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EXPLORATORY DEVELOPMENT OF CORROSION INHIBITING PRIMERS

HYSOL DIVISION OF THE DEXTER CORPORATION
PITTSBURG, CALIFORNIA 94565

JULY 1977

TECHNICAL REPORT AFML-TR-77-121
Final Report for Period 1 April 1976 – 31 March 1977

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NOTICE

This technical report has been reviewed and is approved for publication.

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While present corrosion inhibiting primers give generally good performance in adhesively bonded structures, they require special handling and application conditions to ensure proper pigment suspension and film thickness and uniformity control. In addition, improvements in primer performance and application economies have become increasingly difficult to obtain with known primer resin formulation technology and available corrosion inhibiting pigments. As a possible solution to some of these problems, major emphasis was placed on development of anti-corrosion materials which would be soluble, or at least more easily >

suspendable, then present inorganic chromate pigments. Of the numerous routes examined, most promise was attained with chromate salts of organic amines. However, only a few selected structures were active yet able to resist oxidation during salt formation and purification or were stable during storage or exposure to light. The best of these materials, chromate salts of triphenyl guanidine and melamine, were selected for further evaluation in primer systems as examples of soluble and insoluble corrosion inhibitors. Other routes to potential compatible corrosion inhibitors, including organic inhibitors and chemical modification or cure of the primer resin with inorganic anti-corrosion materials, appeared to be impractical because of difficulty of preparation, instability or low levels of corrosion protection. Some promising corrosion inhibition was shown by several crown ether-chromate complexes, but primer solution stability was low. To provide a more fundamental bases for development of primer resin systems with decreased thickness sensitivity, correlations between chemical composition-critical bulk properties - and performance in adhesively bonded structures were investigated. Model resin systems were selected which were varied in a controlled manner in cross-link density using a constant chain backbone structure and also varied in chain backbone stiffness at constant cross-link density. Informative correlations were found, with a resin vechicle crack toughness parameter showing the closest relation to thickness sensitivity. These results suggest that the thickness sensitivity of primers depends in part on their relative ability to reduce or eliminate the stress concentrations which cab arise around defect areas in the resin film. Using the above bulk property correlations and extended bond performance results, a graded series of anti-corrosion primer systems were defined. These which, though not yet optimized, showed similar to moderately improved properties over selected state-of-the-art primers in storage stability, chromate pigment suspension and reduced thickness sensitivity in adhesive bonds. The relative anticorrosion effectiveness of the various organic and inorganic chromate inhibiton was highly dependent on the specific primer vehicle. In the above systems, the soluble triphenyl guanidine dichromate gave relatively poor performance. Melamine dichromate pigment was more generally effective in preventing corrosion than the common inorganic chromates. However, work beyond the present contract period would be needed to fully evaluate the practicality of its use and to optimize and examine the developed primer systems in expanded performance tests and application methods.

FOREWORD

This report was prepared by the Hysol Division of the Dexter Corporation, Pittsburg, California, under Contract F33615-76-C-5142, "Exploratory Development of Corrosion Inhibiting Primers". The contract was initiated under Project 7340, Task 02, and administered under the direction of the AirForce Materials Laboratory, Wright-Patterson Air Force Base, Ohio, with Theodore J. Aponyi (AFML/MBC), Composite and Fibrous Materials Branch, Nonmetallic Materials Division, as the Project Engineer. Mr. C. Lynn Mahoney, Project Manager, directed the program for Hysol Division of the Dexter Corporation. Mr. Thomas F. Mika served as a technical consultant.

The report covers the period from 01 April 1976 through 31 March 1977.

This report was submitted by the authors in May 1977.

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1.0) PROGRAM OBJECTIVE

The main objective of this present program was to explore new routes to the attainment of improved corrosion inhibiting adhesive primer systems. Reduction of pigment settling problems and film thickness sensitivity, both present in state-of-the-art primers, and adaptability to lower cost methods of application were included as goals. Longer range goals, only partially attainable in this present contract because of time limitations, were final optimization of practical corrosion resistant primers having improved storage stability and application properties along with improved performance in bonded structures under stressed high humidity conditions.

1.1) SUMMARY AND CONCLUSIONS

While present corrosion inhibiting primers give generally good performance in adhesively bonded structures, the inorganic chromate pigments commonly used tend to settle during shipment and storage and require special handling for subdivision and applications. Another problem encountered during their application is related to the opposing properties of improved anti-corrosion performance with increased primer thickness but rapidly decreasing adhesive bond performance, especially in the peeling mode, as primer film thicknesses are increased. Such careful control of thickness presents barriers to use of low cost automated methods of application.

As a potential solution to some of the above problems, a major effort was made to find routes to anti-corrosion materials which would be soluble or at least more compatible or more easily suspendible than present inorganic chromate pigments. Of the numerous routes examined, the major effort, as well as the major promise, was attained with chromate salts of organic amines. Of many organic amine structures examined, those based on guanidines, guanamines and substituted triazines showed the most promise. Even here, however, only a few selected structures were able to resist oxidation during salt formation and purification or were stable during storage or exposure to light.

As the single most promising structural type, trisubstituted guanidines were explored in some detail both through salt preparation with all those commercially available and through synthesis of materials having structures of specific interest. From all this work, chromate salts of triphenyl guanidine and melamine were chosen, on the basis of good salt stability and good anti-corrosion protection, for further evaluation in primer systems as examples of soluble and insoluble corrosion inhibitors.

A number of other routes to potential compatible corrosion inhibitors were explored, including crown ether-chromate complexes, organic inhibitors including materials such as alizarin, chemical modification of the primer resin to contain anti-corrosion promoting groups, and use of inorganic anti-corrosion materials as resin curing agents. Most of these methods appeared to be inpractical because of various problems such as difficulty of preparation, instability, low levels of corrosion protection, etc. Some promising anti-corrosion protection was obtained with several of the crown ether-chromate complexes. However, primer solution stability was low so combination of the complex with the primer solution just before application was necessary.

To provide a more fundamental basis for development of primer resin systems with decreased thickness sensitivity, correlations between chemical composition-critical bulk properties - and performance in adhesively bonded structures were investigated. Model resin systems were selected which were varied in a controlled manner in cross-link density using a constant chain backbone structure and also varied in chain backbone stiffness at constant cross-link density. Informative correlations were found, with a resin vehicle crack toughness parameter showing the closest relation to thickness sensitivity. These results suggest that the thickness sensitivity of primers depends in part on their relative ability to reduce or eliminate the stress concentrations which can arise around defect areas in the resin film.

Using the above bulk property correlations and extended primer performance test results on these model compositions, three resin systems, generally ranging from "hard to soft", were selected for further extended evaluation and optimization. When combined in bonded structures, using a 250°F curing adhesive film, these systems gave good performance but covered the range of high to low in their sensitivity to primer film thickness in adhesive peel performance tests. These good performance properties and the same relative thickness sensitivities were shown when common inorganic chromate corrosion inhibitors were added.

In initial work with chromate salts of organic amines, some selectivity in solvents and curing agents was needed to provide compatibility with primer vehicles. The above three systems were compatible with the selected organic amine-chromate salts, triphenyl guanidine dichromate and melamine dichromate. In scribe panel-salt spray tests, melamine dichromate gave corrosion protection generally superior to the conventional inorganic chromate pigments. The fully soluble triphenyl guanidine dichromate provided only moderate corrosion protection in these systems.

The relative anticorrosive effectiveness of the various inhibitors examined appears to be significantly influenced by the specific primer vehicle used. While melamine dichromate appeared to be more generally effective than the other pigments examined, further work would be needed to evaluate fully optimized systems and to determine the cost effectiveness of its use.

Some improvement in reducing the settling rates of conventional pigments, particularly with zinc potassium chromate, was found through use of primer vehicles containing toughening agents such as reacted butadiene-acrylonitrile elastomers. Several of the selected model primers showed this property. Also, when formulated at high solids content to be suitable for application methods such as roller coating, such systems showed reduced pigment settling and gave good primer coatings.

In overall summary, a graded series of anticorrosion primer systems have been defined which, though not yet optimized, show similar to improved properties over selected state-of-the-art primers in storage stability, inorganic chromate pigment suspension and reduced thickness sensitivity in adhesive bonds. Spray properties and coating properties are good. Such other properties as solvent resistance and bondability after bake, depend on the relative hardness of the primer film, as does the relative primer thickness sensitivity. The goal of finding soluble inhibitors while retaining all the positive properties of present inorganic pigments was not fully attained. The best such material, triphenyl guanidine dichromate, was soluble and stable but gave only moderate corrosion protection. The insoluble melamine dichromate was a very effective corrosion inhibitor but required handling similar to present inorganic pigments.

Further work beyond the contract period would be needed to fully evaluate the practicality of using these organic chromate materials and to optimize and evaluate the developed primer systems in expanded adhesive bond performance tests and in automated application methods.

2.0) INTRODUCTION

2.1) BACKGROUND

Over the past years, much time and effort has been expended by manufacturers of structural aircraft adhesives and a few paint manufacturers, on the development of corrosion inhibiting primers suitable for use in bonded aluminum structures. Though such primers must also function under top coat paints, performance in bonded joints is usually the limiting factor. Such requirements as low thickness sensitivity and high strength performance in peel modes as well as tensile modes over a wide temperature range are added to the corrosion protection requirements of paint primers. A number of the adhesive primers on the market do give good performance in their intended areas of use but they require special application conditions to insure proper pigment suspension, film thickness and uniformity control.

Although formulating efforts have been continued by various suppliers during the past years, further improvements in primer performance and application ease have been increasingly difficult to obtain with the known primer resin formulating technology and available corrosion inhibiting pigments. Such pigments present application problems due to settling in the primer-solvent mix and corrosion performance problems due to non-uniform distribution in the primer film. They also increase primer thickness sensitivity and reduce strengths in bonded structures. While primers with improved performance properties and greater ease of application might result from substitution of pigments with soluble corrosion inhibitors, better resin systems were also needed if primers having extended use temperature ranges or increased resistance to corrosive environments were to be obtained.

2.2) PROGRAM PLAN

To attain the above goals, a program was outlined to develop soluble inhibitors which could provide corrosion protection with a minimum influence on bond performance. In addition, examination of the bulk property and interface characteristics of primers, as they related to performance in adhesively bonded structures, was used to guide formulation optimization.

2.2.1) Approach

The obvious solution to some of the above stated problems, the use of soluble or homogeneously dispersed inhibitors, was a sparcely explored area. While some soluble organic materials and selected chromate salts of organic amines have shown anticorrosion activity in chemical and food process uses and in some paint applications and such inorganic materials as magnesium and potassium chromate have shown both solubility and activity, their examination in practical primer systems with required storage stability, influence on cure and bond performance, etc., has been only slightly touched. Neverthless, the application and performance advantages that appeared possible and the knowledge of a number of potential approaches to chemically prepare such materials suggested that work in this direction was desirable. There were possible trouble areas that could be foreseen. While some corrosion inhibition had been obtained with chromate-free organic systems, it was envisioned that the best chance for success lay with chromate or dichromate-containing organic materials. How this strongly oxidizing group acts when in the free state, as contrasted to its usual inactivation in an insoluble pigment, remained to be seen. What influence this had on resin systems during storage and cure also needed early examination. Methods of incorporating inorganic chromates in a dispersed form was included as part of the program so ways around any encountered stability problems would be possible. In addition, methods of preparing various amine-chromate complexes were so flexible that materials ranging from insoluble pigments through partially soluble to soluble materials should be attainable so that various degrees of separation of chromate from the resin was possible. Even with such insoluble organic chromates, it was thought possible to provide substituents making them much more easily suspendible than the usual inorganic pigments.

The other general area of effort was directed toward providing a better understanding of the performance requirements of primer resin systems as related to chemical structure parameters and bulk material properties. Such information as it relates to primer performance was not available in the literature and it was felt that such an organized approach would provide the best chance for performance optimization beyond present formulation limits.

2.2.2) Specific Plan

The program was divided into four phases as follows:

Phase I A. (Major Effort) Synthesize and screen, using state-of-the-art primer vehicles, soluble organic based inhibitors. Select the most promising types, optimize structures and select three candidates for incorporation in optimized vehicles (Phase IB)

B. (Major Effort) Define required primer resin properties and develop improved primer vehicles. Examine variation in cross-link density and backbond stiffness in seven model systems and compare with two control systems. Correlate changes in molecular architecture with vehicle adhesive performance properties and resin bulk properties. Optimize and select two or more optimum formulations.

Phase II Screen and optimize complete adhesive primer systems using materials developed in Phase IA and IB.

Phase III Briefly evaluate candidate primer(s) optimized in Phase II as a paint primer.

Phase IV Briefly evaluate application methods. Balance formulation(s) and evaluate in falling film (curtain coating) and roller coating apparatus.

3.0 CORROSION PROTECTION

3.1) OBJECTIVE

The objective was development of improved corrosion resistant materials for incorporation in an improved corrosion resistant primer. Corrosion inhibiting materials were to be synthesized that would have greater organic solvent solubility, greater compatibility, or were more easily suspendable than the presently used inorganic chromate pigments.

3.2) BACKGROUND

On the electrolytic potential scale, aluminum is classed among the base metals, and therefore, the unprotected metal is attacked by many materials. The corrosion resistance normally observed is due to a thin protective, non-porous, amorphous aluminum oxide barrier film generally ranging in thickness from 25-35A°. In the presence of moist air or other corrosive environments, additional layers of hydrated aluminum oxide are formed which generally are crystalline and permeable and do not provide good corrosion protection. Often, such corrosion product layers may allow differential oxygen concentrations to develop which can lead to increased corrosion rates through formation of an electrolytic cell.

To reduce corrosion, three general classes of inhibitors are used which:

1) Deposit a thin protective film (silicates, glue, starches, resins,etc.).

2) Neutralize corrosive materials or stabilize materials which could become corrosively aggressive if they decomposed (organic amines, buffers, etc.).

3) Reinforce the natural oxide film or re-establish the film if damaged (chromates, permanganates, hydrogen peroxide, etc.).

Many inhibitors fitting all the above classes have been added to liquids in contact with aluminum in food or chemical process applications. When used in primer films, however, most successful inhibitors have been of the third class with the ability to reduce the electrochemical driving force between anodic and cathodic sites. Most such materials, various inorganic chromates being the most common examples, function as anodic inhibitors and contribute to reformation of the oxide film. However, examination of the cations present with various chromate type inhibitors indicates that the effectiveness of such materials is not alone due to their oxidizing ability but that cathodic polarization can occur if the proper cation is used. In this respect, in primer studies1) the nickel chromate was more effective than the magnesium and calcium chromates which were more effective than sodium or potassium chromate2). There is also evidence that in absence of oxygen, such protection can involve deposition of insoluble materials at cathodic sites which blocks further corrosive action. Non-oxidizing inorganic inhibitors, such as silicates or molybdates or tungstates, which are mild oxidants, probably function by co-precipitation of reaction products of the metal and the anion or by absorption of the inhibitor ions at the metal interface1).

Many organic materials have been added to various fluids to reduce their attack on aluminum but relatively few have been examined as components of primer films. It has been postulated by D. B. Boise3), that a select group of organic compounds giving corrosion protection in primers probably functioned through prevention of crystallization of the protecting amorphous oxide film or through reinforcement of the non-protective crystalline oxide film. Though the best of such materials, alizarin, picrolonic acid, isatin and 4-hydroxy benzophenone, gave poorer results than a control strontium chromate pigment, some further examination of this possible additional mechanism of corrosion protection was made.

Other types of inhibitors that have shown promise in past work include several cyanamide compounds[4], alizarin and alizarin-chromate complexes.[3,5] A number of chromates and dichromates based on N, N', N"-tri-p-chlorophenyl guanidine, α-naphthyl biquanide, and triphenyl guanidine and α- quinoinol[7] etc., have shown promise as has the somewhat related Organokrome[7] pigments formerly produced by Pfizer.

3.3) APPROACH

To be effective in primer applications, inhibitors have to:

1. Be able to control corrosion by mechanisms related to those described above.
2. Have controlled solubility in water to provide protection in defects in the primer surface and yet not undergo depletion at too rapid a rate.
3. Be compatible with the primer vehicle with respect to storage stability, curing chemistry, and performance strength requirements.
4. Provide practical systems compatible with needed application methods.

Essentially all inhibitors used in present adhesive primers are pigments which, while giving good corrosion protection, adversely affect the primer's thickness sensitivity and cause application problems due to rapid settling in the dilute spray solutions commonly used. To improve such inorganic pigment related primer problems, the following general approaches to provide more easily suspended pigments or more soluble or compatible inhibitors have been investigated.

Method I	Organic chromates and dichromates based on amine complexes. Some should be soluble or more readily dispersed than present pigments.
" II	Solubilization of corrosion inhibiting metal salts with organic ligands, especially crown ethers.
" III	Organic and Organo-metallic complex inhibitors.
" IV	Chemical modification of the primer resin vehicle to contain corrosion inhibiting groups.
" V	Cure of the primer resin with corrosion inhibiting metal salts.
" VI	Better pigment suspension methods for special application techniques.

Results obtained with each of the above approaches follows.

3.3.1) Method I Chromate Salts of Organic Amines

The chromate or dichromate anions are present in most of the effective corrosion inhibiting primers used with aluminum. A number of organic chromates and dichromates based on various nitrogen bases have been prepared in the past.6)7). Some of these materials were found to have anticorrosion activity when used in surface coatings for steel6)8). A fewer number have been examined as corrosion inhibitors for aluminum. Many such materials are insoluble and were used as pigment dispersions. Such materials should be much more easily suspended than their inorganic counterparts. By modification of the substituents on organic amine molecules that form chromate salts, it is possible to form organic chromate salts much more soluble in the resin systems and solvents used in primers so that homogeneous primer systems are formed.

This demonstrated ability to form chromate or dichromate salts with organic amines opens up the possibility of forming such complexes with other organic nitrogen containing bases selected from the many available simple amines, nitrogen heterocycles, and related polymers.

Chromium in known effective inorganic chromate corrosion inhibitors is in the +6 oxidation state. Such chromates and dichromates are very strong oxidizing agents and readily attack most organic materials. Numerous organic nitrogen containing bases were evaluated to find the structural combination or combinations that could form stable chromate salts without being oxidized during preparation. Direct reaction of an aqueous solution of chromium trioxide with many amines led to oxidation. More preparative success was found using milder synthesis techniques which involved: 1) mixing aqueous solutions of the pure amine hydrochloride and chromium trioxide, 2) mixing aqueous acetic acid solutions of the pure amine and chromium trioxide, 3) mixing aqueous solutions of the pure amine hydrochloride and sodium dichromate, or 4) forming the complex at ice water temperature. Such methods are described in the Appendix.

3.3.1.1) Chromate Salt Preparation with Various Nitrogen Bases

Preparation of chromate salts was attempted with a wide variety of nitrogen containing organic bases representing numerous structural types. (See Table 1 and the Appendix.) A brief summary of conclusions based on this search are presented below.

Primary aromatic amines do not form stable chromate salts because of the combination of the oxidizing power of hexavalent chromium and the reducing power of the aromatic amine in the same molecule. Modifications to decrease the base strength, such as with diaminodiphenyl sulfone, use of hindering groups, as with methylene-bis-(methylanthranilate), or aromatic nucleus changes, as with 1,5-diaminonaphthalene, still led to oxidation during attempted chromate salt preparation.

Of the three triazoles examined, only benzotriazole formed a stable chromate salt. However, this material is an extremely strong oxidizing agent as evidenced by its leading to ignition of the solvent upon addition to a primer resin vehicle.

