100 degrees C with 17% inhibitor (MPSi and BaBor) incorporated in the epoxy. These samples were then exposed to 0.01 M potassium sulfate for 2 weeks until the water uptake values (by weight) were constant and then PALS measurements were made on these specimens. PALS measurements were also made on the inhibitors MPSi and BaBor using a special cell to hold the powdery solids.

The PALS data for the Epoxy 3 wafers and the inhibitors are given in Table 67. The τ_3, I_3, and $\tau_3 I_3$ values for all of the samples increased in value after water saturation. These results indicated that the electrolyte permeated the Epoxy 3 wafers and caused an increase in the free volume cavity size, the number of free volume cavities, and the free volume fraction. Other work on Epoxy 3 coatings [57] has shown that these coating swelled upon water exposure.

Table 67. Free Volume Characteristics of Epoxy 3, MPSi, and BaBor

Specimen	Electrolyte Uptake	State	t_3 (ps)	I_3 (%)	$t_3 I_3$ (ps)
Epoxy 3	27.8%	dry	2122	14.4	305.6
		wet	2268	15.0	340.0
Epoxy 3 + 17% MPSi	26.1%	dry	2159	12.3	264.8
		wet	2250	13.7	307.8
Epoxy 3 + 17% BaBor	28.2%	dry	2248	11.1	250.3
		wet	2227	14.0	312.6
MPSi	---	dry	1982	2.0	40.8
BaBor	---	dry	2596	2.0	52.0

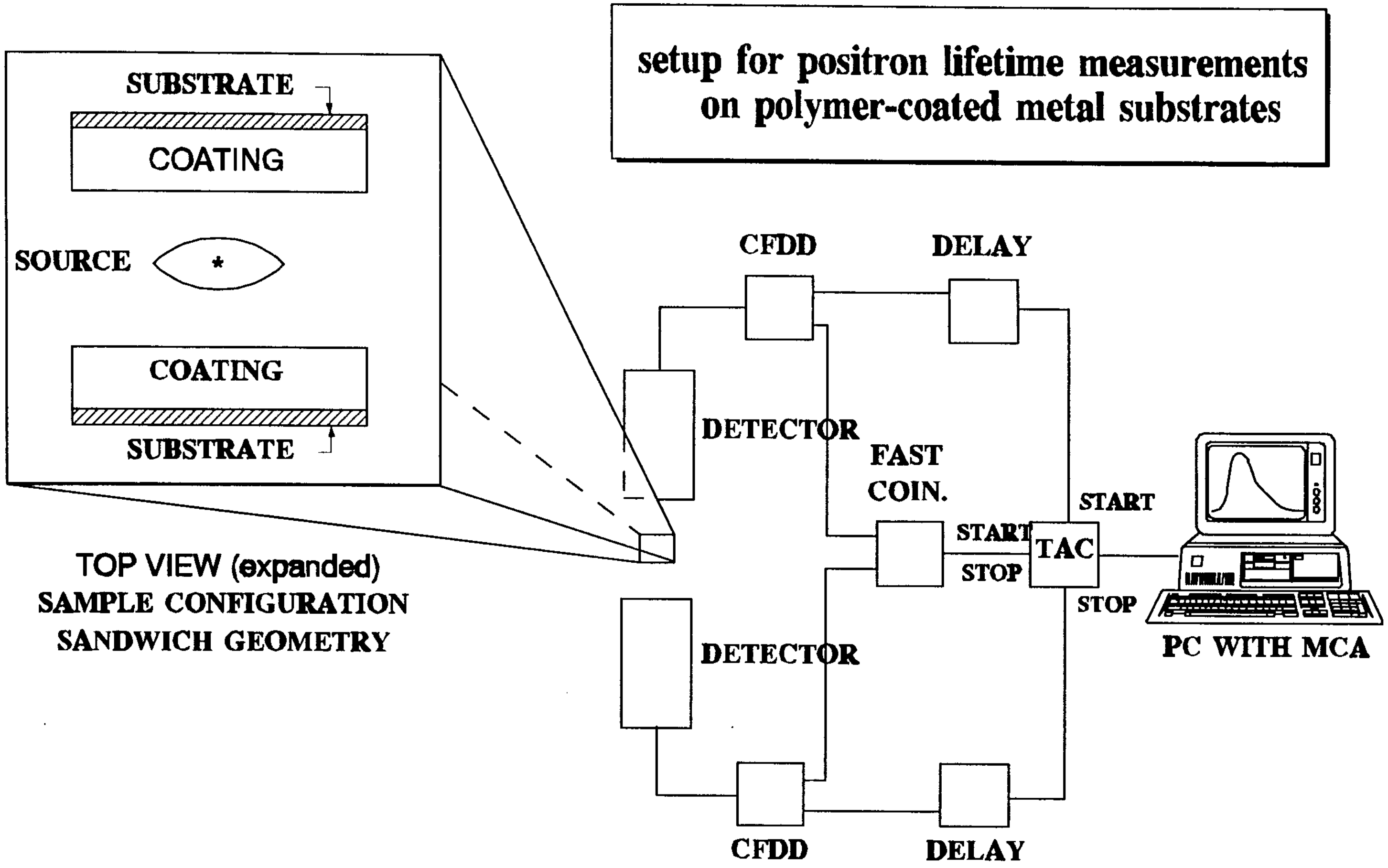


Figure 135. Schematic of positron annihilation lifetime spectroscopy setup.