Preparation of the pyridine chromate salt at room temperature resulted in a red solid which very slowly oxidized on room temperature storage. 8-hydroxy-quinoline and 2-benzylpyridine underwent oxidation during reaction. The highly hindered 2,6-diaminopyridine also oxidized. These data are supported by the findings of Sisler, et al 9). They found that unhindered heterocyclic nitrogen bases, such as pyridine, form chromium (VI) oxide addition compounds at or near room temperature. However, α-picoline and lutidines having a methyl group in the 2-position undergo considerable oxidation by chromium (VI) during preparation, and highly hindered bases, such as 2,6-lutidine, do not react with chromium (VI) oxide under these conditions. Thus, the formation of such chromate salts appears to be strongly influenced by steric hindrance as well as a base strength.

The acridines are nitrogen heterocycles and closely related to the pyridines discussed above. The steric hindrance of acridine is greater than pyridine because of the adjacent rings. Acridine and 3,6-diaminoacridine form stable salts. However, 3,6-bis-(dimethylamino)-acridine did not form a salt probably because of the additional steric effect due to the methyl substitution on the nitrogens.

Of the 2 and 2,4-diamino-s-triazine types, 2-amino-4-morpholino-s-triazine did not form a stable salt. 2,4-diamino-s-triazine did form a stable chromate salt. Comparison of 2,4-diamino-s-triazines with cyclohexylamino, anilino, and p-chloroanilino substitution with the 4 position reveals that chromium (VI) oxide addition was related to basicity of the triazine compound. The least basic 2-amino-4-cyclohexylamino-s-triazine did not form a salt whereas the more basic triazine structures with electron donating substituents formed stable salts.

Of the guanamine structural types, all formed chromate salts except 2,4-diamino-6-chloro-s-triazine. Comparing the structures of 2,4-diamino-s-triazine which does form a chromate salt and 2,4-diamino-6-chloro-s-triazine which does not, it appears that the strongly electron withdrawing chlorine atom decreases the basicity so that a salt is not formed. Other guanamines which have weaker electron withdrawing groups in the 6 position, such as acetoguanamine, stearoguanamine, and benzoguanamine, formed salts. All of the guanamine chromate salts were photosensitive.

Of the 2,4,6 substituted-s-triazines, melamine formed a salt which was very stable to heat and light. However, the solubility of melamine in organic solvents of intermediate polarity was low. Diallylmelamine chromate salt should have had improved solubility but was unstable under room temperature storage. 2,4,6-triphenoxy-s-triazine did not form a salt because of steric hindrance. Other highly hindered trisubstituted s-triazines also would not be expected to form chromium (VI) addition compounds unless the substituents contain nitrogen. Such was the case with 2,4,6-tri-(2-pyridyl)-s-triazine which, although trisubstituted, did form a salt.

Gibson 7) reported the formation of chromate salts of various biguanides. In our work, however, in numerous attempts with various methods of synthesis no chromate salts examined could be prepared with the several biguanide structural types examined.

Imidazoles with aliphatic substitution on the nitrogen, or on one of the ring carbons, or on both the nitrogen and a ring carbon, did not form chromium (VI) oxide addition compounds. Combined aromatic and aliphatic substitution, as in 1-benzyl-2-methylimidazole, resulted in preparation of a red oil. Aromatic substitution on the imidazole ring gives compounds that do form organic chromate salts. This behavior cannot be explained by base strength or steric effect. It could, perhaps, be related to crystal packing structure. 2-(5-Ethyl-2-pyridyl)-benzimidazole oxidizes during reaction because pyridines substituted in the 2-position are labile to oxidation by chromium (VI).

Formation of chromate salts was attempted with some miscellaneous nitrogen containing organic bases. Urea did not form a chromate salt. This was expected because of its very low basicity. The quaternary ammonium salt, cetyltrimethylammonium bromide, formed a chromate salt that exhibited photosensitivity. Triethylenediamine did not form a chromate salt.

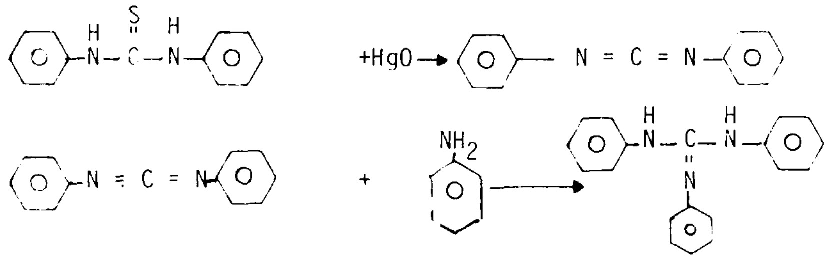
3.3.1.2) Chromate Salts of Guanidine Derivatives

Formation of chromate salts of guanidine and its derivatives proved it to be the most promising structural type. With the exception of 1,1,3,3 tetramethylguanidine and dicyanadiamide, guanidine itself and all 2- and 2,3-substituted guanidines formed addition compounds with chromium (VI) oxide. Of these, salts with aromatic substitution only in the 2- or 2,3-position were either heat or light sensitive. Thus, benzoylguanidine, diphenylguanidine, and diorthotolyguanidine formed chromate salts unstable either to heat or light. However, 1,2,3-triphenylguanidine did form a stable chromate salt. In addition, the salt was relatively soluble in organic solvents of intermediate polarity, such as methyl ethyl ketone.

3.3.1.2.1 Synthesis of Substituted Guanidines

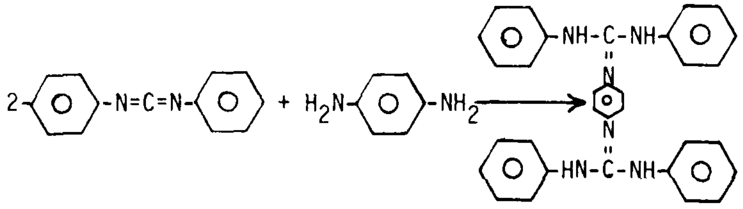
To further investigate the guanidine structural type, commercial chemical suppliers for 1,2,3-aromatic substituted guanidines were sought. Few such guanidines were commercially available. To further develop these observations and obtain optimized amine-chromate salts for anticorrosion applications, synthetic methods for preparing substituted guanidines were investigated.

The literature revealed a synthetic approach which would be clean -- i.e., very little possibility of contaminating side reactions. The route involved the formation of the carbodiimide from the thiourea and reaction of the carbodiimide with an amine to form the trisubstituted guanidine.



The carbodiimide amine reaction goes more easily when catalyzed with aluminum chloride.

Preparation of various structural modifications of trisubstituted guanidines was attempted. A saturated and an unsaturated carbodiimide were evaluated with anilines that had a wide range of basicity. In addition, aromatic primary diamines were reacted with carbodiimides to obtain 1:2 amine to carbodiimide complexes. For example, see below:



The relative reaction rates were found to be dependent upon molecular structure. Dicyclohexylcarbodiimide did not react with aromatic amines when catalyzed with $AlCl_3$ (see Table 2). In contrast, diphenylcarbodiimide formed substituted guanidines when reacted with aromatic amines even without catalysis. The electron donating effect of the saturated rings in dicyclohexylcarbodiimide probably result in a more negative carbon or a weaker positive charge at the reaction site than the electron withdrawing effect of the saturated rings in diphenylcarbodiimide.

A number of anilines and amines varying in base strength from 2,5-dichloroaniline to 4-methoxy aniline were reacted with diphenylcarbodiimide to prepare the corresponding trisubstituted guanidines. See Tables 2 and 3. As the basicity of the amine increased from 2,5-dichloroaniline to 4-chloroaniline, the yield of trisubstituted guanidine prepared with diphenylcarbodiimide improved from 17% to 46%. The lower yields with 2,5-dichloroaniline and 2-chloroaniline could be explained by steric hindrance. However, the gradual improvement of the yield with increasing basicity is evidence that the carbon at the reaction site has a weak positive charge. In addition, the finding that aromatic anilines with strong electron withdrawing groups, such as 3-chloroaniline did not react with the carbodiimide without use of a catalyst is additional evidence that the reactive carbon in the carbodiimide has only a weak positive charge.

Phenylanthranilate did not react with diphenylcarbodiimide because of the bulky ortho substitution on the amine.

Preparation of trisubstituted guanidines from amines more basic than aniline was not very successful. With the exception of the formation of 1:2 amino-carbodiimide compounds with p-phenylenediamine and diaminodiphenylether, no amine more basic than aniline formed the desired trisubstituted guanidine.

3.3.1.2.2 Chromate Salts of Trisubstituted Guanidines

The guanidines synthesized in this work were reacted to form chromium (VI) oxide addition compounds for use as corrosion inhibitors. Chromate salts prepared from substituted guanidines with very acidic anilines ($pKa < 3.46$) in the 1-position were not stable. 1-(2,5-dichlorophenyl)-2,3-diphenylguanidine and 1-(2- chlorophenyl)-2,3-diphenylguanidine formed chromate salts that were unstable to heat. Although 1-(3-chlorophenyl)-2,3-diphenylguanidine did form a stable salt, the yield was low because much of the chromate salt decomposed into the original amine and acid during purification. Chromate salts prepared from substituted guanidines with weakly acidic anilines (pKa 3.46 to 4.63) in the 1-position were stable. Thus, 1-(4-bromophenyl)-2,3-diphenylguanidine, 1-(4-chlorophenyl)-2,3-diphenylguanidine formed stable chromate salts.

Substituted guanidines prepared with aromatic diamines, such that a 1:2 amine to guanidine structure resulted, oxidized during attempted preparation of the chromium (VI) oxide addition compound. Oxidation during formation of the chromate salt was the result of the combination of the strong oxidizing power of hexavalent chromium and the strong reducing power of the aromatic amine in the same molecule.

3.3.1.3 Organic Chromate Salt Stability

Many chromate salts of organic nitrogen containing bases exhibited sensitivity to heat and light. All chromate salts that showed strong heat sensitivity decomposed during the recrystallization stage of the salt preparation procedure. Diorthotolyl guanidine dichromate, which is heat sensitive. was prepared without the recrystallization step because it was (1) stable during normal storage, and was (2) very soluble in organic solvents. Differential scanning calorimetry was used to examine the stability relationships of the organic amine chromates prepared during this work. As seen in Table 4, the salts defined as "unstable" due to decomposition during attempted recrystallization or on exposure to light during storage, generally had lower melting points or decomposition temperatures than the salts determined to be "stable" during their preparation and storage. Most of the "stable" salts exhibited decomposition rather than distinct melting points during such DSC testing. Exceptions to the above observations were found in the high decomposition temperatures observed with the "unstable" acetoguanamine and benzoylguanamine dichromates.

Comparison of structures of organic amine chromate salts that are photosensitive reveals some similarities. See Table 5. Long aliphatic chains, carboyl groups and the guanamine structural type appear to contribute to light sensitivity. Any material that contains the pyridine moeity oxidizes immediately upon addition of the chromic acid during preparation, deteriorates by oxidation or photosensitivity before the recrystallized salt can be isolated, or is photosensitive on standing. The imidazole moeity appears to influence sensitivity to light. In addition, sensitivity to light often increases when aryl groups are replaced by alkyl and methoxyl groups are introduced into phenyl groups. For example, replacement of the phenyl ring in benzoguanamine with a long aliphatic chain to form stearoguanamine changes the time of first evidence of photosensitivity due to diffused light from several days to 10 minutes. Photosensitivity is evidenced by the appearance of green color due to reduced chromium (III) in yellow compounds and the appearance of dark brown color in red or orange compounds.

3.3.1.4 Summary of Chromate Salts of Organic Bases

In summary, the chromate and dichromate anions are present in most of the effective corrosion inhibiting primers used with aluminum. In past work some organic chromates have been found to be effective protectors of steel, but, in this published work, few have been evaluated on aluminum. The ability to form chromate salts with organic nitrogen containing amines opened up the possibility of preparing a wide variety of compounds, some of which had improved solubility in primer resins or solvents.

Since chromium +6 is a strong oxidizing agent, mild synthetic methods were developed to prevent oxidation of the amine during chromate salt preparation.

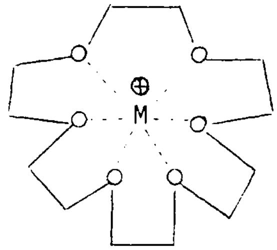
Chromate salt preparation of primary aromatic amine, triazole, pyridine, acridine, 2 and 2,4-diamino-s-triazine, guanimine, 2,4,6-substituted-s-triazine, biguanide, and imidazole structural types were attempted. Of such structures, the guanidines, guanamines and substituted triazines showed the most promise. All the guanamines except 2,4-diamino-6-triazine formed salts. However, all guanamine chromate salts were photosensitive. Of the substitued triazines, melamine, 2,4-diamino-s-triazine, 2-amino-4-anilino-s-triazine, and 2-amino-4(4-chloroanilino)-s-triazine formed stable chromate salts.

The most promising amine structural type for the preparation of chromate slats was guanidine and its derivatives. Few trisubstituted guanidines were commercially available so they were prepared from the reaction of a carbodiimide and an amine. Numerous trisubstituted guanidines were prepared with diphenylcarbodiimide and substituted anilines of varying basicity. Weakly acidic anilines, such as 4-chloroaniline formed trisubstituted guanidines with good yields. Strongly acidic and basic anilines either formed substituted guanidines in low yield or did not react. Chromate salts of trisubstituted guanidines prepared with weakly acidic anilines were heat and light stable.

Many of the organic chromate salts prepared exhibited sensitivity to heat and light. DSC testing revealed that salts considered "unstable" generally had lower melting points or decomposition temperatures than the salts determined to be "stable". The structural similarities of long aliphatic chains, carbonyl groups, guanamine structural type, pyridine moeity, and imidazole moeity appear to contribute to photosensitivity of organic chromate salts.

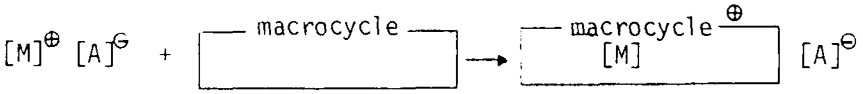
3.3.2) Method II Ligand Systems - Crown Ether Complexes

Macrocyclic polyethers (crown ethers) developed during the past few years10,11,12,13,14,15,16) have the very interesting property of complexing with various alkaline, alkaline earth, and in some cases, transition metal salts to provide solubility in solvents such as benzene or chloroform. In some cases, the solubilizing action is quite specific with selected materials complexing with only one of the above types of metal salts. This characteristic has been attributed to the efficient coordination of the cation by the oxygen atoms in the macrocyclic polyether. X-ray crystallographic data12) have shown that in these macrocyclic polyether-metal salt complexes, the metal ion is enclosed in the cavity of the crown. The complex formation is due to the high negative charge caused by donor atoms pointing toward the center of the crown as indicated below.



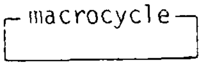
The donor atoms are principally oxygen but some crown ethers with nitrogen and sulfur donors have been made.

The formation of complexes by reacting a macrocyclic polyether with a chromium (VI) containing inorganic chromate is schematically represented as follows:

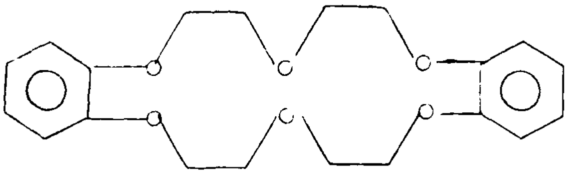


where [M]⊕ is the cation of the salt,

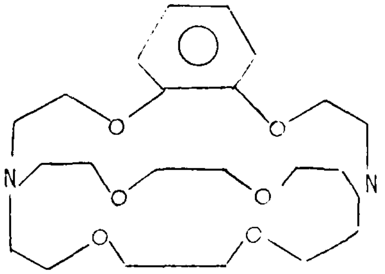
[A]⊖ is the hexavalent chromium containing anion of the salt,

and  is a generalized representation of a crown ether.

Some specific structures of crown ethers are presented below.



Dibenzo-18-crown-6



Kryptofix 222B

In preliminary screening of the chromate complexes of two such crown ethers17), dibenzo-18-crown-6 and dicyclohexyl-18-crown-6, some improved corrosion protection of steel and aluminum surfaces was shown in scribe panel testing of a paint formulation.

3.3.2.1 Preparation of Crown Ether-Chromate Complexes

A number of crown ether-chromate complex preparations were attempted. Such preparations are discussed in the Appendix. Crowns of varying interstitial radii were reacted with cations of varying ionic radii. See Table The formation of crown ether-chromate complexes is dependent on the relationship of the crown interstitial radius and cation ionic radius. In addition, the degree of radii mismatch appears to control the stability of the crown ether chromate complex. Thus, no complex is formed in the reaction of monobenzo-15-crown-5, which has an interstitial crown radius of 0.85-1.10 angstroms, with cobalt chromate, which has a cationic radius of 0.70 A°, because of the dissimilarity in radii. However, copper with a cationic radius of 0.95 angstroms, which is similar to that of monobenzo-15-crown-5, does form a stable complex. An unstable complex results from the crown ether-chromate complex formed from monobenzo-15-crown-5 with potassium dichromate, which has a cationic radius of 1.33 angstroms, again due to the dissimilarity of radii. If the crown radius is increased, as in dibenzo-18-crown-6 which has an interstitial radius of 1.15 to 1.60, a stable crown ether-chromate complex can be formed with potassium dichromate. This relationship appears to hold with different electron donor atoms. Thus, Kryptofix 221 (See Appendix A, Materials Table) did not form a stable complex with potassium dichromate whereas Kryptofix 222B did form a stable complex.

Crown ether-chromate salts were prepared by adding the chromium containing compound to a mixture of the crown ether and an organic solvent. The chromate containing compound must be slightly soluble in the organic solvent for the complex to form. As the chromium containing compound went into solution, the complex was formed. In early laboratory work on this contract, methylene chloride was found to have the appropriate solubility characteristics and was the solvent used for preparation of the crown ether-chromate complexes. However, a complex of dicyclohexyl-18-crown-6 and potassium dichromate was not stable when stored in methylene chloride. Formation of a precipitate was observed after storage at 75°F for several days. Dimethylformamide was, therefore, substituted for methylene chloride because it exhibited the appropriate solubility characteristics and gave storage stable crown ether-chromate complexes.

3.3.2.2 Compatibility with Primer Vehicles

Every crown ether-chromate complex was unstable in model primer vehicle #201 (without pigment) even when stored at 0°F. The incompatibility was shown by (1) darkening of the primer solution indicating oxidation by the chromium VI, (2) a green color in the primer solution indicative of the reduced chromium III, (3) formation of large clear crystals probably indicating that the crown ether-chromate complex had reverted to its starting materials, and (4) formation of a dark thick gelatinous precipitate indicating that the resinous portion of the primer had been oxidized or modified in some way.

To define the cause of incompatibility of the crown ether chromate-complex with the primer vehicle, the complex was evaluated with various components of the primer. A complex of dicyclohexyl-18-crown-6 and potassium dichromate was prepared in dimethylformamide and a small amount added to the various components of the Model #201 primer vehicle to determine compatibility. The complex showed slight instability in MEK as evidenced by the formation of a very small amount of a clear crystalline precipitate.

It had good initial stability in methyl oxitol, but started to darken after four days aging at 75°F. The complex showed good initial stability (less than 24 hours) in methyl oxitol solution of bisphenol A but a methyl oxitol solution of EPON 828 turned bright green overnight. A methyl oxitol solution of an EPON 828/nitrile rubber/bisphenol A condensate and the chromate complex turned dark green within 24 hours. A methyl oxitol solution of a nitrile rubber (CTBN-X) (See Appendix A, Materials Table) and the complex showed good stability for 3 days aging at 75°F. It thus appears that the crown ether complex probably attacks and oxidizes the secondary alcohol on EPON 828, the condensate, and methyl oxitol. The color difference between the EPON 828 and condensate solutions is due to the larger number of secondary hydroxyls on the condensate.

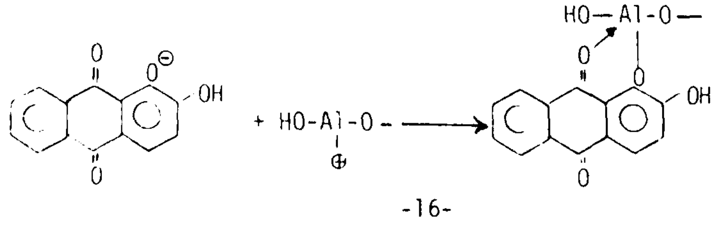
The stability of crown ether chromate complexes in unpigmented Model #201 primer vehicle may be related to photosensitivity. For example, Kryptofix 222B (See Appendix A, Materials Table) did form a stable chromate complex with potassium dichromate in dimethylformamide. However, the complex was unstable in the primer solution and turned very dark after 4 hours storage in light at ambient temperature. A sample of the complex-primer mixture stored in the dark at ambient temperature began discoloring only after 18 hours. A sample of the complex-primer mixture stored in the dark at a temperature of -10°F showed only slight darkening after 360 hours. This data may not be extendable to other crown ethers because Kryptofix 222B crown ether itself is slightly photosensitive.

3.3.2.3 Corrosion Protection of Crown Ether Chromate Complexes

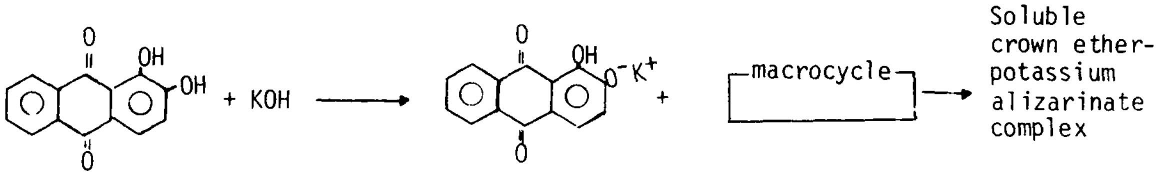
The corrosion protection obtained was related to the age of the primer-crown ether-chromate complex mixture. A panel sprayed with unpigmented Model #201 primer vehicle that had been stored at 0°F for three days after addition of a dicyclohexyl-18-crown-6-potassium dichromate complex failed very quickly (less than 100 hours), about the same time as the unpigmented control (94 hours), in scribe tests in 5% salt fog at 95°F. See Table 6. It thus appeared that the primer model vehicle and the crown ether-chromate complex were incompatible during storage, so the primer had to be handled as a two part system to evaluate corrosion protection of the crown ether-chromate complexes. A panel sprayed immediately after addition of the crown ether-chromate complex to the primer vehicle exhibited much improved corrosion resistance in scribe tests (approximately 350 hours in 5% salt fog at 95°F) compared to the unpigmented control (94 hours). Dicyclohexyl-18-crown-6-potassium dichromate and 18-crown-6-potassium dichromate complexes gave corrosion inhibition equivalent to the strontium chromate control. Dibenzo-18-crown-6-potassium dichromate complex showed 100% improvement over the strontium chromate control. Krytofix 222B-potassium dichromate complex resulted in moderate corrosion resistance (192 hours).

3.3.2.4 Alizarin and Crown Ethers

Alizarin has been reported by several investigators to give moderate corrosion protection on aluminum. The mechanism by which alizarin gives this protection on aluminum is postulated to be the formation of a strong inner chelate with the aluminum oxide surface [3,18]. The mechanism is shown below.



Alizarin is insoluble in organic solvents of intermediate polarity. A mechanism proposed to modify alizarin to improve its solubility in intermediate polarity solvents is represented below.



Alizarin was reacted with potassium hydroxide to form the potassium alizarinate salt. The potassium cation was complexed with 18-crown-6, to form a soluble crown ether potassium alizarinate complex. The pigment was stable by itself and in Model #201 primer vehicle and was soluble in organic solvents. However, the complex gave poorer corrosion protection (240 hrs.) in scribe tests in 5% salt fog at 95°F compared to both alizarin alone (360 hrs.) and the strontium chromate control (350 hrs.). See Tables 5 and 11.

Formation of the crown ether complex may result in steric hindrance or blocking of the formation of the inner chelate between the alizarinate ion and the hydrous oxide surface of the aluminum and thereby decreasing the affective corrosion protection.

3.3.2.5 Summary of Ligand Systems

Macrocyclic polyethers form complexes with various metal salts. These complexes considerably improve the solubility of inorganic cations and anions in organic solvents. Complexes were prepared with crown ethers and inorganic chromium (VI) containing compounds that were very soluble in organic solvents of intermediate polarity, such as methyl ethyl ketone.

Strong crown ether chromate complexes form when the interstitial radius of the crown and the ionic radius of the cation of the metal salt are similar. Moderate dissimilarities in radii result in unstable or weakly coordinated complexes and gross dissimilarities in radii result in failure of the complex to form. However, stability of the crown ether chromate complex was also related to its solubility in a particular solvent. Dimethylformamide was used as the main reaction medium for formation of the complexes because it exhibited the appropriate solubility characteristics and gave storage stable complexes.

A mixture of crown ether chromate complex and Model #201 primer vehicle was not storage stable at 0°F. The incompatibility was evidenced by (1) darkening of the primer solution, (2) green color in primer solution, (3) formation of large clear crystals, or (4) formation of a dark thick gelatinous precipitate. Addition of crown ether chromate complex to various components of the primer revealed degradation of EPON 828, condensate, and methyl oxitol. The crown ether complex probably attacks and oxidizes the secondary alcohols on these materials.

The stability of the crown ether chromate complex-primer vehicle systems may also be related to photosensitivity. A complex prepared with Kryptofix 222B showed improved stability both at 75°F and 0°F storage when stored in the dark.

To circumvent the incompatibility problem and still obtain corrosion protection data on the crown ether chromate complexes, panels were sprayed immediately after addition of the crown ether chromate complex to the primer vehicle. Corrosion resistance in scribe panel tests in 5% salt fog at 95°F of several complexes were equivalent to the strontium chromate control. Dibenzo-18-crown-6 potassium dichromate showed 100% improvement over the strontium chromate control in scribe panel testing.

Alizarin, which is reported to have moderate corrosion resistance on aluminum, functions by the forming of a chelate with the aluminum oxide surface of the metal. Alizarin is not soluble in organic solvents. The alizarinate moeity was made soluble by first reacting with potassium hydroxide to form the potassium salt and then forming a crown ether complex with 18-crown-6. The pigment is stable by itself and in the model primer and is soluble in organic solvents, however, it gave poor corrosion resistance compared to alizarin.

Attempted suspension of inorganic chromates with crown ethers by forming the crown ether chromate complex in situ in the primer did not alter the settling rate of the pigments.

3.3.3) Method III. Organic and Organo Metallic Complex Inhibitors

3.3.3.1 Organic Compounds

It has been postulated by D. B. Boise,[3)] that a select group of organic compounds giving corrosion protection on aluminum probably functioned through prevention of crystallization of the protecting amorphous oxide film or through reinforcement of the more porous non-protective crystalline oxide film. Such materials as alizarin, picrolonic acid, isatin, 4-hydroxybenzophenone, etc. have been shown to have corrosion protection action as components of primers for aluminum.

Scribe testing with the inhibitor in Model #201 primer vehicle in 5% salt fog at 95°F revealed alizarin (360 hrs.) to be comparable to a strontium chromate control (350 hrs.). See Table 11. Alizarin was the most effective corrosion inhibitor of the organic additives tested. Alizarin inhibits corrosion by a mechanism [3)] involving reinforcement of the amorphous oxide film. A chelate is formed from the reaction of the alizarinate ion with the hydrous oxide film.

Other organic materials selected from literature articles and screened gave much poorer corrosion inhibition performance. Isatin (2,3 indolinedione) (140 hrs.) gave less than 50% the corrosion inhibition of the strontium chromate control. The ranking of such materials with generally poor performance, in order of decreasing corrosion protection, was isatin, p-hydroxybenzophenone, ethylenediaminetetracetic acid, picrolonic acid, and ethylenediaminetetracetic acid tetrasodium salt dihydrate. All of the organic additives were soluble in the primer vehicle except alizarin.

3.3.3.2 Organo-Metallic Materials

The literature is replete with evaluations of chromium in the +3 valence state as a corrosion inhibitor, mostly for iron. Also, most of this work has been done with chromium trioxide, mixtures of chromium trioxide with chromium VI salts, such as strontium chromate, or inorganic salts containing chromium III, such as cadmium phosphate-chromate salt. Little appears to have been done with chromium (III) organometallics or with other organometallics. Some organic complexes of antimony, arsenic and chromium have also shown some promise in this type of application 3) (p-tolylarsonic acid, tris-(2-hydroxyacetophenono) chromium, triphenyl antimony, etc). Corrosion protection performance of all examined organo metallic additives, evaluated in Model #201 primer vehicle in 5% salt fog at 95°F, were much poorer than the strontium chromate control (360 hrs.). See Table 11. The rank order of decreasing corrosion protection was tris(2'-hydroxyacetophenono) chromium, tris(ethylenediamine) chromium (III) sulfate, chromium (III) 2-ethylhexanoate, chromium (III) 2,4-pentanedionate, cobalt (III) 2,4-pentanedionate, and triphenyl antimony. All of these organo metallic compounds were soluble or miscible with the primer vehicle, except for potassium trioxalatochromate (III) which phased out of the primer vehicle.

3.3.3.3) Summary of Organic and Organo Metallic Complex Inhibitors

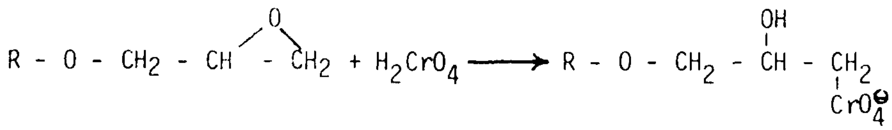
Boise 3) postulated that a select group of corrosion inhibiting organic compounds function by modifying and protecting the amorphous oxide film. Of the organic additives evaluated, only alizarin (360 hrs.) exhibited comparable corrosion inhibition performance to strontium chromate (350 hrs.) in scribe testing with Model #201 primer vehicle in 5% salt fog at 95%. All other additives were much poorer in performance. Of the organo-metallic additives, all were much poorer than the strontium chromate control.

3.3.4) Method IV Chemical Modification of Resin Vehicle

3.3.4.1) Attempted Attachment of Cr^{+6} Containing Groups

Both low molecular weight and high molecular weight epoxide resins can theoretically be chemically modified to contain oxidizing anionic groups of the corrosion inhibiting type. As in the case of reported work on organic chromates 19) some controlled water solubility is believed to be necessary in order for the inhibitor to be effective. Chemical attachment of corrosion inhibiting anionic chromate and phosphate groups should promote water solubility of the epoxy adducts.

To explore this approach, epoxide resins were reacted directly with chromic acid, as indicated below:

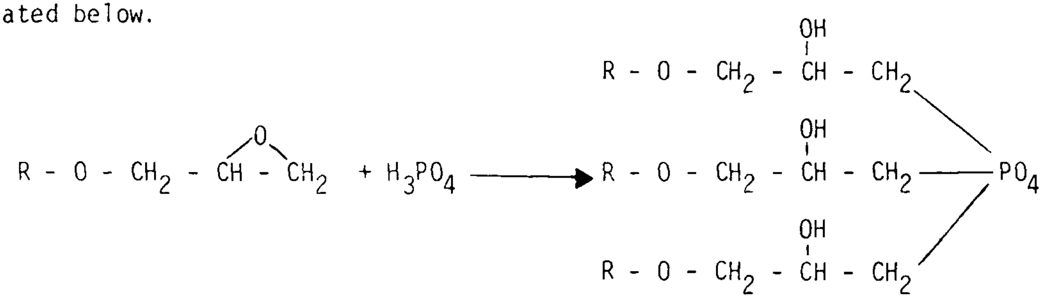


$$R - O - CH_2 - \overset{O}{CH - CH_2} + H_2CrO_4 \longrightarrow R - O - CH_2 - \overset{OH}{\underset{}{CH}} - \underset{CrO_4^{\ominus}}{CH_2}$$

However, reaction of EPON 828 with chromic acid resulted in oxidation. Hexavalent chromium is a strong oxidizing agent and apparently attacked the organic molecule. Oxidation resulted in the production of reduced trivalent chromium which was easily detected by the color change from brown-red to green. The generation of carbonyl groups, as determined by infrared spectrophotometry, was also evidence of oxidation. Infrared spectrophotometry did not show any significant change in epoxide content.

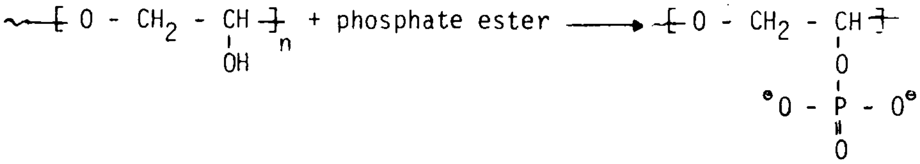
3.3.4.2) Attempted Phosphorylation of Resin Vehicle

Phosphorylation of oxirane rings has been reported to occur on reaction of epoxide resins with phosphorous acid, orthophosphoric acid, and mon, di and trialkyl phosphates.20,21,22,23,24) An unusual anticorrosive paint suggested by duPont24) uses as the vehicle an epoxy resin which has been "phosphorylated" by reaction with orthophosphoric acid. To further explore this area, the epoxide functional groups of epoxy resins were reacted with orthophosphoric acid as indicated below.



Orthophosphoric acid was reacted in acetone medium with a difunctional bisphenol A based epoxide resin (EPON 828) at a stoichiometric ratio that would tie up 50% of the available epoxide, i.e, form the monophosphate. Infrared spectrophotometry revealed that all epoxide had been consumed. Cupery22,23) states that, in order to minimize the possibility of crosslinking of the epoxide, the esterification reaction should be carried out in a solution of the polymer in an organic solvent which is miscible with water. Bradley21) indicated that the ability of glycidyl ether -phosphorous acid containing composition to cure is achieved with 50-150% of the equivalent amount of phosphorous compound present. Bradley21) also points out that mixtures of the phosphorous compound and a glycidyl ether resin gels in several days at room temperature. Our work led to a similar conclusion. A mixture of EPON 828 and orthophosphoric acid at 50% stoichiometry resulted in gelation after several days storage at room temperature. Phosphoric acid apparently cures epoxide resins by 1) reacting with the epoxide and 2) acting as a catalyst for resin homopolymerization.

Attaching a phosphate group to the hydroxyl of an epoxy resin by transesterification was approached as indicated.



$$\sim\left[O - CH_2 - \underset{\underset{OH}{|}}{CH}\right]_n + \text{phosphate ester} \longrightarrow \left[O - CH_2 - \underset{\underset{{}^{\ominus}O - \underset{\underset{O}{\|}}{P} - O^{\ominus}}{\underset{O}{|}}}{CH}\right]$$

Reaction of EPON 1001 with triethylphosphate, using para-toluenesulfonic acid catalysis to get transesterification, resulted in no desired product.

Mono-, di-, and tri-esters of phosphorous acid can be obtained from reactions of alcohols with PCl_3 alone or in the presence of an organic base as hydrogen chloride acceptor 25). EPON 1001 was reacted with ethyl dichlorophosphate without catalysis but gave an insoluble polymer. Infrared spectrophotometry indicated that some phosphorylation and some loss of epoxide had occurred. EPON 1001 was also reacted with ethyl dichlorophosphate without acid catalysis in the presence of pyridine as a hydrogen chloride acceptor but again gave an insoluble polymer. Infrared spectrophotometry indicated some phosphorylation had occurred. Use of titanium butoxide IV catalysis gave no desired product. The formation of insoluble polymer probably occurs through reaction of the epoxide ring with the chloride ion, freed in the esterification reaction of the phosphate ester with the hydroxyl of the epoxide resin, attacking the epoxide and thus causing homopolymerization.

3.3.4.3) Summary of Chemical Modification of Vehicle

Hexavalent chromium is a strong oxidizing agent and attacked the resin molecules during the attempted preparation of chromate containing epoxide resins. The characteristic appearance of the reduced chromium +3 green color and the appearance of the carbonyl group in IR spectra was evidence that oxidation had occurred. Phosphorylation of the epoxide group with phosphoric acid at 50% of stoiciometry resulted in gelation of the epoxide resin because the phosphoric acid acted as a catalyst for resin homopolymerization. Several methods of attaching a phosphate group to the hydroxyl of an epoxide resin by transesterification resulted in no desired product.

3.3.5) Method V Cure of Epoxy Resins with Metal Salts

In epoxy resin technology, a variety of metal salts are described as curing agents. Metal salts soluble in the epoxide resin react in a 1:1 stoicio-metry (1 mole of epoxide to 1 mole of metal salt) to give an adduct which contains both the cation and anion of the salt as indicated.

$$MeX + \overset{\overset{O}{\diagup\;\diagdown}}{CH_2 - CH} - CH_2 \longrightarrow MeOCH_2 - \overset{\overset{X}{|}}{CH} - CH_2 -$$

In a brief exploration of this approach, an attempt to react an epoxide resin with an inorganic chromate failed to show any evidence of reaction. Differential scanning calorimetry (DSC) was used to detect evidence of reaction between EPON 828 and magnesium dichromate. As the DSC was temperature programmed from 70°C to 250°C, no evidence of an exotherm indicating reaction was recorded.

3.3.5.1) Summary of Curing Epoxy Resins with Metal Salts

Differential scanning calorimetry used to detect reaction of a metal salt with an epoxide resin showed no evidence of reaction.

3.3.6) Method VI Pigment Suspending Agents

Various techniques to reduce the settling of inorganic pigments in dilute primer systems were evaluated. Organic titanates have shown some success in suspending inorganic fillers and pigments in very low viscosity systems. One of the functional moeities of these materials reacts with hydroxyls which are the result of water that is either chemically or physically bound on the surface of the filler particle.

A number of organic titanates were evaluated at 0.25% by weight based on the pigment in primer Model Vehicle #201 at 10% solids. None showed improvement over the control (Table 7).

Thixotropic or gel type thickeners swell in the primer vehicle to form a stable colloidal gel network which immobilizes the pigment and inhibits pigment settling. The increased thixotropy obtained with thixotropic or gel type thickeners is normally accompanied by a viscosity increase. These thickeners are generally completely organic in nature.

Thixatrol ST, Thixatrol GST, MPA-MS, MPA-1078X, and Tenlo 70 (see Materials Table) suspending aids were evaluated in primer Model Vehicle #201. These suspending aids were ball milled with a Model Vehicle #201 concentrate, the concentrate was then "let down" to 10% solids, and the pigment settling rate and ease of pigment cake breakup was measured. See Table 8.

The strontium chromate control required 21 hours for the pigment to settle. When such products as Thixatrol GST at 0.8% w and 5.0% w based on total primer solids and MPA-1078X at 0.7% based on total primer solids were added, a 100% improvement in pigment settling time was obtained. However, much greater levels of improvement in pigment settling tendencies would be needed to remove this problem.