The creation of additional free volume in Epoxy 3 correlates to the low impedance values observed in these coatings [57]. Water permeation into the Epoxy 3 free volume is driven by the chemical interaction between the hydrophilic groups on the resin backbone and water, resulting in the expansion of the coating's free volume [57]. The decrease in the Epoxy 3 free volume upon addition of the inhibitor was due to the replacement of epoxy material by inhibitor, which has a free volume that is 12% (MPSi) and 15% (BaBor) of the Epoxy 3's free volume.

4.5.4 Differential Scanning Calorimetry Results. Differential Scanning Calorimetry (DSC) measurements were made on the epoxy system to determine the degree of cure (D_c) of each system. The DSC measurements were based on the principle that the curing of the epoxy is exothermic. For example, the isothermal exotherm of the epoxy was measured for 2 hours at 100 degrees C (ΔH_{iso}). Then the epoxy was cooled to 50 degrees C and slowly heated (10 K/min) to 300 degrees C. This dynamic exotherm (ΔH_{dyn}) was assumed to be due to the curing of any material not cured during the isothermal scan. The degree of cure was then calculated by

$$D_c = \Delta H_{iso} / (\Delta H_{iso} + \Delta H_{dyn}) \; .$$

The degree of cure of the room temperature cured epoxy was calculated by

$$D_c = [(\Delta H_T)_{init} - (\Delta H_T)_{fin}]/[(\Delta H_T)_{init} + (\Delta H_T)_{fin}]$$

where $\Delta H_T = \Delta H_{iso} + \Delta H_{dyn}$, and init and final refer to before and after the epoxy cured 1 week at room temperature.

The DSC measurements were obtained with a Mettler DSC 30 interfaced with a Mettler TC101A TA processor to determine degrees of cure for each coating system. A small amount (10 - 20 mg) of coating mixture (epoxide and polyamide resin) were placed in a tared pan. Isothermal scans were run at 100 degrees C for 2 hours and were immediately followed by dynamic scans. Computer analysis of the area under the respective curves gave ΔH_{iso} and ΔH_{dyn}.

The D_c data for the epoxy systems used in this study are given in Table 68. This data shows that Epoxies 1, 2, and 3 cured at 100 degrees C for 2 hours were 93.5% cured and above. This result indicates that 2 hours at 100 degrees C was sufficient to completely cure these epoxy systems. The Epoxy 1 system cured at room temperature for 1 week was 65.7% cured. However, the impedance data after 3 months suggests that the Epoxy 1 system cured 7 days at

Table 68. Degree of Cure (D_c) of the Epoxy Coating Materials

Specimen	Cure	D_c (%)
Epoxy 1	7 d at room temperature	65.7
Epoxy 1	2 h at 100°C	97.5
Epoxy 2	2 h at 100°C	93.5
Epoxy 3	2 h at 100°C	99.2
Epoxy 3 + 17% BaBor	2 h at 100°C	99.1

room temperature was an excellent barrier to 0.01 M potassium sulfate electrolyte. This observation coupled with the fact that the Epoxy 3 system which was 99% cured and was an extremely poor barrier to the electrolyte, demonstrates that the degree of cure of an epoxy system is not indicative of the coating's barrier properties.

4.5.5 X-Ray Photoelectron Spectroscopy Results. X-ray Photoelectron Spectroscopy (XPS) measurements were made on aluminum substrates exposed to inhibitor solutions to determine the type and concentration of elements present on the surface. An 800 micron diameter hole was drilled in the center of CCC, chemically cleaned, and solvent cleaned aluminum panels. The edges of these panels were then taped and the panels were immersed in individual beakers containing the following solutions: 0.01 M potassium sulfate, 0.01 M potassium sulfate saturated with MPSi, 0.01 M potassium sulfate saturated with BaBor, 0.01 M potassium sulfate + 0.003 M potassium chloride, 0.01 M potassium sulfate + 0.003 M potassium chloride saturated with MPSi, and 0.01 M potassium sulfate + 0.003 M potassium chloride saturated with BaBor. These were allowed to stand for 48 hours, at which time the panels were removed and rinsed in the following manner: dipped in successive baths of distilled water (twice) and then in ethanol. The specimens were dried with warm air and stored in individual petri dishes in a silica gel desiccator.

The specimens were cut down to 1 square cm in area for XPS measurements. The XPS measurements were made with a Scienta ESCA-300 equipped with a monochromatic $AlK\alpha=1486.7$ eV X-ray source having a resolution of 0.1 eV, which detects elements 20 - 100 Angstroms below the surface. XPS spectra were measured in 3 locations: in the hole, just outside the hole, and far from the hole.

The XPS elemental data are given in Tables 69 - 71 and the XPS spectra are given in Appendix I in Figures 220 - 270. The elemental composition of the aluminum surface inside and outside the hole is consistent with the elements found in the electrolyte solution (Table 72), in the CCC (Cr), and in the aluminum alloy (Table 64). The following are the trends (exceptions noted) observed in the XPS data. S was present in all locations (inside hole, just outside hole, far from hole) for those specimens that were exposed to uninhibited electrolyte solutions. S was not present on specimens exposed to inhibited electrolyte. Zn, P, and Ca were found in all location of specimens exposed to electrolyte containing MPSi. Ba and Si were found in all locations on specimens exposed to BaBor saturated electrolyte. Sr, B, Cl, and K were not found in any locations on the specimens. N was found outside the hole on the CCC aluminum specimens.

S on the aluminum surface where inhibitor was not present indicates that S is part of the corrosion product, perhaps in the form of aluminum sulfate. S was not found on the aluminum surface when inhibitor was present in the electrolyte showing that the inhibitors prevent the formation of corrosion product (up to 48 hours). Zn, P, and Ca on the aluminum surface in MPSi inhibited solutions and Ba and Si on the aluminum surface in BaBor solutions show that these elements from the inhibitors participate in corrosion inhibition. The lack of Sr, B, Cl, and K indicate that these elements do not participate directly in corrosion or corrosion inhibition, perhaps because they are too soluble. The N found in the CCC came from an unknown source.

4.5.6 Scanning Electron Microscopy Results. Scanning Electron Microscopy (SEM) data was obtained to determine the relative positions of the elements on the surface of the aluminum exposed to inhibitor solutions. Three of the specimens used for impedance measurements in Section 4.5.1.2 were cross-sectioned through the defect for SEM analysis. These specimens were Epoxy 1 on CCC aluminum with an 800 micron diameter defect exposed to the following solutions: 0.01 M potassium sulfate, 0.01 M potassium sulfate

Table 69. Atomic Percentages of Elements* on 2024 T3 Al Inside the Hole

Substr.	Inhibitor	Electrolyte	N	S	Si	Al	Cr	Zn	Ca	P	Pb	Mg	Fe	Ba	K	Cu
chem	none	K_2SO_4/KCl	-	6.7	-	19.1	-	-	-	-	-	-	-	-	-	-
chem	MPSi	K_2SO_4/KCl	-	-	-	22.8	-	-	-	-	0.2	-	-	-	-	-
chem	BaBor	K_2SO_4/KCl	-	-	11.3	25.3	-	-	-	-	-	-	-	1.7	-	-
solv	none	K_2SO_4/KCl	-	6.2	-	23.1	-	-	-	-	-	-	-	-	-	-
solv	MPSi	$K_2SO_{4/KCl}$	-	-	-	14.1	-	0.9	1.1	9.1	-	-	-	-	-	-
solv	BaBor	K_2SO_4/KCl	-	-	4.9	13.8	-	-	-	-	-	4.3	-	1.0	-	-
CCC	none	K_2SO_4/KCl	-	4.3	-	19.6	-	-	-	-	-	-	-	-	-	-
CCC	MPSi	K_2SO_4/KCl	4.7	-	2.8	7.7	2.3	0.3	-	2.3	0.2	-	-	-	-	-
CCC	BaBor	K_2SO_4/KCl	-	-	9.1	26.8	-	0.3	-	-	-	-	-	1.7	-	-
chem	none	K_2SO_4	-	4.1	-	21.5	-	-	-	-	-	-	-	-	-	-
chem	MPSi	K_2SO_4	-	-	-	27.9	-	3.1	-	8.0	-	-	-	0.2	-	0.1
chem	BaBor	K_2SO_4	-	0.4	10.2	27.0	-	0.4	-	-	-	-	-	0.6	-	-
solv	none	K_2SO_4	-	1.3	-	21.2	-	-	-	-	-	6.9	-	-	-	-
solv[1]	MPSi	K_2SO_4	-	-	3.5	17.2	-	2.9	1.4	6.8	0.2	3.3	-	-	-	-
CCC	none	K_2SO_4	3.8	2.6	-	15.3	1.1	-	-	-	-	-	-	-	-	-
CCC	MPSi	K_2SO_4	-	-	-	15.1	-	2.5	-	5.4	0.2	-	-	-	-	-
CCC	BaBor	K_2SO_4	1.9	-	9.3	21.2	-	-	-	-	-	-	-	0.6	1.6	-

CCC = chromate conversion coated Al
chem = chemically cleaned Al
solv = solvent cleaned Al
* The percentages add up to 100%. The balance is C and O.
1. The solv cleaned Al specimen exposed to BaBor K_2SO_4 was lost in the XPS vacuum chamber.

Table 70. Atomic Percentages of Elements* on 2024 T3 Al Just Outside the Hole

Substr.	Inhibitor	Electrolyte	N	S	Si	Al	Cr	Zn	Ca	P	Pb	Mg	Fe	Ba	K	Cu
chem	none	K_2SO_4/KCl	-	7.0	-	18.0	-	-	-	-	-	-	-	-	-	-
chem	MPSi	K_2SO_4/KCl	-	-	-	29.4	-	0.9	-	2.7	0.4	-	-	-	-	0.4
chem	BaBor	K_2SO_4/KCl	-	-	9.3	28.4	-	-	-	-	-	-	-	1.6	-	0.2
solv	none	K_2SO_4/KCl	-	6.7	-	19.4	-	-	-	-	-	-	-	-	-	-
solv	MPSi	$K_2SO_{4/KCl}$	-	-	-	13.0	-	1.4	2.8	7.5	-	10.2	-	-	-	-
solv	BaBor	K_2SO_4/KCl	-	-	4.8	9.4	-	-	-	-	-	8.0	-	0.9	-	-
CCC	none	K_2SO_4/KCl	4.8	2.1	-	14.7	1.9	-	-	-	-	-	-	-	-	-
CCC	MPSi	K_2SO_4/KCl	7.6	-	2.0	6.7	4.5	0.7	-	1.9	0.3	-	0.9	-	-	-
CCC	BaBor	K_2SO_4/KCl	7.3	-	3.6	5.9	5.2	0.3	-	-	0.5	-	2.0	1.8	1.7	-
chem	none	K_2SO_4	-	3.7	-	20.6	-	-	-	-	-	-	-	-	-	-
chem	MPSi	K_2SO_4	-	-	-	35.4	-	2.9	-	5.2	-	-	-	-	-	0.4
chem	BaBor	K_2SO_4	-	-	9.0	30.1	-	0.3	-	-	-	-	-	1.0	-	0.2
solv	none	K_2SO_4	-	1.3	-	20.6	-	-	-	-	-	5.8	-	-	-	0.5
solv[1]	MPSi	K_2SO_4	-	-	4.0	12.5	-	2.6	2.4	2.3	0.2	7.0	-	-	-	-
CCC	none	K_2SO_4	10.9	-	-	6.6	5.4	-	-	-	0.2	-	2.2	-	-	-
CCC	MPSi	K_2SO_4	9.0	-	-	4.8	5.4	2.3	-	2.1	0.2	-	2.4	-	-	-
CCC	BaBor	K_2SO_4	6.2	-	5.0	7.6	5.2	0.6	-	-	0.3	-	2.8	0.6	1.7	-