All materials evaluated showed considerable improvement in preventing hard caking of the pigment (see Table 8) The relative ease of breaking the pigment cake was measured by the number of inversions of the primer solution required to disperse the pigment in the primer solution after seven days primer storage at 0°F. Thixatrol ST at 5.0% and MPA-MS at 5.0% based on total solids indicate a fourfold improvement in ease of breaking the pigment cake. Thixatrol GST at 0.8 and MPA-MS at 0.7% and 5.0% based on total primer solids showed a threefold improvement. However, even with this amount of improvement, resuspension of settled pigments remains as a practical problem in use of such primers.

3.3.6.1) Summary of Pigment Suspending Agents

Although significant improvements were thus obtained in increased pigment settling times and particularly in increased ease of breaking the pigment cake, these improvements fall far short of solving pigment suspension problems.

3.3.7) Screening of Corrosion Inhibitors

Organic chromate corrosion inhibitors that exhibited reasonable heat stability were analyzed and evaluated to determine their structure, solubility in water and methyl ethyl ketone and pigment stability during long term storage in diffused light at 75°F. Those reasonably stable in light were evaluated in primer solutions for stability during storage at -10°F, baked primer MEK wipe resistance, and scribe panel testing in 5% salt fog at 95°F.

Inorganic chromates, organic inhibitors, and organo metallic inhibitors were also evaluated in MEK wipe resistance and scribe panel testing in 5 salt fog at 95°F.

3.3.7.1 Primer Thickness Versus Corrosion Resistance

A primer film thickness versus corrosion resistance experiment was designed to determine the affect of primer film thickness on corrosion rate in 5% salt fog at 95°F. The primers were sprayed at thicknesses of 0.1, 0.2, 0.3 and 0.4 mils on 2024 T-3 bare, dichromate etched aluminum, flashed 30 minutes at 75°F, baked one hour at 250°F, scribed with a carbide tipped cutting tool, and placed in a salt environment (per ASTM B 117-64).

EA 9201, EA 9202, EA 9205, EA 9210, ADX-238.1, and BR-127 primers were evaluated. Primer films at 0.1 mils thickness generally showed initial failure in the film (far from the scribe line) because of discontinuities in the film. The discontinuities could be the result of poor spraying techniques, pigment or filler particles, or solvent escape during flashing and baking of the primer film. Primer films at 0.2, 0.3 and 0.4 mils thickness showed initial failure in the scribe with the film holding up well throughout the entire test. There appeared to be no significant improvement in corrosion resistance in the scribe at a film thickness of 0.4 mils compared to a 0.2 mil film. Based on this information, 0.2 mil primer film thickness was chosen for all corrosion inhibitor screening.

3.3.7.2 Organic Chromate Inhibitors

The structures of the organic chromate salts were defined using a sodium thiosulfate titration method to determine the chromium VI content. Most salts formed 2:1 amine to dichromate complexes, i.e., 2 moles of organic base to 1 mole of dichromate. Only 2,4-diamino-6-[2'-undecylimidazole-(1')]-ethyl-s-triazine dichromate and 2,4,6-5 tri-(2-pyridyl)-s-triazine dichromate formed 1:1 base: dichromate salts. This raises an interesting point of structure, since during synthesis at ambient temperature the first evidence of salt formation was a yellow solid which often slowly progressed to form an orange solid. Lower temperature reaction (5°C) gave more yellow solid and the formation of the orange colored salt was much slower. Perhaps this phenomena can be explained by the initial formation of the 1:1 salt. This salt formation requires change from the octahedral configuration of chromium in solid CrO_3 to the tetrahedral form of the chromate amine 1:1 salt. Conversion further to a 2:1 salt can occur if steric and other factors are not restrictive. This conversion from a 1:1 salt to a 2:1 salt involved a configuration change from tetrahedral to trigonal bipyramide and a coordination number change from 4 to 5.

Solubility in water and methyl ethyl ketone was determined for each of the salts prepared. See Table 9. The water solubility of most salts ranged from 0.1 g/100 ml to 3.0 g/100 ml at 75°F. There appeared to be no relationship between film performance (MEK wipe resistance and corrosion inhibition in scribe tests in 5% salt fog at 95°F) and water solubility in the range investigated.

Methyl ethylketone solubility was determined with an eye toward an inhibitor soluble in the primer solvent vehicle and, thus, elimination of the pigment dispersion step of current state-of-the-art primer production. 1,2,3-Triphenylguanidine dichromate and diorthotolylguanidine dichromate were soluble in the primer solvent vehicle. All other organic amine-chromate salts were solvent insoluble and required ball milling for pigment dispersion. There appeared to be no correlation between MEK solubility and corrosion inhibition in scribe panel salt fog tests.

The storage stability (at -10°F) of the various amine-chromate salts in Model #201 were evaluated using the inhibitor at 0.25% chromium VI, based on solids, in a Model #201 primer vehicle. Instability was evidenced by (1) a change in the color of the primer from orange to brown or black, (2) agglomeration of the pigment, and (3) appearance of gel particles. Acridine dichromate, 2,4-diamino-6-heptadecyl-s-triazine dichromate, 2,4-diamino-6-phenyl-s-triazine dichromate, melamine dichromate, guanidine dichromate, and guanylurea dichromate gave good storage stability in the primer vehicle at -10°F.

Since degradation of primer solutions upon storage at -10°F generally occurred slowly, spraying of the panels shortly after primer preparation eliminated the effects of primer deterioration in all film testing. The MEK wipe resistance of the baked primer films was generally good. There was little correlation between MEK wipe resistance and primer solution stability.

There appeared to be a strong correlation between solubility of the organic chromate pigment and MEK wipe resistance of the baked primer film. All organic chromate inhibitors with solubilities of greater than 0.4 g/100 ml of MEK resulted in baked primer films with fair to very poor MEK wipe resistance. An exception was 2-amino-4-(4-chloroanilino)-s-triazine dichromate which gave good MEK wipe resistance. All organic chromate inhibitors with solubilities of less than 0.4 g/100 ml of MEK resulted in baked primer films with good MEK wipe resistance, except 2-phenylimidazole which gave fair MEK wipe resistance.

The corrosion inhibition of organic chromate pigments in Model #201 primer vehicle at 0.25% chromium VI based on solids was determined with scribe panel tests in 5% salt fog at 95°F. (See Table 11). A dry primer film thickness of 0.2 mils was used. In this primer vehicle, guanidine dichromate (1340 hours) exhibited corrosion inhibition four times greater than the strontium chromate control (350 hours). 1-(4-chlorophenyl)-2,3-diphenylguanidine dichromate (790 hours), 2,4-diamino-6-phenyl-s-triazine dichromate (enzoquanamine)(650 hours), and melamine dichromate (645 hours) gave corrosion inhibition double that of the strontium chromate control (350 hours). 2,4,6-Tri-(2-pyridyl)-s-triazine dichromate (460 hours) 2,4-diamino-6-acetyl-s-triazine dichromate (acetoguanamine 430 hours) 2,4-diamino-s-triazine dichromate (360 hours), guanylurea dichromate (360 hours), and 1,2,3-triphenylguanidine dichromate (305 hours) gave corrosion inhibition equivalent to the strontium chromate control. Corrosion inhibition of all other organic chromate salts evaluated was inferior compared to the strontium chromate control.

3.3.7.2.1 Primers Made With Organic Chromate Inhibitors

Organic chromate salts prepared from nitrogen containing bases show some instability in the presence of strong amines present as catalysts in some primer resin vehicles. As a result, organic chromate corrosion inhibitors formed precipitates in some of the model vehicles. For example, triphenylguanidine dichromate,, when added to Model #201 primer vehicle (see Appendix) resulted in immediate formation of a black precipitate. To determine the cause, triphenylguanidine dichromate was added first to the primer solvent system only and then to mixtures of the primer solvent system and one of the constituents of the resin system. Other constitutents commonly used in primers were also evaluated in this manner. Such film forming agents, as polyethyleneimine (PEI-18 Dow Chemical), and curing agents, diethylenetriamine, formed precipitates with the organic chromate pigments. However, not all nitrogen containing bases used as curing agents result in precipitation with organic chromate salts. Dicyandiamide, substituted for triethylenediamine as the curing agent of Model #201 primer vehicle, was stable upon addition of the organic chromate pigment. The cause was probably related to basicity. Primer resin curing agents more basic than the amine used in creating the chromate complex promote the breakup of the chromate complex and a new chromate complex is formed with the stronger amine.

3.3.7.3 Inorganic Chromate Inhibitors

Chromium VI containing pigments inhibit corrosion by virtue of the strong oxidizing power of the chromium VI. However, the inhibition of corrosion on aluminum by chromium VI containing compounds is not solely due to the oxidizing ability of the chromium VI. Two other factors related to the physical or chemical nature of the pigment appear to effect corrosion inhibition.

The relative water solubility of the inorganic chromate appears to be important in providing corrosion inhibition. Scribe panel testing of various inorganic chromates at concentrations of 0.25% chromium IV based on primer solids in Model #201 primer vehicle (in 5% salt at 95°F) revealed that pigments with high water solubility, such as potassium chromate and magnesium chromate, failed more quickly compared to pigments of low water solubility, such as strontium chromate, zinc chromate, and cobalt chromate. (See Tables 10 and 11.) Pigments of high water solubility showed initial corrosion failure in the film (far from the scribe) while while those with low solubility showed initial corrosion only in the scribe. This information, reported by others1),2) and verified by this work, can be explained, in part, by a mechanism of too rapid leaching of the soluble pigment from the film and thereby reducing the chromium VI concentration and decreasing the time of effective corrosion protection.

The nature of the cation of such inorganic chromates has been reported to influence corrosion protection of aluminum.1) Comparison of the times to corrosion failure in salt spray for strontium chromate, zinc chromate, and cobalt chromate, which have nearly equivalent solubilities in water at 75°F, revealed a wide variation from strontium chromate with 350 hours to failure to cobalt chromate with 1240 hours to failure. It has been inferred1),2) that selected cations can retard crystallization of the protective amorphous aluminum oxide layer and thus retard migration of corrosive materials to the aluminum metal surface.

3.3.7.4 Organic and Organometallic Inhibitors

Of the organic and organometallic materials evaluated, only alizarin (360 hours) showed comparable corrosion protection, in scribe panel testing (5% salt fog at 95°F with Model #201 primer vehicle) to the strontium chromate control (350 hours). (See Table 11). All other materials of this type that were evaluated, gave poorer corrosion protection than the control.

3.3.7.5 Selection of Pigments

Four pigments that exhibited the best combination of overall properties were selected for further evaluation. (See Tables 10 and 11.) Cobalt chromate was chosen based on its excellent corrosion inhibition in scribe panel testing.

Strontium chromate was chosen as a control. Melamine dichromate exhibited the best overall properties of all organic chromates evaluated. However, melamine dichromate had to be ball-milled for pigment dispersion.

Guanadine dichromate, 1,2,3-triphenylguanidine dichromate, and diorthotolylguanidine dichromate were soluble in the primer vehicle. Guanidine dichromate gave good overall properties with the exception that with salt spray exposure, the primer film discolored and showed evidence of becoming brittle and cracking. As a result, 1,2,3-triphenylguanidine was chosen to represent the soluble organic chromate salt inhibitors.

Of the organic and organometallic inhibitors evaluated, only alizarin gave corrosion protection (360 hours) equivalent to strontium chromate control (350 hours). However, alizarin has poor MEK wipe resistance and was eliminated on that basis.

3.3.7.6 Corrosion Inhibition Versus Model Vehicle Composition

The corrosion inhibition shown by cobalt chromate, strontium chromate, mealamine dichromate, and 1,2,3-triphenylguanidine dichromate was evaluated in scribe panel tests (in 5% salt fog at 95°F) with each of Model Primer Vehicles #201, #210, #7, and #127. (See Table 11.) (See Appendix for description of model primer vehicles.) The corrosion protection attributable to a particular pigment was highly dependent on the composition of the primer vehicle. For example, strontium chromate gave corrosion protection for 350 hours in Model #201 vehicle compared to 1870 hours of corrosion protection in the Model #127 vehicle. Cobalt chromate gave 1240 hours of corrosion protection in Model #201 and only 430 hours protection in Model #7. The relative order of performance of the various pigments also changed as the resin vehicle type was changed. It thus appears that optimization of the corrosion resistance properties of any pigment or any primer vehicle depends on the proper marriage of these two ingredients.

3.3.7.7 Summary of Corrosion Inhibitor Screening

1. A primer thickness versus corrosion performance study revealed that the corrosion rate in scribes made through the primer film was not related to primer thickness as long as the film was 0.2 mils or greater.

2. A 2:1 complex of amine: chromate was found to be the predominate structure of the organic chromate salts synthesized in this work. This structure suggests a coordination number of 5 for chromium.

3. The solubility of the inhibitor in MEK and H_2O, the stability of the pigment containing primer at -10°F, the MEK wipe resistance of the baked primer film and the corrosion protection in scribe panel tests in salt fog were used to evaluate inhibitors. Melamine dichromate, 1,2,3-triphenylguanidine dichromate, and cobalt chromate were chosen as having the best overall properties.

4. Organic chromates were found to react with certain strong amine curing agents in the primer vehicles both inorganic and organic.

5. The corrosion protection of pigments was found to be dependent on the composition of the primer vehicle.

4.0) PRIMER RESIN VEHICLE OPTIMIZATION

4.1) SPECIFIC OBJECTIVE

In this effort to develop corrosion inhibiting primers (CIP) which would perform better than state-of-the-art systems in paint and adhesive bond applications on aluminum aircraft structures, the specific primer vehicle plays a most significant role. Improvements in over-all corrosion protection would also result from the employment of better anti-corrosion agents. However, the primer vehicle plays more than an indirect role as a media for dispersion and application and,through its film forming and barrier coat properties,greatly influences anti-corrosion protection. Other important properties whose improvement are almost entirely dependent upon the vehicle are reduced thickness sensitivity to peel forces, increased resistance to bond failure under environmental stress, increased service temperature and, to some extent, adaptability to lower cost and/or improved methods of application.

The above objectives suggest the following goals for the development of an optimized vehicle in which an inhibitor could be suspended or dissolved:

1) Develop a vehicle which can be applied at dry film thicknesses up to 0.5-0.75 mils and, when cured with a bondable film adhesive, perform in peel tests over a temperature range of -67°F upwards.
2) Be accompanied by excellent resistance to attack by common aircraft solvents.
3) Maintain a use temperature of at least 180°F and preferably 350°F.

4.2) BACKGROUND

A characteristic of many state-of-the-art adhesive primers is the need to control primer thickness below an acceptable level if maximum joint properties are to be maintained. This requirements becomes more critical for primer systems which cure to such a state so as to offer maximum chemical resistance - i.e., in highly crosslinked epoxy-based coatings. Too, bondability may decrease even further in subsequent bonding cycles after which the primer coat has undergone additional baking.

The effect of primer thickness on peel strength may be illustrated by the following where two Hysol 250°F curing adhesive tapes were tested with American Cyanamid's BR-127 corrosion inhibiting primer:

	Bell Peel, ppi			
	Tape A		Tape B	
Primer Thickness, mils	-67°F	77°F	-67°F	77°F
0.13	54	73	45	57
0.21	39	62	28	53
0.31	39	65	15	43
0.38	22	62	18	32

As can be seen above,at approximately 0.13 mils thickness, bond peel strength at -67°F falls off significantly. When used by the aircraft manufacturer, very careful application control must be used which can result in an added expense. While formulation techniques are known by which this primer thickness sensitivity can be reduced, these changes are usually accompanied by a loss of solvent and temperature resistance which make the system less universally useable.

4.3) TECHNICAL APPROACH

If we assume that the adhesion of a primer vehicle to both the metal substrate and a bonding adhesive is adequate to force fracture within the primer matrix, then the bulk properties of that primer matrix should affect the performance of the entire system when tested in a peeling mode. This will be discussed more fully in Section 5.0. Secondly, the chemical relationships of the primer vehicle to both the bonding adhesive and the metal substrate must be considered since either of those areas of interaction may affect system peel performance.

As a means of exploring the several interactions discussed above, a series of model vehicles having a theoretically wide range of bulk properties and inherently different adhesive properties were chosen. As a result it was possible to correlate variable primer bulk properties with adhesive performance.

4.4) SELECTION AND PREPARATION OF MODEL VEHICLE SYSTEMS

4.4.1) Selection Of Model Resins

Seven specific model resin systems were chosen as a means of determining the effects of variable bulk resin properties on adhesive performance. In addition, two vehicle systems used commercially as wash and shop primers were prepared for evaluation with the other models. The following generally describes the models and may be used for easy reference in this and subsequent sections of the report.

Description Of Model Resin Vehicles

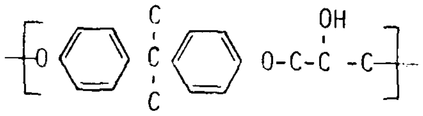
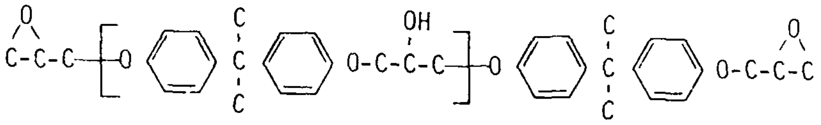
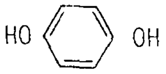
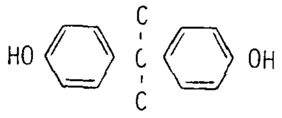
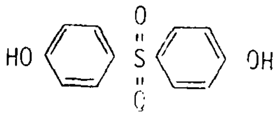
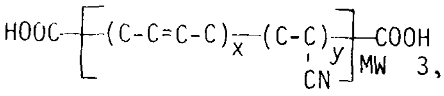
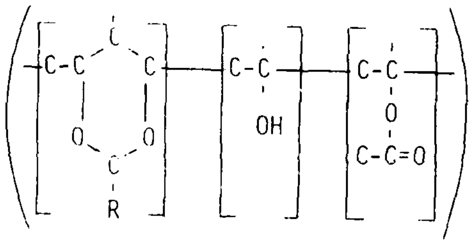
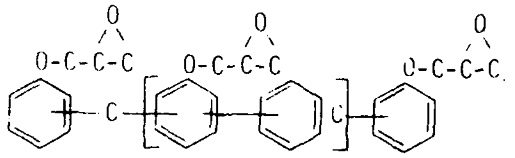
Model Number	Resin(s)[1)]	Vehicle Theo. WPE
1	Phenoxy (~MW 30,000)[2)]	300
2	Epon 1007 (~MW 5,000)[2)]	280
3	Epon 828 (MW 350)[2)]	180
4	Resorcinol-Epon 828 Adduct	490
4'	Hydroquinone-Epon 828 Adduct	490
5	Bisphenol A-Epon 828 Adduct	560
6	Bisphenol S-Epon 828 Adduct	580
7	Hycar CTBN-Bisphenol A-Epon 828 Adduct	680
8	Phenoxy (~MW 200,000)-Melamine Formaldehyde	-
9	Polyvinyl Butyral (~MW 50,000)-Phenol Formaldehyde	-

1) See appendix for description and source.
2) 40 pbw with 60 pbw epoxy novalac (DEN 438, MW 750)

Above, Models 1 through 3 were chosen to examine the influence of changes in the crosslink density of the cured primer using a novalac type hardener at a 1:1 equivalent ratio of phenolic hydroxyl and epoxide groups. Models 4 through 7 examine changes in chain stiffness while maintaining constant crosslink density.