CCC = chromate conversion coated Al
chem = chemically cleaned Al
solv = solvent cleaned Al
* The percentages add up to 100%. The balance is C and O.
1. The solv cleaned Al specimen exposed to BaBor K_2SO_4 was lost in the XPS vacuum chamber.

Table 71. Atomic Percentages of Elements* on 2024 T3 Al Far From the Hole

Substr.	Inhibitor	Electrolyte	N	S	Si	Al	Cr	Zn	Ca	P	Pb	Mg	Fe	Ba	K	Cu
chem	none	K_2SO_4/KCl	-	6.7	-	19.1	-	-	-	-	-	-	-	-	-	-
chem	MPSi	K_2SO_4/KCl	-	-	-	31.4	-	0.8	-	4.3	0.3	-	-	-	-	0.4
chem	BaBor	K_2SO_4/KCl	-	-	8.9	29.9	-	-	-	-	-	-	-	1.3	-	0.2
solv	none	K_2SO_4/KCl	-	5.8	-	19.7	-	-	-	-	-	-	-	-	-	-
solv	MPSi	K_2SO_4/KCl	-	-	-	12.9	-	1.2	2.4	7.5	-	10.1	-	-	-	-
solv	BaBor	K_2SO_4/KCl	-	-	4.8	8.2	-	-	-	-	-	7.8	-	0.9	-	-
CCC[1]	none	K_2SO_4/KCl	4.5	2.4	-	11.0	2.2	-	-	-	-	-	-	-	-	-
CCC	MPSi	K_2SO_4/KCl	6.6	-	-	7.2	4.7	0.6	-	1.5	0.3	-	0.6	-	-	-
CCC	BaBor	K_2SO_4/KCl	8.1	-	4.1	5.9	5.6	0.3	-	-	0.5	-	1.5	1.7	1.1	-
chem	none	K_2SO_4	-	2.5	-	23.9	-	-	-	-	-	-	-	-	-	-
chem	MPSi	K_2SO_4	-	-	-	33.0	-	2.5	-	4.6	-	-	-	-	-	0.4
chem	BaBor	K_2SO_4	-	-	9.5	28.8	-	0.1	-	-	-	-	-	0.9	-	-
solv	none	K_2SO_4	-	1.5	-	20.2	-	-	-	-	-	5.4	-	-	-	0.3
solv[2]	MPSi	K_2SO_4	-	-	2.4	10.6	-	2.1	2.6	3.4	0.2	8.5	-	-	-	-
CCC	none	K_2SO_4	11.5	1.5	-	3.4	5.3	-	-	-	0.2	-	1.9	-	-	-
CCC	MPSi	K_2SO_4	7.2	-	-	5.2	6.3	2.0	-	-	0.3	-	1.1	-	-	-
CCC	BaBor	K_2SO_4	8.0	-	3.6	6.8	5.7	0.5	-	-	0.5	-	2.1	0.8	3.0	-

CCC = chromate conversion coated Al
chem = chemically cleaned Al
solv = solvent cleaned Al
* The percentages add up to 100%. The balance is C and O.
1. 0.7% Cl
2. The solv cleaned Al specimen exposed to BaBor K_2SO_4 was lost in the XPS vacuum chamber.

Table 72. Concentrations of Elements in Electrolyte Solutions (ppm)

Solution	Ba	B	Ca	Cl	Cr	Pb	P	K	Si	Sr	S	Zn
0.01 M K_2SO_4	0.02	0.2	0.13	45	0.02	0.05	<0.01	740	0.70	<0.1	300	0.03
0.01 M K_2SO_4 + 0.003 M KCl	<0.01	0.3	0.68	100	0.03	0.02	<0.01	870	<0.1	<0.1	306	0.01
0.01 M K_2SO_4 + MPSi	6.49	1.4	86.3	30	<0.04	<0.005	50	420	53.7	16.8	160	161
0.01 M K_2SO_4 + BaBor	1120	184	1.88	40	<0.07	0.03	0.06	760	73.0	29.9	298	55.4
0.01 M K_2SO_4 + 0.003 M KCl + MPSi	6.82	4.8	103	180	<0.07	0.02	59	1200	64	19.9	428	181
0.01 M K_2SO_4 + 0.003 M KCl + BaBor	319	652	0.33	150	<0.07	0.02	<0.05	970	42.3	6.0	<6	12.1

saturated MPSi, and 0.01 M potassium sulfate saturated BaBor for 2 months. The SEM measurements were made with a Joel JXA-733 Electron Probe X-ray Microanalyzer. SEM pictures and elemental maps were made of the bottom and the side of the defect for each specimen. SEM detects elements up to 1 micron below the surface.

The SEM pictures and elemental maps are given in Figures 271 - 276 in Appendix J. The elemental maps of the control show the presence of S on the aluminum surface in the hole, indicating that S is a component of the corrosion product. Cu and Fe were also present and are components in the 2024 aluminum alloy. Si, Sr, and K were present on the aluminum surface on the side of the hole in the specimens exposed to MPSi, while only Si was present at the bottom of the hole. Ba, Si, S, Sr, and K were present on the aluminum surface on the specimen exposed to BaBor. These results indicate that with specimens exposed to BaBor; Ba, Si, K, and S are the components of the resistive film on the aluminum surface and that with specimens exposed to MPSi; Si, Sr, and K are components of the resistive film on the aluminum surface.

4.5.7 Inductively Coupled Plasma Results. Inductively Coupled Plasma (ICP) experiments were performed to determine which elements were present in the electrolyte solutions. The solutions analyzed were those used in Section 4.5.5. The ICP analyses were done by Benchmark Analytics in Hellertown, PA. The results are shown in Table 72.

The results in Table 72 are consistent with the elements that should be present in the solutions. However, there are elements that were present in the inhibitor solutions that appear to be contaminants. For example, small quantities of Ba and B were found in solutions that did not have BaBor present, and Zn, Si, Sr, and Ca were found in solutions not containing MPSi.

5.0 IMPORTANT FINDINGS

5.1 Electrocoating Material Development. The following important findings were realized from this portion of the program:

1. Established working relationships with two electrocoat material suppliers. However, the first shipment of materials did not arrive until June 3, 1994, one year into this two year program. BASF submitted a cathodic material that we ultimately used in our own development work. PPG submitted one cathodic material and one anodic material.
2. Completed the evaluation of several current, commercially available electrocoat materials. The overall performance of all three materials is good and only slight differences were observed. While corrosion performance was not satisfactory, most other performance results far exceeded the military specification requirements.
3. Established a NAWCADWAR electrocoat process line and finalized the proper operating procedures necessary to produce good quality coatings similar to the specimens produced by MDA.
4. Developed a pigment paste grinding technique to reproduce the standard BASF formulation and to properly disperse pigment pastes for future formulations.
5. NAWCADWAR sent BASF and PPG their non-toxic, corrosion inhibiting, pigment packages for incorporation into their electrocoat materials. BASF attempted to introduce the pigments into their cathodic material, while PPG worked with their anodic material. Neither company was successful with introducing these packages into their electrocoats.
6. NAWCADWAR produced five pigment pastes containing individual corrosion inhibiting pigments. The five inhibitors selected were those used to make the NAWCADWAR proprietary pigment packages including MW-101, SZP-391, Phos Plus, KW-84, and Sicron-RZ.
7. Mixed working electrocoat baths using the above five inhibitor containing pigment pastes. A voltage ladder determined the correct voltage for the desired film thickness for each inhibited bath. Also, the bath non-volatile content and the pigment to binder ratio are monitored to check the bath stability. A total of 20 panels were coated from each bath.
8. Completed performance evaluations on the electrocoated panels which contain inhibitors. These panels and panels coated by MDA, for use as controls, underwent 2000 hours in neutral salt spray and 1000 hours in SO_2 salt fog exposure cabinets. They all passed water resistance and tape adhesion tests.
9. Corrosion performance of these inhibitor containing systems has not been improved. In neutral salt fog none of the systems improved and two actually degraded. The results of the systems in the SO_2 salt fog was altered from the standard system. Although blistering of the coating was reduced an aggressive underfilm corrosion was observed that is not present in the standard system until after a much longer exposure.
10. Electrocoats on pretreated aluminum are excellent barrier coatings in 3.5% NaCl.
11. Exposure of scribed electrocoated aluminum to SO_2 salt spray causes a loss of barrier properties in the visibly undamaged area of the coating. The loss of barrier properties caused by SO_2 salt spray becomes evident in immersion EIS tests when an activation procedure is employed. These systems could usually be modeled mathematically rather well with EIS and progress was made in developing physical models.

12. A knowledge of the electrochemical behavior of the underlying pretreated aluminum helps explain the complete electrocoated system.

5.2 UV Cure Coatings Material Development. The requirements of this program were very difficult for suppliers to meet. Of the original companies surveyed, many declined to participate, or dropped out of the program, because the anticipated amount of business was insufficient to justify the amount of development necessary to provide UV curable coatings that would meet all of the necessary requirements.

There are however, several coatings companies that exhibited continuing interest in developing a UV curable coating for this application. The first problem encountered was that most of the coatings were too viscous to be sprayed. When the Z14L pigment mix was incorporated into the coatings, and subsequently applied to test panels, an adverse affect on flexibility and solvent resistance was observed. In addition, the amount of pigment necessary to provide opacity exceeds the concentrations that were tested, thus presenting further technical challenges. The various pigments absorb, reflect and transmit UV light at different wavelength bands than some of the photoinitiators, and the amount of UV light transmission generally decreases as pigment concentration increases.

One pigmented coating that did perform well in screen tests, 3M 631, is not a zero VOC coating. In addition, solvent had to be added to incorporate the pigment. Another coating that performed well and is promising for further development, Herberts 094-58-1, is a UV curable powder coating.