The general variance anticipated for the model bulk and adhesive properties is suggested by the base polymer structures illustrated below:

Base Model Resin Chemical Structure

Model Number	Base Resin	Chemical Structure
1	Phenoxy PAHJ	 MW 30,000
2	Epon 1007	 MW 5,000
3	Epon 828	Same as Epon 1007, MW 350
4	Resorcinol	
4'	Hydroquinone	
5	Bisphenol A	
6	Bisphenol S	
7	Hycar CTBN	 $\mathrm{HOOC}-[(\mathrm{C-C=C-C})_x-(\mathrm{C-\underset{CN}{C}})_y]-\mathrm{COOH}$ MW 3,500
8	Phenoxy Eponol 55	Same as Phenoxy PAHJ, MW 200,000
9	Butvar 76	 MW 50,000
	DEN 438	 MW 750

Initially, work was completed using resorcinol in Model #4. This was later changed to hydroquinone for its molecular symetry to examine changes in chain stiffness while maintaining constant cross-link density. Epon 828 was reacted with a constant hydroxyl equivalent (0.298) of each diphenol to give reaction products having approximately the same epoxide equivalent - in the range of Epon 1001 (WPE 450-550). Preparation of each diphenolic adduct of Epon 828 is given in the Appendix. Test results of specific lots used throughout the program are given in Table 12.

4.4.2) Selection Of A Phenolic Hardener

From previous studies, phenol formaldehyde resins of the novolac (two-step) type have given superior properties when used to cure epoxy primer and coating systems. However, their effectiveness can vary according to the epoxy resin and catalyst used and the novolac's molecular weight and whether it was modified with certain oils or other ingredients.

To aid in proper selection, a pre-screening experiment was conducted on three novolacs and three resole (one-step) type phenol-formaldehyde resins which also perform as epoxide curing agents.

First, Model #1, as described in Section 4.4.1 above, was employed as the epoxy resin system for these curing agent selection studies. Each phenolic resin was then combined with the epoxy resin at 20% solids (weight) in a mixture of methyl ethyl ketone (MEK), tetrahydrofuran (THF) and diacetone alcohol (DAA)(55/30/15 by weight). Each of these systems were tested with three separate catalysts by drawing down a coating on FPL etched 0.020 inch 2024-T3 clad aluminum and baking to a nominal 0.5 mil dry thickness at 250°F for one hour. Coating thickness was measured on a Dermitron Non-Destructive Thickness Tester.

Phenolic resins evaluated were SP-6700, BRZ-7541, Varcum 4326, Methylon 75108, BRRA 4020 and Varcum 5416. Tertiary amine catalysts evaluated were Curing Agent D, BDMA and TPPEI. See Appendix for description.

Due to the failure of this model to provide MEK resistance with any of the phenolic combinations using a catalyst concentration at 0.5 phr (parts per hundred resin, epoxy) the series was repeated using a catalyst concentration of 1.0 phr. However, MEK resistance was still not improved.

Solutions were then prepared using the same phenolic resins and catalysts except Dow DEN 438 resin was used alone as a model to improve MEK resistance. The same equivalent proportions of phenolic to epoxide were used and the catalyst concentration was 1.0 phr. Table 13 shows the results.

Varcum 4326 resin was chosen at this stage for further use with the model systems. It is a low molecular weight phenol-formaldehyde resin used commercially as a starting resin in the manufacture of epoxy novolacs and contains less than one percent free phenol. It is also easily mixed in hot melt epoxy systems which aided in the preparation of castings for use in the measurement of bulk properties. The equivalent weight was indicated to be 104 (0.94 OH- equivalents/100 grams) from the manufacturer's theoretical molecular weight (approximately 600-650). Attempts to verify the phenolic hydroxyl content by current titration methods were unsuccessful.

It is perhaps important to emphasize that, throughout the course of this program - mostly in the first six months of effort - the employment of a proper phenolic resin hardener, as well as various catalyst types, periodically came under review. While the final choice of hardener and catalyst was Varcum 4326 and TPPEI, respectively, considerable data was generated with other combinations which will be described later. It was decided that, since Varcum 4326 and TPPEI were best for casting specimens for bulk property tests, correlations between the latter and model adhesive property, performance would also be more meaningful if the same hardener/catalyst system was used.

To verify the curability of the designed models prior to the final preparation of specimens for bulk property measurements, a program was conducted which included the following categories:

1. Variation in phenolic hardener stoichiometry.
2. Variation/substitution of catalysts.
3. Substitution of phenolic hardeners based on commercially accepted systems.

The above were programmed using the Model #2 resin vehicle (Epon 1007/DEN 438). Comparisons were made by testing casting, coating and adhesive properties. Castings were examined for extent of cure by measuring their glass transition temperatures (Tg) and coefficients of thermal expansion (α) after three levels of cure. A more detailed description of the measurement of Tg and expansion coefficient and an interpretation of their use in defining completeness of cure is presented in a following paragraph of this section. Also, flexure strength was measured using a simple, in-house, method. Routine pencil scratch hardness and chemical (MEK) resistance were conducted as well as MMCD peel strength.

The foregoing was based on the assumption that the hardener/catalyst system which affords the desired cure for Model #2 will do likewise for the remaining models. It was not known whether a full cure was necessary for future primer candidates but it was more desirable to measure bulk properties of vehicles which were fully cured, provided some correlation could still be made with their adhesive properties.

Systems 1 through 3 in Table 14 and systems 1 and 2 in Table 15 showed that the current hardener/catalyst concentration for Model #2 (control) was optimum. However, MEK resistance and hardness values suggested that TPPEI (triphenyl phosphine ethyl iodide) in System 3, Table 15, was a better catalyst than Curing Agent D. By Tg and α measurements, System 3, Table 15, was not fully cured, however. While not necessarily significant, it is interesting that clear castings were obtained with TPPEI and BDMA (benzyl dimethylamine).

As a further comparison to Varcum 4326, another novolac (two-step) phenolic, BRZ-7541, and three resole (one-step) phenolics commercially used in resin systems similar to Model #2, were examined for coating properties. Table 14 shows System 4 to also have better MEK resistance than the control. It gives a clear casting but is still not fully cured after a 350°F cycle. Table 16 shows only Resinox P-97 in System 2 to have improved MEK resistance.

As a result of the data reported in Tables 14,15 & 16 coating properties were repeated for the control system and systems substituting TPPEI catalyst for Curing Agent D and BRZ-7541 and Resinox P-97 hardeners for Varcum 4326. Further, BRZ-7541 and Resinox P-97 were evaluated with TPPEI. Also, each of the above systems were tested for adhesive properties as primers for EA 9628 film.

Table 17 shows fair system repeatability even though systems 1, 2 and 5 had been allowed to stand at room temperature for approximately one week prior to the test. Note also that System 3 retained the best MMCD peel strength after one bake cycle although there appears to be no correlation between other systems which also had poor coating properties after baking.

4.4.3) Measurement Of The Effect Of Curing System Variables On Cure Rate And Completeness Of Cure

As discussed, the effect of varying both the novolac curing agent (Varcum 4326) and the catalyst type and concentration on the curability at 250°F of Model System 2 (Epon 1007/DEN 438) was examined using thermal mechanical analysis (TMA) of castings cured for varying periods at 250°F with and without a 350°F post cure to establish the presence of a full cure.

A thermal mechanical analysis spectrum, using the penetration mode, essentially is a presentation of a compressive modulus versus temperature. The major change in slope of this curve is interpreted as the glass transition temperature. In the case of a fully cured system, the slope of this curve, before and after the Tg, is constant. The Tg shown then is the maximum possible, Tg_{∞} as characterized by Gillham et al[26]). If the system is capable of further cross-linking, the curve above the Tg describes a shallow "S" shape as further cure is brought about. This "S" shape comes about due to a new order of molecular mobility becoming free. As defined by Gillham, this system, after the initial cure, is in the vitrified or glassy state; the Tg is associated with the gel point of the system while the "S" transition marks the transition from the glassy to the more reactive rubbery state. Typical TMA curves for Model #2 in both the incomplete and complete cure states are shown in Figures 1 and 2, respectively.

This type of analysis of full cure as applied to a number of curing systems (Table 14) shows the effect of curing agent stoichiometry, at constant catalyst concentration, on the cured resin properties. A post cure of 350°F is required to affect full cure at both 90 and 100% stoichiometry as interpreted by the lack of a "S" portion to the TMA curve. The 100% stoichiometry system is not fully cured even with the 350°F bake. This interpretation is reinforced by the increase in the Tg of the 250°F cures upon post cure. Additionally, the systems do not become resistant to wiping with a methyl ethyl ketone (MEK) saturated rag until post cured.

An increase in the concentration of the catalyst, Curing Agent "D", from 1.16 parts per hundred resin (phr) to 1.55 phr (a 34% increase) also did not affect full cure with a 250°F schedule (Table 15). Again, the Tg and MEK wipe resistance data support this conclusion.

A further means of measuring the degree of cure is by using reflective infra-red (IR) spectroscopy. In this test,a primer is coated at a thickness of 0.3 to 0.4 mils dry and an initial IR scan made. After subsequent bake cycles, scans are again made and the extent of cure followed by the change in the epoxide stretching peak at 10.9 u. Table 18 shows the difference in model primer vehicle curability using Curing Agent D as a catalyst (3.0 phh). Models 1, 3 and 4 approached maximum cure after just 30 minutes bake at 250°F. 90-95% epoxide consumption is judged very near to optimum by this test. There also appears to be a correlation between hardness, MEK resistance and degree of cure (at 350°F) for Models 1 through 3 - as degree of cure increases, so do hardness and resistance to MEK rub. Polymer structure is likely the most important factor in these differences. EA 9628 was included for a comparison.

4.5) DETERMINATION OF MODEL VEHICLE ADHESIVE PERFORMANCE

To determine any differences in the model system's abilities to function as primer coats for subsequent bonding with adhesive films, the metal-metal climbing drum peel test was employed (ASTM D1871-70). The peeling skin was prepared using a phosphoric acid anodizing technique. The bonding film for these tests was 0.045 psf EA 9628 supported with a nylon knit fabric. Metal surface preparation and specimen layup and cure technique are fully described in the Appendix as are verifications of our thickness measuring techniques.

The first peel performance data was developed using Curing Agent "D" catalyst at a concentration of 3 phh (parts per hundred hardener). Tables 22 and 23 show that most of the primers dried at room temperature (unbaked) are insensitive to moderate increases in primer thickness. However, after baking, only a few models (5 and 7) held peel strength at the higher thickness. It is apparent that Models 5 (BPA Adduct) and 7 (BPA-Hycar CTBN) give the best all-around peel properties.

To determine the adhesive performance of each model vehicle using TPPEI catalyst substituted for Curing Agent D, typical metal-metal climbing drum peel panels were prepared using EA 9628 film on phosphate anodized 2024-T3 clad aluminum. The results listed in Tables 24 and 25 show all systems to be bondable after an air dry at room temperature with only Model 7 (BPA-Hycar CTBN adduct) retaining strength at both 75°F and -67°F after bake and at increased coating thicknesses (0.2 versus 0.4 mils).

To extend our knowledge on the effect of primer thickness with each model after a standard bake of one hour at 250°F, additional MMCD specimens were prepared using an adhesive cure of one hour at 250°F and a post cure of one hour at 350°F. This procedure was used to develop numbers on which to base thickness sensitivity curves for each model vehicle - these curves to be correlated with crack-toughness (^{G}Ic) data in Section 5.0. The data in Tables 26 and 27 reveal that models 2 and 4 through 7 have good 75°F strength retention at higher coating thicknesses even after the post cure. The -67°F data reveal that models 4', 5 and 7 retain good strength to 0.5 mils coating thickness with model 7 having some strength as high as 1.9 mils.

Catalyst systems other than Curing Agent "D" were also examined. Both benzyldimethyl amine (BDMA) and the ethyliodide complex of triphenylphosphine (TPPEI) were added at 1.16 phr. A comparison with Curing Agent "D", Table 15) shows that, by TMA scans, neither affected full cure at 250°F. The TPPEI system did not appear to be fully cured even after post curing at 350°F. In the case of the BDMA system, this conclusion is supported by the Tg and MEK wipe data. However, the MEK wipe resistance of the TPPEI catalyzed system contradicts the TMA results. This coating test showed that excellent resistance is afforded after a 60 minute cure at 250°F. In the other systems examined, a strong direct correlation of MEK wipe resistance to full cure was found.

As the final step in the selection of a preferred hardener-catalyst system, the catalysis of the phenolic-epoxide reaction by TPPEI was studied at two catalyst concentrations (Table 19). The TMA curves showed that use of either concentration did not give complete cure with the two hour at 250°F cycle. An example of this is shown in Figure 1. As can be seen, the trace shows a minor penetration of the specimen somewhat above the glass transition temperature (130°C). This indicates that the rubbery modulus of the system is low enough to allow major deformations under the load applied. At ca. 145°C, a linear expansion curve is reestablished indicating that cure is complete. A complete cure is indicated by the TMA after a one hour at 350°F post cure. The TMA curve (Figure 2) does not exhibit any penetration characteristics.

This behavior of incomplete cure after a two hour at 250°F cure cycle was characteristic of TPPEI concentrations varying from 0.4 to 1.2 parts by weight. This may indicate that the catalyst concentration is effective only in controlling reaction rate prior to vitrification and that the extent of cure at that point is independent of TPPEI concentration.

The extent of reaction at the point of vitrification must be close to complete as reflected in the MEK wipe resistance. Even though the TMA indicates incomplete cure, a thin film of this material shows as good as, if not better, resistance after a two hour at 250°F cure as with a 350°F post cure.

To test the affect of TPPEI concentration on coating properties, Model #2 was again used. The level of TPPEI, a true catalyst, affects the speed at which coating chemical resistance and hardness are developed. Table 20 shows that a higher concentration may be detrimental. From this, all model vehicles were prepared using a concentration of 2 parts per hundred hardener (phh) for use in bulk and adhesive property testing.

4.4.4) Application And Modification Of Model Vehicle Systems

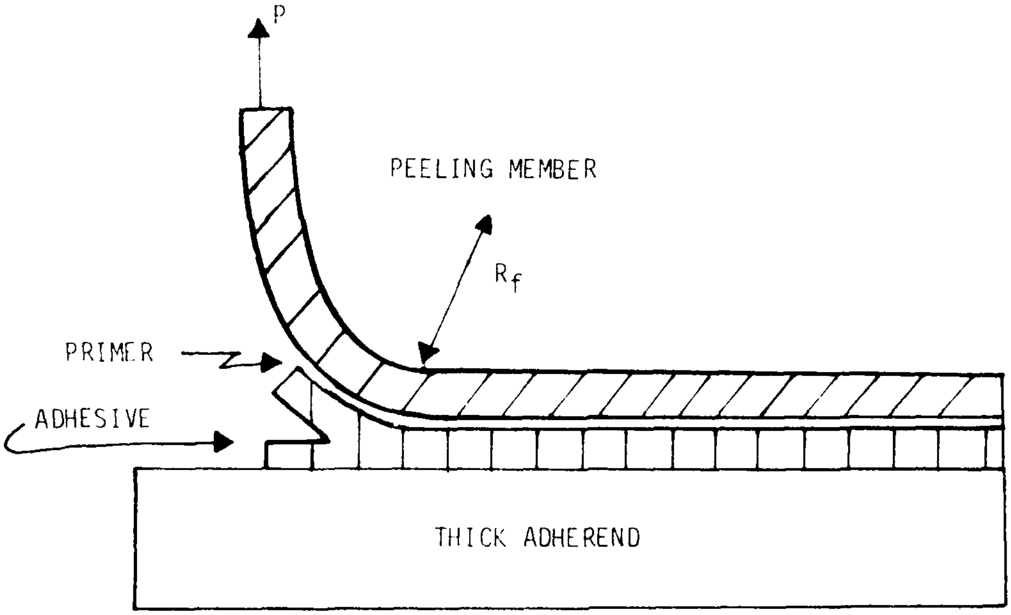
Prior to the preparation of castings for measuring model bulk properties, screening of several anti-foam agents was necessary in order to effect void free specimens. Monsanto's PC-1344 was most advantageous in the technique employed for casting preparation which is described in the Appendix. For primer applications, General Electric's SR-82 at 1 phr was the most effective as a flow control agent. A solvent blend of methyl ethyl ketone/tetrahydrofuran/diacetone alcohol (55/30/15) was selected and used throughout the program. A yellow dye, Chinoline Yellow SS, was employed at 0.1 phr as a spray aid. Techniques for spraying the model primer vehicles were established and generally described in the Appendix. The specific formulation for each of the model vehicles is given in Table 21.

5.0 BULK PROPERTY - PRIMER PERFORMANCE CORRELATION

5.1) BACKGROUND

To date, no literature information has been published dealing with the relationship of resin system bulk properties (i.e., molecular architecture) and primer performance which might aid in the design of improved systems. In order to logically select and objectively evaluate variations in primer vehicle formulations, a simple qualitative model of a metal to metal peel test has been formulated. This model assumes that sufficient adhesion at the adhesive-primer and primer-metal interfaces is established such that all failure processes are within the bulk of either of the organic layers. This assumption is supported by our observation that the thickness sensitivity of a primer vehicle can be decreased by techniques,which modify the cohesive properties of the resin system, such as decreased crosslink density.

A proposed diagram of the peeling process in an adhesive bond is as follows:



A fracture model similar to this but containing only an adhesive layer has been used by both Duke27) and Yamamoto28) in effectively describing adhesive peel properties. Duke found that the flexible adherend was subject to plastic deformation as the failure process proceeded and developed a permanent curve described by the radius of curvature, R_f. His calculations predict a dependence of R_f on both the stress-strain and geometric factors (bond and adherend thickness) of both the adhesive and adherend. Likewise, he has developed a relationship between the peeling strength and adhesive and adherend properties:

$$P = (t\epsilon_m \sigma_y{}^2 Sy/3)^{1/3} \quad bT^{2/3}$$

where

P = peeling force
t = adhesive thickness
ϵ_m = maximum adhesive strain
σ_y = adhesive yield stress
S_y = adherend yield stress
b = bond width
T = adherend thickness

On analysis, his equation appears to predict reality fairly well.

Unfortunately, most studies on peel adhesion described in the literature, have used pressure sensitive adhesives with stress-strain and viscoelastic parameters widely different than those of the epoxy adhesives of interest. Because of this, the present description of the peeling process as it relates to primer applications is very qualitative but it does examine those adhesive material parameters found important in the above references.