5.3 Powder Coatings Development

5.3.1 The Z14L corrosion inhibitor system can be effectively incorporated into powder coatings and will have a positive/beneficial influence on corrosion resistance and overall coating performance if the pigmentation concentration is at an adequate level.

5.3.2 TPE and statistical analysis can be effectively used to analyze data. It is particularly useful with large data sets.

5.4 Powder Coatings Applications Development

5.4.1 Coating of Non-conductive Substrates. A method to powder coat non-conductive susbstrates was developed with the use of quaternary salts. These materials enhance the surface conductivity of the non-conductive substrate allowing the powder coating to adhere to the surface. The properties of the coatings are not affected by the surface enhancing agents.

5.4.2 IR Curing. The use of IR energy to cure powder paints is a viable alternative to convection curing. Parts that have been powder coated can be cured in as little as 90 seconds without any degradation of the properties of the epoxy powder paint. However, non-conventional shapes make it difficult to obtain even heating on the surface of the substrate which results in uneven curing of the powder coating. To resolve this issue, parts with non-conventional shapes would require IR curing equipment which takes into account the shape of the part.

The ability to minimize internal temperatures of parts cured with IR energy was not supported by this development work. However, parts with a thick cross-section should demonstrate cooler internal temperatures dependent on the material of the part. Various powder paint systems will also require different cure times and temperatures when IR curing is applied. During this development work, times as long as ten minutes were required to cure initial test samples while other paint systems only required 90 seconds to obtain the desired 410°F surface temperature as demonstrated by subsequent test results.

5.5 Inhibitor Characterization and Analysis. This section is organized into 7 subsections which describe the important findings of each phase of the technical results.

5.5.1 EIS Findings. The EIS findings are summarized as follows:

1. The Epoxy 1 systems on CCC aluminum cured at room temperature and 100 degrees C without defects showed no change in low frequency impedance with respect to time (up to 3 months), inhibitor type (in electrolyte), or filter indicating that water and ions do not penetrate this system.

2. The Epoxy 1 systems with an 800 micron diameter defect showed changes in low frequency impedance with respect to time (changes in 24 hours), inhibitor type (in electrolyte), and coating cure temperature. The changes in impedance were used to rank the inhibitors' effectiveness. MPSi and BaBor were found to be the most effective.

3. The more porous Epoxy 2 on CCC aluminum showed little change in low frequency impedance with respect to time, inhibitor type, and inhibitor location (coating or electrolyte) because the conductivity through the coating was not sufficiently low enough to see impedance changes due to the coating-metal interface.

4. Epoxy 2 with an 800 micron defect showed no significant low frequency impedance changes with respect to time, inhibitor type, and inhibitor location (coating or electrolyte) due to the fact that the defect impedance was insignificant relative to the coating impedance.

5. Epoxy 3 on CCC aluminum substrates showed changes in low frequency impedance after 720 hours in potassium sulfate and potassium chloride, but no change after 168 hours in potassium chloride. No changes in 3 mHz impedance were found after 168 hours indicating that the CCC was not degraded by the electrolyte.

6. Epoxy 3 on bare aluminum substrates showed low frequency changes with respect to time, inhibitor type, inhibitor location, and type of substrate (chemically and solvent cleaned). BaBor and MPSi were found to function as inhibitors when in the electrolyte, but not when incorporated in the film.

7. Epoxy 1 on CCC, chemically cleaned, and solvent cleaned with an 800 micron defect showed changes in low frequency impedance with respect to time and inhibitor type. BaBor and MPSi were found to function as inhibitors when in the electrolyte in the presence of chloride.

5.5.2 Polarization Resistance Findings. The polarization resistance values determined on the Epoxy 3 system on CCC, chemically cleaned, and solvent cleaned aluminum panels were nearly identical to the resistance values determined with EIS. Since increases in polarization resistance values have been correlated with inhibitor performance [50], EIS results are indicative of inhibitor effectiveness.

5.5.3 PALS Findings. The PALS parameters indicate that the electrolyte permeated the Epoxy 3 wafers and caused an increase in the free volume cavity size, the number of free volume cavities, and the free volume fraction. Other work on Epoxy 3 coatings [57] has shown that these coating swelled upon water exposure. The creation of additional free volume in Epoxy 3 correlates to the low impedance values observed in these coatings [57]. Water permeation into the Epoxy 3 free volume is driven by the chemical interaction between the hydrophilic groups on the resin backbone and water, resulting in the expansion of the coating's free volume [57]. The decrease in the Epoxy 3 free volume upon addition of the inhibitor was due to the replacement of epoxy material by inhibitor, which has a free volume that is 12% (MPSio) and 15% (BaBor) of the Epoxy 3's free volume.

5.5.4 DSC Findings. The DSC data show that Epoxies 1, 2, and 3 cured at 100 degrees C for 2 hours were 93.5% cured and above. This result indicates that 2 hours at 100 degrees C was sufficient to completely cure these epoxy systems. The Epoxy 1 system cured at room temperature for 1 week was 65.7% cured. However, the impedance data after 3 months suggests that the Epoxy 1 system cured 7 days at room temperature was an excellent barrier to 0.01 M potassium sulfate electrolyte. This observation coupled with the fact that the Epoxy 3 system which was 99% cured and was an extremely poor barrier to the electrolyte, demonstrates that the degree of cure of an epoxy system is not indicative of the coating's barrier properties.

5.5.5 XPS Findings. The XPS results show the following trends. S was on the aluminum surface where inhibitor was not present indicating that S is part of the corrosion product, perhaps in the form of aluminum sulfate. S was not found on the aluminum surface when inhibitor was present in the electrolyte showing that the inhibitors prevent the formation of corrosion product (up to 48 hours). Zn, P, and Ca were found on the aluminum surface in MPSi inhibited solutions and Ba and Si were found on the aluminum surface in BaBor solutions showing that these elements from the inhibitors participate in corrosion inhibition. The lack of Sr, B, Cl, and K on the aluminum surface indicate that these elements do not participate directly in corrosion or corrosion inhibition, perhaps because they are too soluble. The N found on the CCC came from an unknown source.

5.5.6 SEM Findings. The SEM elemental maps of the control show the presence of S on the aluminum surface in the hole, indicating that S is a component of the corrosion product. Cu and Fe were also present and are components in the 2024 aluminum alloy. Si, Sr, and K were present on the aluminum surface on the side of the hole in the specimens exposed to MPSi, while only Si was present at the bottom of the hole. Ba, Si, S, Sr, and K were present on the aluminum surface on the specimen exposed to BaBor. These results indicate that with specimens exposed to BaBor; Ba, Si, K, and S are the components of the resistive film on the aluminum surface and that with specimens exposed to MPSi; Si, Sr, and K are components of the resistive film on the aluminum surface.

5.5.7 ICP Findings. The ICP results are consistent with the elements that should be present in the solutions. However, there are elements that are present in the inhibitor solutions that appear to be contaminants. For example, small quantities of Ba and B were found in solutions that did not have BaBor present, and Zn, Si, Sr, and Ca were found in solutions not containing MPSi.

6.0 SIGNIFICANT HARDWARE DEVELOPMENTS

NONE

7.0 SPECIAL COMMENTS

Two techniques were developed to study corrosion inhibitor mechanisms in epoxy coated systems on aluminum with EIS. The first technique was exposure of a nonporous coating with a designed defect to inhibitor saturated electrolyte. The second technique comprised the use of a porous coating where the location of the inhibitor (in the coating and/or electrolyte) was varied.

The mechanisms of two corrosion inhibitors were determined. The inhibitor BaBor inhibits corrosion on aluminum substrates by forming a barrier layer on the surface. The barrier layer is comprised of Ba, Si, S, and K, which may be in the form of barium silicate, barium sulfate, and potassium silicate. B was not found on any aluminum substrates indicating that B does not actively participate in the corrosion inhibition mechanism. BaBor functions as described above when a defect is present in a barrier coating. In a poor barrier coating, BaBor from the saturated electrolyte forms a resistive film on the surface of the epoxy coating. Since BaBor deposits resistive films on both aluminum and epoxy surfaces and appears to be highly insoluble in aqueous electrolyte, the insoluble resistive barrier is not a result of a chemical reaction between elements in BaBor and the aluminum surface. When BaBor is incorporated in a porous coating, it is unable to form a resistive barrier on the aluminum surface because the insoluble material is not transported to the coating-metal interface.

MPSi also functions as an inhibitor by forming a resistive film on the aluminum surface. The barrier is comprised of Zn, P, Ca, Sr, Si, and K, which may be in the form of silicates and phosphates. Thus, when a defect is present in a barrier coating, MPSi functions by forming a resistive barrier on the defect's aluminum surface. In a poor barrier coating, MPSi from the electrolyte forms a resistive film at the coating-metal interface. In order to do this, MPSi in the saturated electrolyte must pass through the porous coating in the form of ions. This observation suggests that MPSi does not form an insoluble inorganic coating like BaBor, but reacts with the aluminum substrate to form a resistive barrier. When MPSi is incorporated in a poor barrier coating, it is unable to form a barrier at the coating-metal interface. Therefore, in a porous coating MPSi is unable to form ions because there is insufficient electrolyte to solvate the inhibitor.

The inhibitors MPSi and BaBor only function when they are saturated in an electrolyte. Neither inhibitor is able to migrate to the coating-metal interface when incorporated in a porous coating, while only MPSi is able to migrate through a porous coating when saturated in the electrolyte. Therefore, incorporation of these inhibitors in an extremely good barrier coating (i.e., powder, electrocoat, or UV-curable coatings) would render the inhibitor ineffective because it would not be transported to the coating-metal interface by the electrolyte. Assuming that an inhibitor can be incorporated into a powder, electrocoat, or UV-curable coating, the following scenario would have to occur for the inhibitor to be effective: If upon impact a defect in the coating was created that (1) exposed the metal substrate to electrolyte, (2) exposed the inhibitor in the coating to electrolyte, and (3) the inhibitor was able to saturate the volume of electrolyte in contact with the metal surface; then the inhibitor might be effective based on the work described in this report.

The investigation into the pretreatment inconsistency problem resulted in the identification of several potential methods for analysis. A number of analysis techniques were evaluated for their potential to characterize the chromate conversion coating surface pretreatment used in this study. These methods included: Color Analysis; Coating Adhesion Tests; EIS and Polarization Analysis; Surface Wetting Characterization; X-Ray Fluorescence; Pendulum Hardness; Photoelectron Emission Testing; and Galvanic Cell/$CuSO_4$ Spot Testing; along with the standard tests (salt spray testing and primer adhesion wet tape tests).