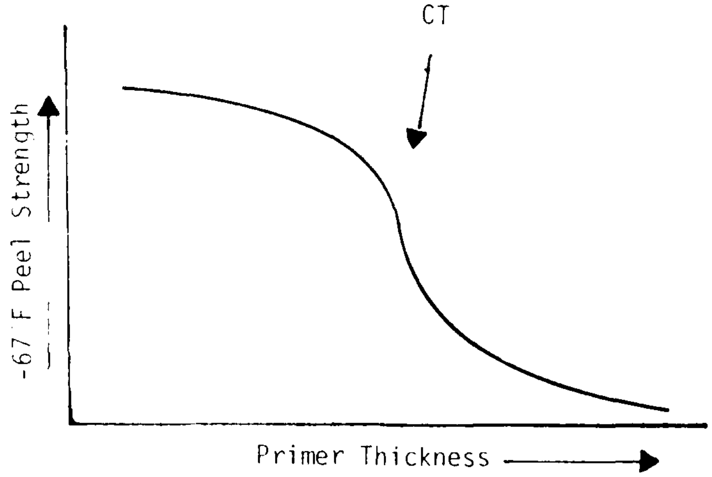
As stated by Duke27), the plastic collapse of the peeling adherend causes the stress to be transferred into the adhesive and primer layers in a tensile mode. As such, these layers can be considered as flexed films with large amounts of tensile strain on them. As the strain level increases, failure will occur in either the primer or adhesive layer depending upon the stress-strain properties of each. If fracture is initiated in the primer layer, the energy required to fail the bond will be dependent upon the crack toughness; i.e., the energy required to create a unit area of new surface, of the primer. If fracture initiates in the adhesive layer, progress of the process can continue in the adhesive or transfer to the primer layer. The final location is dependent upon the stress-strain properties of the primer as well as the relative level (compared to the adhesive) of crack toughness. This can best be understood by examining the behavior of the joint as primer thickness is increased. At constant R_f, the strain in the outermost (i.e.-most distance from the peeling member) layer of primer increases as the thickness of that material increases. The adhesive layer is subjected to even greater levels of strain and failure should initiate in this material. However, if the primer is significantly weaker than the adhesive, the primer thickness could reach a level such that the critical strain for failure is reached in the primer, prior to the adhesive,and the crack would initiate there. The crack locus would be maintained in the primer layer and the "peel" strength would be characteristic of the primer. Ideally, it would be desirable to increase the strength, elongation to failure or crack toughness of the primer vehicle such that the critical strain is never approached in the desired primer thickness range. Failure would then occur in the adhesive layer.

An attempt has been made to develop a working model by correlating the thickness sensitivity of several model primer systems with such parameters as ultimate tensile strength, elongation to failure and crack toughness. If such a correlation was shown to exist, then it could be used as a guide to the development of improved primer vehicles.

Current methods of increasing primer vehicle strain to failure and/or crack toughness involve reduction of cross-link density. This change also results in reduced cohesive strength which has led to reduction of system solvent and thermal resistance. Attempts to eliminate this situation includes maintainance of high cohesive energy density levels at reduced cross-link density by increasing chain stiffness. This type of system should have both high cohesive energy as well as large elongations to failure. Increasing the chain stiffness should also increase solvent resistance and glass transition temperature as shown by Van Hoorn[29)]. Improvement in crack toughness was attempted by heterophase reinforcement of the resin system by such agents as the liquid acrylonitrile-butadiene rubbers . This modification of the epoxy matrix has been shown to significantly increase both the crack toughness and tensile elongation to failure of the system without gross reduction of glass transition temperatures or Young's modulus.

5.2) RESULTS

The experimental objective of this portion of the effort was to quantitatively correlate the thickness sensitivity of primer systems with cured resin bulk properties. A quantifiable parameter characterizing the thickness sensitivity was necessary and the thickness at which the -67°F metal to metal peel strength started to decrease was chosen. This "critical thickness" (CT) is defined by the following generalized curve.



5.2.1) Model Systems

A number of model resin systems were chosen to investigate the effect of three variables in molecular architecture on both bulk properties and primer thickness sensitivity. These variables were:

1) Cross-link density - the resin systems consisted of a mixture of DEN-438 [an epoxidized novolac (functionality ≅ 3.5)]and a bisphenol A diepoxide varying in molecular weight. The diepoxides used were:PHENOXY^R PAHJ (See list of Products in Appendix) (Mol. Wt. = 30,000),EPON^R 1007 (Mol.Wt. - 5000),

and EPON 828 (Mol.Wt. = 350). These formulations are given in Table 28.

2) Chain Stiffness at Constant Cross-link Density - Changes in chain stiffness while maintaining constant cross-link density were examined. This was accomplished by reacting EPON 828 with a constant equivalent percent of several diphenols; hydroquinone, bisphenol A and bisphenol S. The distance between cross-links was designed such that the EPON 828/ bisphenol A reaction product had an equivalent weight similar to EPON 1001/1002 (eq.wt. = 500-650). Use of these three diphenols should have given chains of widely different chain stiffness as reflected in their thermal properties. Thus Van Hoorn29) has shown that a high molecular weight-phenoxy type polymer based on bisphenol A has a Tg of 100°C while that of the bisphenol S based polymer is 170°C. Ehlers31) found that EPON 828 cured with hydroquinone had a vicat softening temperature of 75°C while with bisphenol S the softening temperature was 90°C. These differences are further confirmed by in-house data comparing the 250°F tensile lap shear strengths of an amine cured modified epoxy adhesive produced in part by pre-reaction with several diphenols32).

Diphenol	Resorcinol	Bisphenol A	Bisphenol S
Tensile Lap Shear at 250°F (lb/in^2)	1075	1235	3350

These formulations are also shown in Table 28.

3) Rubber Heterophase - Significant improvements in the toughness of epoxide resins without serious effects on Tg or solvent resistance have been made by incorporating a liquid reactive rubber into the formulation30). Bascom et al 33) has found that addition of up to 15% of CTBN, a carboxyl terminated liquid acrylonitrile butadiene rubber, into a bisphenol A epoxide adhesive increased the crack toughness (G_{Ia}) value to approximately 35 x 10^2 J/m^2 from the 1.2 x 10^2 J/m^2 value characteristic of the non-rubber containing system. A model system was built by reacting Hycar^R CTBN (a carboxyl terminated butadiene-acrylonitrile rubber) with the EPON 828 bisphenol A resin described previously. (Table 28).

All model systems were cured with a solid novolac resin (Varcum^R 4326, functionality ≈ 6, softening point = 75 to 80°C). The cure was accelerated with a triphenyl phosphine-ethyl iodide complex (TPPEI). 34) All model systems were cured for 2 hours at 250°F plus 1 hour at 350°F.

5.2.2) Determination of Critical Thickness.

The critical thickness (CT) of the model primer systems was obtained from data developed measuring the -67°F metal to metal climbing drum peel strength. EA 9628, a high peel 250°F service adhesive system was used as a reference adhesive. Details of the primer application procedure are included in the Appendix.

The results are shown in Figures 3 through 5. As can be seen, the curves are all "S" shaped with high strength at low primer buildups. For reference, the peel strength of EA 9628 at -67°F on unprimed metal is 50-55 in.lb./in. Primer model 2 (the EPON 1007-DEN-438 model) exhibits these strengths only below approximately 0.05 mils. At primer thicknesses greater than this peel strength decreases rapidly (20 in.lb./in. at 0.3 mils). A critical thickness (CT) of 0.10 mils was obtained. The strength decrease with thickness of Model #5 is less drastic. Peel strengths were 40 in.lb./in. at a primer thickness of 0.30 mils, decreasing to about 17 in.lb./in. at 0.95 mils. This system had a critical thickness (CT) of 0.40 mils. In a like manner, a critical thickness of 0.05 mils was found for Model #3, 0.20 mils for Model #6, and 0.55 mils for Model #4. (Figure 4). The peel strength versus primer thickness curve of Model #7, (Figure 5) was very flat and no critical thickness value was readily apparent. A critical thickness of 1.40 mils was determined using the midpoint between high and low values.

Data for Model #1 (the phenoxy-DEN-438 system) were not presented since acceptable castings for bulk property measurements could not be prepared.

A tabulation of the critical thickness (CT) values is shown in Table 29. As was outlined earlier, the formulation of the model systems followed three distinct concepts: cross-link density, chain stiffness at constant cross-link density and rubber heterophase particle toughening. The critical thickness (CT) values found can be segregated into three groups which correspond to the three different molecular architecture variables being examined. Thus the lowest values (TC = 0.05 and 0.10 mils) were obtained from the variable cross-link formulation set. A second set (TC = 0.20 to 0.55 mils) came from the variable chain stiffness formulations, while the heterophase toughening experiment gave a lone TC value at 1.50 mils.

Therefore, all three variables affect the primer critical thickness. The chain stiffness experiments were formulated at a significantly lower cross-link density than the variable cross-link density formulations and have a significantly greater value of critical thickness. Flexible chains, as given by hydroquinone, impart a lower thickness sensitivity to a primer vehicle than do the stiffer chains formed with Bisphenol S. Finally, toughening the formulation by precipitated rubber particles, holds the highest promise in reducing thickness sensitivity.

The selection of these molecular architecture variables has therefore given a wide range of critical thickness primer systems with which to develop correlations with bulk resin properties.

5.2.3) Bulk Property Determination

5.2.3.1) Tensile Properties

Tensile ultimate strength, initial modulus and elongation at failure were determined per ASTM D 638-64T(10). Special techniques had to be developed to obtain high quality void free castings for such performance measurements. Details of the preparation of castings of the model resin systems can be found in the Appendix. Data for Model #1 (Phenoxy PAJH-Den 438 mixture) was not developed because the very tough consistency of the uncured resin system precluded manufacture of void free castings.

The tensile properties were determined at 75°F and are shown in Table 30. In contrast to the range seen with the critical thickness (CT) values, there is a surprising uniformity in the tensile properties. The ultimate strengths may be divided into two groups. The first, including both the difunctional-multifunctional and the bisphenol reaction product resin systems (Models 2 through 6), gave nearly identical tensile strengths of 10,500 lb/in^2. In contrast, model #7, the rubber heterophase system, had an ultimate strength of 7900 lb/in^2. This system also showed, in contrast to the remainder of the tests, considerable stress whitening at the fracture locus.

In a like manner, the range of initial tangent modulii is small, ranging from a low of 404,000 lb/in^2 for Model #4 (the hydroquinone-EPON 828 resin) to a maximum of 595,000 lb/in^2 (Model #3, EPON 828-DEN 438 mixture). Model #7, which had the lowest ultimate tensile, showed an intermediate level of modulus (440,000 lb/in^2). The elongation to failure ranged from a low of 2.5% (Model #3) to a maximum of 6.2% (Model #5).

5.2.3.2 Crack Toughness

The crack toughness of the model systems was determined using the tapered double cantilevered beam technique of Mostovoy and Ripling (35) Details and discussion of this test are given in the Appendix. Both the crack toughness for opening (G_{Ic}) and arresting (G_{Ia}) were determined. G_{Ia} and G_{Ic} values for the model systems are listed in Table 31. As can be seen, there is a large range of values varying from a low ($G_{Ic} = 1.00$, $G_{Ia} = 0.59$) for Model #3 (EPON 828-DEN 438) to a high ($G_{Ic} = 5.30$, $G_{Ia} = 3.46$)for Model #7 (EPON 828-bisphenol A-DEN 438).

There is a trend of increasing crack toughness (both arrest and critical) with increasing critical thickness (CT). Thus the highly crosslinked systems such as Models 2 and 3 (EPON 1007-DEN 438) with TC values of 0.05 and 0.10 mils, respectively have G_{Ic} values of 1.00 and 1.53 lb/in. In contrast, Models 4 (the hydroquinone-EPON 838 resin) and 7 with TC values of 0.55 and 1.50 mils exhibit G_{Ic} values of 2.33 and 5.30 lb/in respectively. Similar differences in the arrest toughness (G_{Ia}) were also seen.

5.2.3.3 Glass Transition Temperature

The glass transition temperature of the model systems were determined by Differential Scanning Calorimeter Techniques (Figure 6.) using pieces of the cured tensile castings. The results are shown in Table 32. The trends seen are those that would be expected from examining the molecular structure of the systems' components. Thus, Model 6, the system with the bisphenol S in the backbone, has a

Tg of 115°C while the Bisphenol A and hydroquinone containing backbones (Models 4 and 5) had Tg's of 90 and 86°C respectively. Also, the Hycar CTBN containing system had a Tg of 88°C essentially equivalent to the 90°C of the non-CTBN containing control system, Model 5. This result also follows from reported results showing little or no effect on Tg due to the inclusion of rubbery heterophase particles.

The high molecular weight diepoxide/DEN 438 blend systems (Models 1 and 2) show two transition temperatures, 85° and 132°C. The blend of EPON 828 and DEN-438 exhibits only one Tg, however, at 123°C. The results might be interpreted as being due to a separating of Models 1 and 2 into two phases. The first would contain the high molecular weight diepoxide (Tg - 85°C) while the second could represent the cured DEN-438. This interpretation is supported by two observations. Van Hoorn found the Tg of the phenoxy type polymer to be approximately 100°C by torsion pendulum measurements. Secondly, as the molecular weight of the diepoxide decreases to that of EPON 828, only one Tg is found. This diepoxide would be expected to be more compatible with DEN-438 than the higher molecular weight materials. Also, the Tg of the EPON 828/ DEN 438 system (123°C) suggests that the higher temperature transition of Models 1 and 2 is due to the cured 438.

5.3) CORRELATIONS

Correlations between the critical thickness parameter (CT) and both the bulk tensile properties and the two crack toughness values were attempted.

5.3.1) Tensile Correlations

Variation of either the crosslink density or chain stiffness of the cured resin systems did not result in any significant variation in ultimate tensile strength (Table 30). This occurred in systems which varied in CT from 0.05 to 0.55 mils. There does not appear to be any strong correlation, therefore, between these two parameters. The fact that the system with the greatest CT value (Model #7, CT - 1.5 mils) also exhibited the lowest tensile strength (7900 lb/in^2) may be fortuitous or may be indicative of a trend.

In a like manner, there does not appear to be any correlation between either the tensile modulus or elongation to failure and the system's CT value. Examining the modulus values, those systems with the highest CT values have modulii intermediate in the range seen. Thus Model #7, with a CT value of 1.50 mils has a modulus of 440,000 lb/in^2 and Model #4 (CT - 0.55 mils) exhibited a modulus of 404,000 lb/in^2. The same lack of correlation was noticed for the elongation to failure values.

It may be that the tensile test as it was used [ASTM D638-64T(10)] was too insensitive to detect the correlations with critical thickness. Visual examination of the failed tensile dogbones of Model #7, showed a great deal of stress whitening and necking down of the specimen in the immediate area of the fracture. Both of these phenomenon are indicative of a good deal of strain, yet the elongation to failure (4.1%) was no different than the other systems which failed in the normal brittle manner (2.5 to 6.2%). A one inch guage extensometer was used in conjunction with these tests and perhaps the strain indicated by the stress cracking or necking became much less noticeable when averaged over this guage length.

5.3.2) Crack Toughness

Correlations of the primer critical thickness (CT) with both the critical crack toughness (G_{Ic}) and arrest crack toughness (G_{Ia}) are shown in Figures 7 and 8 respectively. The correlation of CT with G_{Ic} is very good for all models except Model #5. A straight line (slope = 0.35) can be drawn through the points. Regression analysis showed a correlation coefficient of 99.1% for this set of data. Likewise, a straight line can be drawn through the CT versus G_{Ia} data (slope = 0.52, correlation = 97.71%). The data from Model #5 fits into this correlation.

It is very interesting that a strong correlation of primer vehicle thickness sensitivity was found with crack toughness, a parameter derived from a process occurring at and after failure rather than tensile elongation, derived from the system prior to failure. The original qualitative model was built on the concept of a critical level of strain governing the thickness sensitivity.

One plausible reason for this situation is, as discussed earlier, that the tensile testing sensitivity was too low to detect the properties desired. The other is that the parameter controlling thickness sensitivity is defect sensitivity. All plastic articles contain defects, be they voids or dirt particles. These defects tend to magnify the stress level in a small volume around them far beyond that detectible on a gross scale. A system then, such as the liquid rubber, Model #7, which can distribute these stresses over a larger volume, is less thickness sensitive.

5.4) CONCLUSIONS

This work has shown that the determination of the primer vehicles crack toughness parameters can be used to estimate the thickness sensitivity of the system. At this stage of development, the correlation is somewhat rough and would need more data sets before an exact relationship could be derived. These results do fit a rationale which predicts that the thickness sensitivity of a vehicle depends upon the ability to reduce or eliminate the stress magnifications due to defects in the resin.

Unfortunately, the CTBN modified bisphenol A-EPON 828 resin, the least crack sensitive model used, suffers from solvent sensitivity. This is probably due to the incomplete precipitation of the CTBN into the rubbery heterophase particle during cure. It would be expected that further formulation should be directed toward improved toughening techniques.

6.0) PRIMER VEHICLE PERFORMANCE OPTIMIZATION

6.1) OBJECTIVE

The purpose of the primer vehicle optimization phase was to provide a series of optimized vehicles which would give a range of performance properties best suited for the subsequent inclusion with preferred corrosion inhibitors. Through use of the model vehicle bulk and performance property correlations, it was possible to formulate these optimized vehicles by modification of the models themselves.

6.2) APPROACH

Certain performance criteria are essential to the overall performance of a resin vehicle as a primer and as a top coat. Among such criteria are the primer's resistance to solvent and moisture environments, scratch hardness, wetability and general adhesion to the bonding substrate or film adhesive. Basically, it was necessary to define these and other properties and then modify the model vehicles as necessary to give an acceptable balance.

The optimization of the model vehicles prior to the incorporation and evaluation with optimized inhibitors can be based only partly on correlations with model bulk properties. The general performance of the vehicle systems, in metal-metal climbing drum peel tests as outlined below, does seem to correlate with a general ordering of "toughness" based on crack propagation data and inferred chemical structures.

Rank Toughness	Model	Rank Peel (EA 9628)
Low	3 (Epon 828)	8 (Lowest)
↑	2 (Epon 1007)	5
	6 (BPS Adduct)	6
	1 (Phenoxy)	7
	4' (Hydroquinone Adduct)	3
	4 (Resorcinol Adduct)	4
↓	5 (BPA Adduct)	2
High	7 (BPA-Rubber Adduct)	1 (Highest)

Although it is not known whether peel performance is more influenced by their relative degree of toughness or by surface characteristics for adhesion, Models 7, 5, 4 and 4' appeared to be the best candidates for optimization.

The system intermediate in toughness and peel performance, Model 5, was chosen for further study with the intent of altering its properties by resin substitution, change of curing agent type and comparison of catalysts. The purpose of this investigation was to define the best combination of peel strength, thickness insensitivity, and chemical and moisture resistance before selecting candidates for evaluation with corrosion inhibitors. The program is described in Table 33.

6.3) SUMMARY OF RESULTS

The formulations were prepared using the standard model solvent system of methyl ethyl ketone/tetra-hydrofuran/diacetone alcohol (55/30/15) except where solubility of ingredients necessitated changes. The systems were sprayed onto phosphate anodized aluminum as usual, baked for 1 hour at 250°F and cured with EA 9628.

Results are given in Table 34 and are compared with BR-127 and Model Vehicles 4, 4', 5, 6 and 7. System 15 sprayed poorly due to the insolubility of melamine and testing was discontinued.

While the peel strength for the EA 9628 control was below normal with this set of tests, the overall results were comparatively valuable and provided a basis for further optimization. Systems 3, 8, 13, 14, 17, 18 and 20 gave reasonable peel strength at high coating thicknesses and, except for 13 and 20, acceptable MEK resistance after cure. System 20 consistently gave the best MMCD peel strength at room temperature or -67°F for any given primer thickness. In an attempt to improve its MEK resistance and hardness, the system was modified to include a higher functionality epoxy resin (Ciba 0500), an alternate catalyst (DMP-30 at 2 phh), and another curing agent system (metaphenylene diamine/2-ethyl-4-methyl imidazole at 3.9/0.5 phr). The new formulations were tested along with the former systems and reported in Table 35. In this test series systems 14, 17 and 20 gave the best peel properties with systems 3, 4, 5 and 20A next.