The evaluation parameters consisted of: 2024 T-3 Aluminum alloy (cleaned & deoxidized with non-chromate materials); Alodine 1200 chromate conversion coating; MIL-P-23377 Epoxy Primer and a minimum of three replicates per condition. Variances in coating weights (25, 46 & 80 mg/ft^2) and pretreatment aging (1 hour, 24 hours, 7 days, etc.) were investigated using these techniques.

The Pendulum Hardness and Photoelectron Emission Testing were discontinued due to a lack of promising results. The Color Analysis, Coating Adhesion Tests, EIS and Polarization Analysis, Surface Wetting Characterization, X-Ray Fluorescence, and Galvanic Cell/CuSO4 Spot Testing all showed some promise as potential methods for pretreatment analysis. In addition, several of these techniques also held potential for field use. Unfortunately, parameters such as contamination and overall quality were not defined by the initial investigation.

8.0 IMPLICATIONS FOR FUTURE RESEARCH

8.1 Electrocoatings Material Development. The following implications for future research were realized from this portion of the program:

1. Continue investigating the formulation of corrosion inhibitors into electrocoat materials. Arrangements have been made between NAWCADWAR and BASF for the continued supply of development materials.
2. Attempt a second round of formulations using the NAWCADWAR inhibitors at lowered loading levels and increased neutralization. However, if these inhibitors are not providing protection now they probably will not at reduced levels.
3. Continue the search for alternate corrosion inhibiting substances.
4. Continue the effort to develop a pigment screening procedure using conductivity or other analysis methods.
5. Obtain access to anodic materials as their properties may be better for the incorporation of inhibitors. Apply the above to the anodic material development.

8.2 UV Cure Coatings Material Development. As testing for this program came to a close, Sokol Enterprises, Inc. developed a UV coating formulation that remains untested by HAC. Sokol was provided with a list of the requirements, and reports that the new formulation passes adhesion, solvent resistance, flexibility and fluid resistance tests. This development occurred just when the test phase of this program was discontinued, but it is promising enough to warrant future testing and modification.

Further work needs to be done in the area of matching photoinitiators and specialty bulbs, with the specific pigments or pigment mixes used in UV curable coating formulations.

Since it was found that addition of the Z14L pigment mix resulted in flexibility loss of most coatings, additional formulation research of the base resin systems to improve flexibility is mandated. Since the 3M 631 coating (not zero VOC) exhibited good characteristics when pigmented, it is evident that the technology does exist, however more extensive research is required.

8.3 Powder Coating Development

8.3.1. Two Herberts epoxy powder coatings (H096-22-3 & H096-22-4) were identical formulations except that they were cured at 275°F and 300°F, respectively. The TPE data clearly indicates superior performance at the 300°F cure temperature. Optimum cure temperature analysis should be performed in future related efforts.

8.3.2. Weatherable resin chemistries such as polyurethane, polyester, and continued work with acrylics, should be developed and combined with other non-toxic corrosion inhibitive pigment systems in order to develop materials more applicable to exterior exposed equipment systems.

8.3.3. Coating removal rate with novel environmentally friendly methods (i.e., non-methylene chloride based chemical strippers, plastic media blasting, CO_2/flashlamp removal, etc.) should be analyzed since many types of aerospace equipment are required to be stripped of their coating systems on regular intervals.

8.4 Powder Coating Applications Development

8.4.1 IR Cure. The implications of future research in reference to IR curing of powder coatings is highly dependent on the specific applications. Material properties of the cured powder paint will not change when cured with IR energy assuming a full cure is achieved. Therefore, specific applications must be evaluated on a case by case basis dependent upon the shape and material of the part to be powder coated. This case by case requirement makes generic research on IR curing of powder coatings difficult.

8.5 Inhibitor Characterization and Analysis. Future research should be directed at developing corrosion inhibitors which can be incorporated in powder, electrocoat, and/or UV-curable coatings that will prevent corrosion on aluminum when a defect in the coating exposes the substrate. Therefore, the mechanisms of inhibitor transport to the substrate should be studied.

When a defect is present in a coating, the electrolyte migration to the substrate is dependent on (1) the amount of inhibitor directly available to the electrolyte in the defect, (2) the solubility of the inhibitor in the electrolyte, (3) the permeability of the coating to the electrolyte, and (4) any factor which affects the mass transport of inhibitor in the electrolyte to the substrate. The following is a suggested approach to study the above mentioned factors:

1. Inhibitor Availability;
   The parameters affecting the amount of available inhibitor in a coating such as the concentration of inhibitor in the coating, surface wetting properties of the coating on the inhibitor, the physical and chemical interactions of the inhibitor with the coating material, etc.

2. Inhibitor Solubility;
   The conditions affecting inhibitor solubility such as electrolyte pH, electrolyte ion concentration, electrolyte temperature, etc. Also, the kinetics of inhibitor solubility, i.e., how long does it take for the inhibitor to saturate a given type and volume of electrolyte.

3. Permeability of the Coating;
   The factors affecting the permeability of the coating to electrolyte such as the chemical and physical properties of the coating material.

4. Mass Transport of the Inhibitor;
   The conditions affecting the mass transport of inhibitor to the substrate surface such as the rate and type of movement of the substrate relative to the electrolyte and vice versa in a dynamic environment, the evaporation and condensation of electrolyte on the substrate, etc.

8.6 Conversion Coating Analysis. Future research should be directed at further development of the most promising conversion coating analysis methods to optimize both a laboratory method and a field method which can operate on a wide range of inorganic coatings.

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