6.3.1 Moisture Equilibrium (ME) Tests

In a study of vehicle moisture barrier properties as a means to judge potential for corrosion resistance, a series of moisture equilibrium tests were conducted. A test method involving the moisture pickup of vehicle coated aluminum panels was evaluated and found to have advantages in (1) testing systems applied from solvent, (2) evaluating the affect of thin film cures as opposed to cured castings and (3) to arrive at a result rapidly.

Panels were subjected to total immersion in deionized water controlled to 120 ± 2°F in a stainless steel water bath. The pH of the water was monitored throughout each test series and ranged from 7.8 to 8.8.

Aluminum test panels were prepared by spraying to a dry film thickness of 2-4 mils and measured for moisture pickup after baking the coatings for two hours at 250°F to simulate a pre-bake and normal cure cycle of about one hour each. Results for the model systems are given in Table 36 and shown in Figure 9. In this test, specimens were started in a 120°F, condensing humidity chamber. After about 148 hours, the chamber malfunctioned (ceased to condense) and the specimens were removed to a total immersion bath.

Model 3 absorbed the least moisture. This would be expected since it is the highest cross-linked system. By the same logic, Models 2 and 3 are next, followed by the adducts of BPA, hydroquinone and resorcinol. Model 7, the lowest crosslinked system, had surprisingly low equilibrium moisture absorption.

Next, the new vehicle systems described in Section 6.3 were tested. Results in Table 37 and Figure 10 show no improvement in moisture resistance by the modification of Systems 5 (Model 5) and 20 (Model 7).

6.3.2) Correlation Of Primer Surface Contact Angle With Bondability

Past studies have shown that certain primers, particularly CIP versions give decreasing peel strength with increasing primer thickness when baked and used under structural adhesive film. Our work under this contract has also shown this trend. Moreover, some primer systems were observed to fail mor adhesively from the bonding film as primer thickness increased. Some commercial bonding primers have shown this failure tendency. Possible causes could be related to some changes in the primer surface properties as thickness increased. For example, reaction volatiles could entrap themselves near the surface of a thicker coating, or, the polymer structure could change at the surface due to mass effects causing a higher cross-linked structure or a dis-orientation of polar bonding sites away from the surface, or any of the like, which might result in lower peel strengths.

Having previously observed film adhesives to fail more adhesively from baked BR-127 primer as primer thickness increased, this primer was sprayed onto phosphate anodized, 2024-T3 clad aluminum panels and baked for one hour at 270°F. Contact angles were measured and thickness, hardness and MEK wipe resistance determined. The panels were assembled into MMCD peel specimens using EA 9628 film and cured for one hour at 250°F, (50 psi) after a one hour autoclave heatup.

Tests A and B in Table 38 represent surface characterizations and bond results determined at two different times and show fair agreement. Significantly, the usual decrease in peel strength with increasing primer thickness was observed but with essentially no difference in critical surface tension, γ_c, which is a measure of the wettability of the primer surface by selected liquids. The γ_c of BR-127, approximately 31 dynes/cm, is much the same as for most conventional DGEBA resins (re Epon 828) cured with an aromatic amine such as metaphenylene diamine (MPDA, giving 24 dynes/cm). Further, MMCD peel failure modes show that EA 9628 bonded well to the primer surface at all thicknesses which suggests that the thickness/strength effect results from the bulk properties of the BR-127 system and stress distribution in the primer layer as thickness increases and not from a change in surface wettability as determined at room temperature. Depending on the curing agents used, γ_c for a number of cured epoxy resins shows higher values in the interior than the exterior surface (i.e. Epon 828-MPDA 43 dynes/cm interior, 34 dynes/cm exterior). This is believed to be due to the turning away or dis-orientation of polar groups (i.e. hydroxyl groups) from the air exposed surface. It is probable that some correlation between γ_c and bondability could be shown by taking measurements at temperatures above ambient or more near those used during heatup and cure since these would seem to be the most significant values.

Finally the γ_c usually decreases as the cure proceeds which makes the surface less susceptible to wetting, generally. This is exemplified by the fact better bonds are often achieved on non or partially baked primers. A study to compare the primer γ_c with the surface tension of the bonding film, γ_L on an increasing elevated temperature curve would yield interesting and quite possibly helpful data regarding bonding parameters with tapes and primers.

6.3.3) Ranking Of Properties

To gain a perspective on the comparative performance of the various modified primer vehicles, they were ranked within each category tested. The categories were MMCD peel, MEK resistance, pencil hardness and moisture equilibrium. Judgement as to the ranking of a particular vehicle system within a test category was made after careful scanning of all data. Table 39 represents the ranking.

A further display shows how the vehicle systems ranked in overall performance, see Table 40. The data, weighted toward MMCD peel performance, clearly shows that systems ranking in the top 50% contain the adduct of BPA or BPA-rubber with and without Ciba 0500 resin addition. These systems are Systems 5, 8, 14, 17, 20 and 20a. Of these, systems 14 and 17 employ curing agents or catalysts other than the standard Varcum 4326 and TPPEI.

6.3.4) Solvent Resistance Studies

Several primer vehicles, including the original models, were sprayed to a thickness of 0.5 mils on chromic acid etched 2024-T3 clad aluminum and baked for two hours at 250°F. Initial pencil hardness was measured and a coated panel placed in each of six common solvents for seven days at 75°F. After exposure, the panels were wiped free of surface fluid and the hardness re-measured. Results are given in Table 41.

As seen, BR-127 tests well in all solvents, retaining its pencil hardness of 7H. Model #3 is also excellent as expected from its high cross-link density. Recall, however, that Model #3 has very low peel strength above 0.05 mils coating thickness. Otherwise, the data clearly show Models 8 and 20A to perform the best. It should also be observed that DMP-30 catalyst gives improved resistance to solvents when comparing Models 5 (containing TPPEI) and 18. To a lesser degree, the same can be observed when comparing Models 7 (also containing TPPEI) and 20C. It is believed that DMP-30 gives a more complete cure due to (1) speed of reaction, and (2) curability of any remaining epoxide by homopolymerization. The disadvantages of this catalyst would be stability in solution and bondability.

6.3.5) Final Optimization of Primer Vehicle Systems

In repeat tests to confirm selected primer vehicle performance with EA 9628 adhesive, systems were sprayed to a dry film thickness of 0.4 to 0.6 mils on improved phosphate anodized aluminum skins, baked 1 hour at 250°F and cured. Table 42 shows the following systems to give the best range of MEK resistance and peel strength at these thicknesses.

5A - Model #5, increased catalyst concentration
6A - Model #5/DEN 438, decreased catalyst concentration
8A - Model #5/Ciba 0500, decreased catalyst concentration
20-1 - Model #7, increased catalyst concentration
20A-1 - Model #7/Ciba 0500, decreased catalyst concentration

System 6A is a repeat of previous tests using lower catalyst concentration (2.0 pph TPPEI has been routinely used) to reduce the initial bake cycle hardness to promote a better bond. System 14 (Model #5, gallic acid as the hardener) was tested using higher hardener and catalyst concentrations in an attempt to improve MEK resistance. MMCD peel was retained but MEK resistance was not improved, however.

From the data gathered in the foregoing experiment, as well as that collected from previous work, an optimum vehicle system would most likely fall within the boundaries of System 8A and 7. This is better illustrated below in a table showing the vehicle ingredients which give coatings ranging from hard to soft.

	Hard →		(X)[a]		→ Soft
System	8A	20A-1	(X)	5	7
Ingredients					
BPA, equiv./100g EPON 828	0.3	0.3	(X)	0.3	0.3
Hycar CTBN, phr (EPON 828)	0	20.0	(X)	0	20.0
Ciba 0500/Adduct (wt)	30/70	30/70	(X)	0	0
TPPEI, phh (Novalac)[b]	1.0	1.0	(X)	2.0	2.0
Novalac Conc., phr	41.0	39.0	(X)	18.0	15.0
Properties (0.5 mils)					
MMCD Peel, in lb/in					
@ R.T.	~60	~60	(X)	~60	~60
@ -67°F	<15	<15	(X)	> 30	> 30
MEK Resis. (Baked/Cured)[c]	E/E	G/E	(X)	P/E	N/G

a) X - optimum ingredient/property
b) Varcum 4326
c) E - Excellent N - None
G - Good P - Poor

The above lends itself to a good designed experiment, whereas each of the ingredients, including BPA, are varied through reasonable concentration levels and tested for their response to the important properties desired (peel, MEK resistance, moisture resistance, etc.). While there are many other diphenols, epoxide resins, hardeners and catalysts which might give even better optimized properties, such an experimental design within the scope of the ingredients presently being examined might have provided an excellent route to an optimized vehicle system. Although this approach is useful as a time saver, if properly done, the work would have extended itself far enough past the end of the contract period to be impractical. As an alternative to the experimental design and its associated computer read-out and useful contour maps, we chose an alternate method which gave a reasonable indication of optimized vehicle properties (X) in a shorter time and still allowed for the formulation and testing of an inhibitor-containing primer.

In the test program,a series of five primer vehicles were formulated within the theoretical performance boundary of Models 8A and 7 as described in the foregoing table. The systems are shown in Table 43 as X_2 through X_5 and their test results compared with Models 5, 7, 8A and 20A-1 using BR-127 (vehicle) as a control. An optimum system was not readily apparent but the data suggests it to be within the area of Systems X_2, X_3 or X_4. From close scrutiny of peel specimen bondline thickness and failure modes plus the history generated that vehicles containing rubber modifications (in this case X_2 and X_3) were best in moisture resistance, System X_3 was selected for further evaluation as the optimized median vehicle. Therefore, it was designated as Model 22. It is manufactured according to the procedures for Model 7 in the Appendix.

Model 22 Formula:

Adduct:	EPON 828	100 pbw	85 pbw
	Hycar CTBN	10	
	BPA	34	
	TPPEI	0.25	
Ciba 0500			15
Varcum 4326			28
TPPEI			0.28
Solvent:	MEK/THF/DAA (55/30/15)		5.3

Not knowing the vehicle performance changes which could occur upon incorporating the series of corrosion inhibitors, it was elected to test the inhibitors with three vehicle systems ranging in general properties from hard to soft, specifically Models 8A, 22 and 7. These vehicles were freshly prepared and screened a final time with EA 9628. Results are given in Table 44. They show the median system, Model 22, to lean more toward the "hard" primer vehicle in this test series, particularly in MMCD peel at -67°F. Time did not permit further re-testing of the vehicles in the X_2 through X_4 series, although this was favored, and evaluation of the inhibitors proceeded with the three systems as discussed.

6.3.6) Effect Of R.T. Storage On Various Vehicle Systems

Several primer vehicles were observed after having been stored at 75°F in tin containers. Results of these observations are given in Table 45. The data suggests that the Varcum 4326 hardener used in the finalized vehicle systems is relatively stable with several catalysts, including the selected TPPEI catalyst. Also, systems containing Ciba 0500 (i.e. Model 8A) have good stability also. It should be noted here that the "fair" rating for Model 8A coatability resulted from a low level of sediment observed in the can after storage and would be masked by any pigments. It is not likely to affect bondability.

7.0) EVALUATION OF CORROSION INHIBITORS WITH OPTIMIZED PRIMER VEHICLES

Initially, ten vehicles were selected for evaluation with the four candidate inhibitors outlined in Section 3.0. They are:

10 Vehicles	4 Inhibitors
Model #1 (Phenoxy)	Strontium Chromate
Model #2 (EPON 1007)	Cobalt Chromate
Model #3 (EPON 828)	Melamine Dichromate
Model #4' (Hydroquinone adduct)	1,2,3 triphenylquanidine dichromate*
Model #5 (BPA adduct)	
Model #7 (BPA-rubber adduct)	
Model #8A (Model #5/Ciba 0500, 1 phh cat.)	*Soluble
Model #20-A1 (Model #7/Ciba 0500, 1phh cat.)	
Model #127 (BR-127 vehicle)	
Model #201 (EA 9201 Vehicle)	

In addition to the above inhibitors, zinc potassium chromate and magnesium dichromate (soluble) were incorporated in Models 5, 7, 8A and 20A-1 and evaluated.

Finally, Model 22 was evaluated along with Models 8A (hard) and 7 (soft) in the final optimization phase.

The CIP primers were evaluated for corrosion protection by their performance in the salt spray scribed panel test and by MMCD peel for thickness sensitivity.

7.1) EFFECT OF PRIMER VEHICLE AND INHIBITORS ON SALT SPRAY CORROSION (SCRIBED PANEL TEST).

The unpigmented primer vehicles were sprayed onto 2024-T3 bare aluminum panels which had been chromic acid etched. The panels were baked for 2 hours at 250°F, cross-scribed with a carbide tip tool and placed in a 95°F, 5% salt spray chamber for observation. Figure 11 illustrates the comparison between vehicles and their tendency to allow corrosion. Each scribe was examined microscopically and the individual beads of corrosion (undercut) counted with time. As can be seen, at some point a vehicle will have accumulated sufficient corrosion that two or more beads become one and the total number in the scribe will decrease. It is interesting to observe the relatively fast rise and resulting high levels of corrosion for some systems (Models 1 through 4' and BR-127). The fact that Model 3, the highest cross-linked system, is so poor most likely is explained by its inherent brittleness and cracking by the scribing tool. Also, that the systems containing diphenolic adducts (Models 4' through 20A-1) are noticeably better in resistance to corrosion. Further, that systems containing rubber modification (Models 20A-1 and, particularly Model 7) have about the lowest rate and level of corrosion development. These observations seem to fit with moisture equilibrium measurements for these vehicles which were described previously.

To test the effect of the inhibitors, each was ball-milled (except soluble inhibitors) in each of the ten vehicles for 16 hours using standard milling techniques except where the supply of inhibitor was too small for mass grinding. In this case, i.e., melamine dichromate and cobalt chromate, somewhat lower pigment-binder/solvent ratios were used. All grinds appeared excellent. Final primer blends were:

% Solids	10.00
Cr^{+6} conc., wt %	2.56

With each vehicle/inhibitor system, six chromic acid etched .063 inch thick 2024-T3 bare aluminum panels were sprayed to a nominal 0.3 mils, baked for two hours at 250°F and cross-scribed. One panel was retained for reference, one placed in a 90°F D.I. H_2O fog chamber and the remaining four panels placed in a 95°F, 5% salt spray chamber for observation.

Table 46 shows the results after a 2000 hour salt spray cycle and suggests the following ranking of inhibitors' corrosion resistance:

1. Melamine dichromate (best)
2. Strontium chromate
3. Zinc potassium chromate
4. Cobalt chromate
5. Magnesium dichromate
6. Triphenyl guanidine dichromate (worst)

The best inhibitor in this test series at the 2000 hour mark was melamine dichromate. Strontium chromate was rated next best. Further, four vehicles containing melamine dichromate have at least one test panel continuing past 2000 hours salt spray exposure as opposed to only two vehicles containing strontium chromate.

Additional panels were prepared for further exposure using the three optimized vehicles (7, 8A and 22) with melamine, cobalt, strontium and zinc chromates at two levels of inhibitor concentrations (2.56 and 3.84%). BR-127 standard primer was used as a control. Corrosion resistance was compared using both a 250°F and 350°F baking cycle. Table 47 shows the results. Although this series ran for only 1200 hours, melamine dichromate again appears the best inhibitor overall. Cobalt chromate performed rather well considering that the general appearance of the panels was poor, the inhibitor being rather widely dispersed. After 1200 hours, the three test vehicles performed about equally and, except when containing zinc potassium chromate, gave equal to or better performance than BR-127.

7.2) EFFECT OF INHIBITORS ON MMCD PEEL STRENGTH

The incorporation of solid particles such as inorganic fillers or pigments can greatly affect adhesive peel performance through alteration of the primer bulk resin or surface adhesion properties. As a preliminary study of their relative sensitivity, primer vehicle models 5, 7, 8A, 20A-1, 201 and BR-127 were prepared with six inhibitors and sprayed at 0.5 mils thickness on phosphate anodized 2024-T3 clad aluminum. After baking for 1 hour at 250°F, they were bonded with EA 9628. Results of room temperature peel tests are given in Table 48. At the concentrations employed, the inhibitors generally had very little affect on peel strength. Where low strengths were measured, it appears to be the result of an accelerating affect by the inhibitor on the cure rate. For example, observe the increased MEK resistance for some systems over their unpigmented versions and that,when solvent resistance was good (G) to excellent (E),adhesion was reduced. This was especially true for melamine and triphenyl guanidine dichromates.

As a means to better measure the effects of primer thickness and salt spray exposure on the CIP primers, the primers were spray applied and baked for only 0.5 hours at 250°F prior to bonding with EA 9628. They were compared with an unbaked version.

7.2.1) Primer Thickness Effects

Tables 49, 50 and 51 show the results of primer thickness tests using two levels of inhibitor. When the primers were left unbaked prior to bonding, most systems suffered little or no reduction in -67°F or 75°F peel strength with increased primer thickness. Exceptions were BR-127, which is seldom recommended for use unless pre-baked for at least one hour at 250-270°F, and Vehicles 8A and 22 containing melamine dichromate or strontium chromate at the higher concentration (Tables 49, 50, and 51). Also there was little difference between inhibitors themselves except melamine and triphenyl guanidine dichromates which were compounded at higher comparative pigment/binder ratios for the same concentration of chromium $^{+6}$ ion. Further, only slight strength reduction was observed when the inhibitor concentration was increased by 50 (Tables 49 and 50.)

When comparing primers which were pre-baked prior to bonding, more definitive differences occurred. As expected, Vehicle 8A lost strength noticeably as the primer thickness increased. More subtle losses were observed with the other vehicles except for 22 which was clearly the best in these tests. At -67°F, Vehicle 22 showed thickness sensitivity about equal to Vehicle 7 which would, however, be expected to perform well at thicknesses approaching 1 mil. Again, vehicles having higher pigment/binder ratios were only slightly lower in strength. This property is considered noteworthy since it would allow use of more inhibitor for increased corrosion resistance with only minor loss of peel.

Although the pre-described tests represent a limited data base, there appears to be evidence which suggests that Vehicle 22, (containing zinc potassium chromate) has overall peel properties equal to or better than the other included primer systems.

Further work is needed to fully define the bond performance of these pigment containing primer systems.

7.3) EFFECT OF INHIBITORS ON VEHICLE SHELF STABILITY

Six inhibitors were incorporated into several primer vehicle systems and observed after storing in glass and tin containers at 75°F. Observations on the systems' color, settling rate and pigment resuspension are given in Table 52. Without regard for adhesive performance, the following conclusions may be made (1.5 months observation):

Most stable inhibitor (In Decreasing Order)	Strontium chromate, zinc potassium chromate, TPGD, magnesium dichromate, cobalt chromate, melamine dichromate.
Most stable vehicle	Not defined. BR-127 was least stable, however, when comparing rate of color change, solution viscosity and formation of pigment hard cake.
Slowest settling pigment	Zinc potassium chromate slightly better, others same.
Best pigment suspending vehicle (decreasing order)	Model 7,20A-1, 5, 127, 8A. (rubber containing systems best).
Effect of container type	No difference.

7.4) CONCLUSIONS

Although further testing, such as MMCD peel versus exposure to salt spray, effect of various primer bake cycles, secondary bond performance, salt spray scribe corrosion tests, effects of temperature, salt spray, humidity and chemical exposure on tensile lap shear performance, and the like is needed, Model 22 with zinc potassium chromate appears to be the better CIP primer resulting from this program. While it merits further comparison testing with commercial state-of-the-art CIP primers, this system appears to have good properties. These are:

1. Low sensitivity to coating thickness when tested with EA 9628 adhesive.
2. Good low temperature (-67°F) peel properties when used with EA 9628 adhesive.
3. Low pigment settling rate observed periodically, not reported.
4. Good stability when stored at room temperature.

8.0) PRIMER APPLICATION STUDIES

During the course of this program, all primer variations have been spray applied for testing of coating and adhesive performance properties. The majority of these systems were observed to apply excellently by the spray technique described in the Appendix. It was an intent to screen at least one optimized CIP primer in any or all of the following methods of application: 1) curtain coater, 2) roller coater and electrostatic spray.

Model 22 (containing zinc potassium chromate) was chosen for screening by the various methods. While this system was shown to apply effectively by roller coating, it was not possible to evaluate the other methods due to time constraints. However, from experience with Hysol's curtain coating adhesives (EA's 9500 and 9559) we consider that Model 22 or either of the other final primer systems selected -- Models 8A (hard) or 7 (soft) -- would lend themselves to routine processing by curtain coating. This judgement especially applies for the systems when inhibited with either zinc potassium or strontium chromates, for any of the soluble inhibitors and, of course, for the vehicles themselves if used as unpigmented adhesives. It is not known to what extent the systems will lend themselves to electrostatic spray techniques.

8.1) EVALUATION BY ROLLER COATING

Model 22 primer was prepared with zinc potassium chromate at 10.8% pigment (pigment/binder ratio - .121) and 72.3% non-volatiles in methylethyl ketone/tetrahydrofuran/diacetone alcohol (65.2/26.7/8.1 by weight). Brookfield viscosity was approximately 1200 cps using a Model HBT Viscometer with a #1 spindle at 20 RPM. The primer was introduced onto a 14 inch wide, direct type, Wagner Litho roller coater and used to coat a series of 0.020 inch thick phosphate anodized 2024-T3 clad aluminum sheets. Using conventional techniques of varying roll gap and speed, the primer was too viscous to coat the panels evenly at thicknesses below about 3 mils dry. Reducing the viscosity gradually with a mixture of the same solvents permitted even coats at thicknesses from 0.1 to about 1.0 mil. It was determined that a pan viscosity of 15-20 cps could affect coatings as low as 0.1 mils.

The appearance of the best coatings was equal to or better than samples of BR-127 primer which had been coated using reverse roller coating, that is, totally covered but with moderate, longitudinal striations. It is believed that application by reverse roller coating would improve the coverage to some extent.

Clean-up of the coater was excellent using only methylethyl ketone.

9.0) APPENDIX

9.1) MATERIAL DESCRIPTION AND SOURCE

9.1.1) List of Resins

Trade Name	Description	Supplier[a)]
Butvar 76	Polyvinyl Butyral, solid, AMW[b)] 50,000	Monsanto
Ciba 0500	Epoxy, liquid, WPE[c)] 110	Ciba-Geigy
DEN 438	Epoxy novalac, semi-solid, WPE 178	Dow Chemical
EPON 828	Epoxy, liquid, WPE 190	Shell Chemical
EPON 1007	Epoxy, solid, WPE 2250	Shell Chemical
Eponol 55B40	Phenoxy, solid, AMW 200,000(40% N.V. in MEK)	Shell Chemical
Phenoxy PAHJ	Phenoxy, solid, AMW 30,000	Union Carbide

a) Source used. Other suppliers may be available.
b) Average molecular weight.
c) Weight per epoxide (average)

9.1.2) List of Hardeners and Catalysts

Trade Name	Description	Supplier[a)]
BDMA	Benzyldimethylamine, liquid	Sherwin-Williams
BRRA 4020	Phenolic resole, solid, Hydroxyl eq.wt.200	Union Carbide
BRJ-473	Phenolic resole (70% SP8010 in MEK)	Schenectady
BRZ-7541	Phenolic novalac, semi-solid,Hydroxyl eq.wt. 107	Union Carbide
Curing Agent D	2-Ethylhexoate salt of DMP-30, liquid tertiary amine	Shell Chemical
Cymel 245-8	Melamine formaldehyde resin, liquid	American Cyanamid
DETA	Diethylenetriamine	Dow Chemical
Dicy	Dicyandiamide, solid, eq.wt. 21	American Cyanamid
DMP-30	Tris(dimethylaminomethyl)-phenol,liquid	Rohm & Haas
EMI-24	2-Ethyl-4-methyl imidazole, liquid	O'Kura & Co.
Gallic Acid	3,4,5-Trihydroxybenzoic acid, solid	Harshaw
LR 082-82	Proprietary catalyst,solid tertiary amine	Hysol
Methylon 75108	Phenolic resole, liquid hydroxyl eq.wt.118	General Electric
MPDA	Metaphenylene diamine, solid,eq.wt. 27	Dow Chemical
Phosphoric Acid	85% Ortho phosphoric acid	Baker
Resinox P-97	Phenolic resole, liquid (50% N.V.)	Monsanto
SP-6700	Phenolic novalac, solid,hydroxyl eq.wt.182	Schenectady
SP-8010	Phenolic resole, solid	Schenectady
TPP	Triphenyl phosphine, solid	-
TPPEI	Triphenyl phosphine ethyl iodide,solid	-
Varcum 4326	Phenolic novalac,solid,hydroxyl eq.wt. 104	Reichhold
Varcum 5416	Phenolic resole, solid, hydroxyl eq.wt. 118	Reichhold

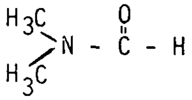
a) Source used. Other suppliers may be available.

9.1.3) List of Modifiers

Trade Name	Description	Supplier[a)]
Bisphenol A (BPA)	2,2'-Bis(p-hydroxyphenyl) propane, solid, hydroxyl eq.wt. 110	Shell Chemical Co.
Bisphenol S (BPS)	4,4'-Dihydroxydiphenyl sulfone, solid, hydroxyl eq.wt. 125	Crown Zellerbach
BR-127	Proprietary corrosion inhibiting primer	American Cyanamid
Calco Chinoline Yel. SS	Dye, solid	American Cyanamid
D.C. 840	Silicone flow control agent	Dow Corning
EA 9201	Proprietary CIP Primer	Hysol
EA 9210	Proprietary CIP Primer	Hysol
EA 9628	Proprietary 250°F curing structural adhesive tape	Hysol
Hycar CTBN	Carboxyl terminated butadiene acrylonitrile rubber, liquid carboxyl - 0.053 equiv./100 g.	B. F. Goodrich
Hydroquinone	1,4-Benzenediol solid, hydroxyl eq.wt. 55	Mallinckrodt
Nuosperse 657	Flow control agent, liquid (73% N.V.)	Nuodex Products
PC-1344 Defoamer	Flow control agent, semi-solid	Monsanto
Resorcinol	1,3-Benzenediol, solid, hydroxyl eq.wt. 55	Mallinckrodt
SR-82	Silicone flow control resin	General Electric
PEI-18	Polyethyleneimine	Dow Chemical
ETDP-234	Di-cumylphenoxy, ethylene, iso-stearoyl titanate	Kenrich Petrochemicals
TTR-27	Isopropyl, triricinoyl titanate	Kenrich Petrochemicals
TTOP-12	Isopropyl, tri(dioctylphosphate) titanate	Kenrich Petrochemicals
TTOPI-41B	Tetraisopropyl, di(dioctylphosphite) titanate	Kenrich Petrochemicals
GTDOPP-1385	Titanium di(dioctylpyrophosphate) oxyacetate	Kenrich Petrochemicals
Thixatrol ST	Organic thixotropic additive	National Lead
Thixatrol GST	Organic thixotropic additive	National Lead
MPA-MS	Organic thixotropic additive in mineral spirits	National Lead
MPA-1078X	Organic thixotropic additive in xylene	National Lead
Tenlo 70	Suspending aid	Diamond Shamrock

a) Sources used. Other suppliers may be available.

9.1.4) List of Solvents

Trade Name	Description	Source[a]
Butyl alcohol	n-Butanol	Baker
Butyl cellosolve	2-Butoxyethanol	Central Solvents
Cellosolve acetate	Ethylene glycol monomethyl ether acetate	Union Carbide
Diacetone alcohol (DAA)	4-Hydroxy-4-methyl-2-pentanone	Matheson Coleman & Bell
Ethyl alcohol (den.)	Ethanol (den.)	Shell Chemical
MEK	Methyl ethyl ketone	Shell Chemical
Methyl oxitol (MOX)	Ethylene glycol monomethyl ether	Shell Chemical
MIBK	Methylisobutyl ketone	Shell Chemical
THF	Tetrahydrofuran	American Drug & Chemical
Toluene	Methyl benzene	Mallinckrodt
Benzene		Mallinckrodt
Chloroform	$HcCl_3$	Mallinckrodt
Methylene chloride	CH_2Cl_2	Mallinckrodt
Dimethylformamide		Mallinekrodt
Methanol	CH_3 - OH	Mallinckrodt

a) Source used. Other suppliers may be available.

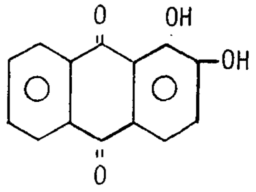
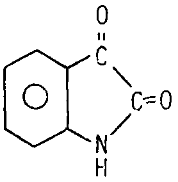
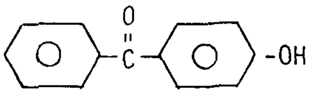
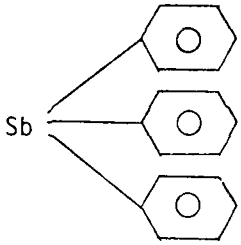
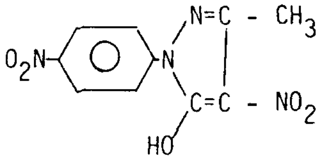
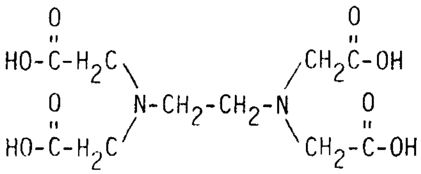
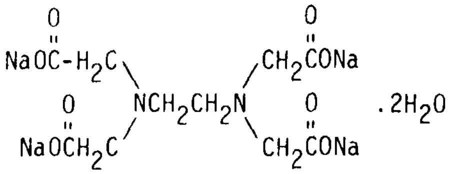
9.1.5) List of Organic and Inorganic Inhibitors and Chemicals[a]

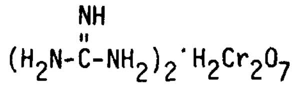
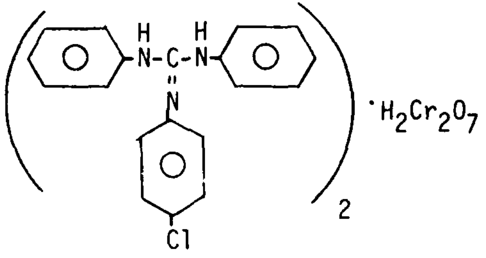
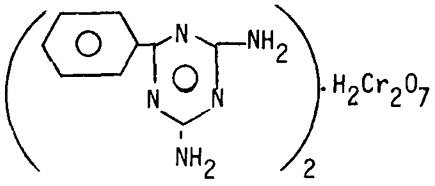
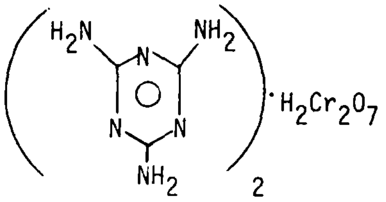
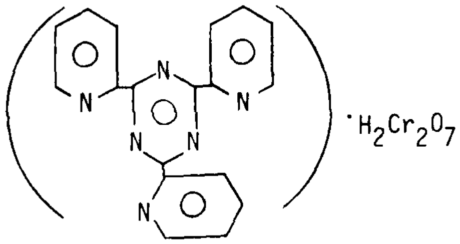
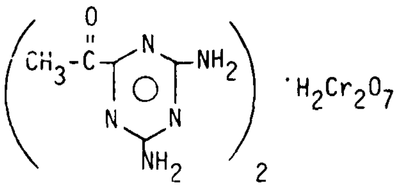
9.1.5.1) Inorganic Inhibitors

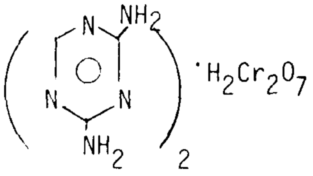
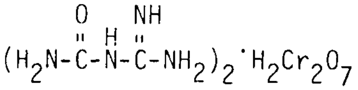
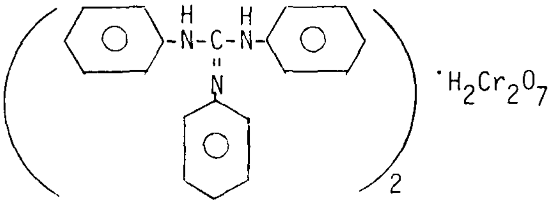
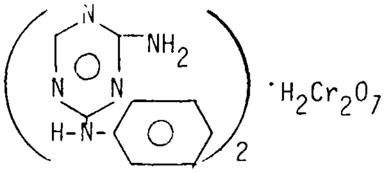
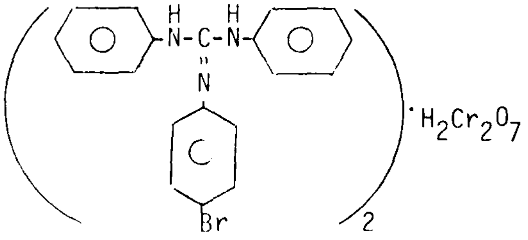
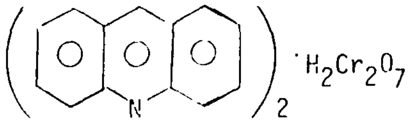
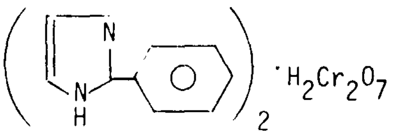
Trade Name	Description	Source
Cobalt Chromate	$COCrO_4$	Ventron Corporation
Zinc chromate	$ZnCrO_4$	ICN Pharmaceuticals
Calcium chromate	$CaCrO_4$	ICN Pharmaceuticals
Strontium chromate (X-2865)	$SrCrO_4$	Hercules
Barium chromate	$BaCrO_4$	Ventron Corporation
Potassium chromate	K_2CrO_4	Ventrol Corporation
Magnesium chromate	$MgCrO_4$	Allied Chemical
Magnesium dichromate	$Mg_2Cr_2O_7 \cdot 6H_2O$	Baker
Nickel chromate	$NiCrO_4$	ICN Pharmaceuticals
Zinc potassium chromate (Y-539D)	$ZnKCrO_4$	DuPont
Zinc molybdate	$ZnMoO_4$	Sherwin Williams
Ammonium molybdate	$(NH_4)_2 MoO_4$	Mallinckrodt
Potassium trioxalatochromate (III)	$K_3Cr(C_2O_4)_3$	Ventron Corporation

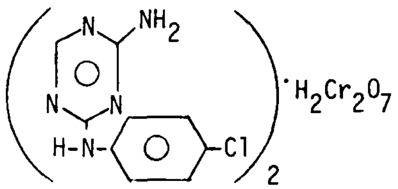
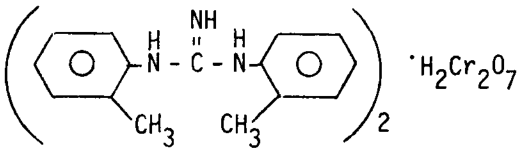
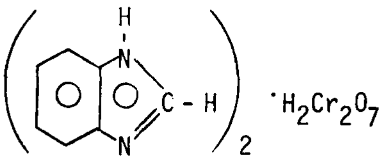
a) Source used. Other suppliers may be available.

9.1.5.2) Organic Inhibitors

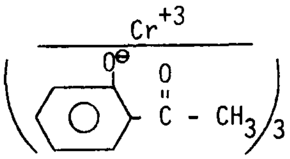
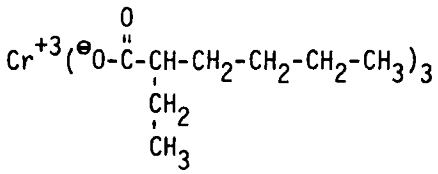
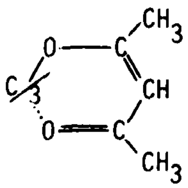
Name	Description	Source$^{a)}$
Alizarin		Aldrich Chemical
Isatin (2,3 indolinedione)		Aldrich Chemical
4-Hydroxybenzophenone		Aldrich Chemical
Triphenyl antimony		Aldrich Chemical
Picrolonic acid		Eastman Chemical
Ethylenediaminetetracetic acid		Aldrich Chemical
Ethylenediaminetetracetic acid, tetrasodium salt dihydrate		Aldrich Chemical

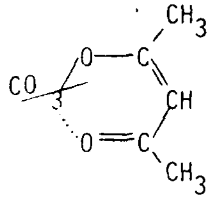
Name	Description	Source$^{a)}$
Guanidine dichromate	 $(H_2N\text{-}\overset{\overset{NH}{\|}}{C}\text{-}NH_2)_2\cdot H_2Cr_2O_7$	Hysol
1-(4-Chlorophenyl)-2,3-diphenylguanidine dichromate		Hysol
2,4-Diamino-6-phenyl-s-triazine dichromate (Benzoguanamine)		Hysol
Melamine dichromate		Hysol
2,4,6-Tri-(2-pyridyl)-s-triazine dichromate		Hysol
2,4-Diamino-6-acetyl-s-triazine dichromate (acetoguanamine)		Hysol

Name	Description	Source[a)]
2,4-Diamino-s-triazine dichromate		Hysol
Guanylurea dichromate	 $(H_2N-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-\overset{NH}{\overset{\|}{C}}-NH_2)_2 \cdot H_2Cr_2O_7$	Hysol
1,2,3-Triphenylguanidine dichromate		Hysol
2-Amino-4-anilino-s-triazine dichromate		Hysol
1-(4-bromophenyl)-2,3-diphenylguanidine dichromate		Hysol
Acridine dichromate		Hysol
2-Phenylimidazole dichromate		Hysol

Name	Description	Source a)
2-Amino-4-(4-chloroanilino)-s-triazine dichromate		Hysol
Diorthotoylguanidine dichromate		Hysol
Benzimidazole dichromate		Hysol

10.1.5.3) Organometallic Inhibitors

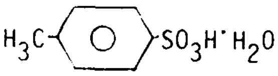
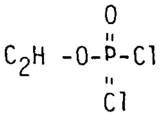
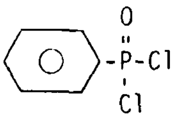
Name	Description	Source a)
Tris-(2-hydroxyacetophenono) Chromium		Eastman Chemical
Tris-(ethylenediamine) Chromium III sulfate	$[Cr(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$	Ventron Corporation
Chromium (III) 2-ethylhexanoate	 $Cr^{+3}(^{\ominus}O-\overset{\overset{O}{\|}}{C}-\underset{\underset{\underset{CH_3}{\vert}}{CH_2}}{\underset{\vert}{CH}}-CH_2-CH_2-CH_2-CH_3)_3$	Ventron Corporation
Chromium (III) 2,4 pentanedionate		Ventron Corporation

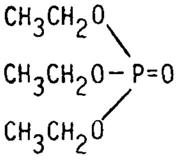
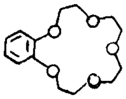
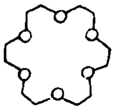
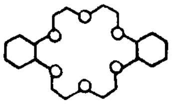
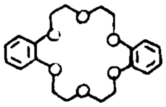
Name	Description	Source$^{a)}$
Cobalt (III) 2,4 pentanedionate		Ventron Corporation

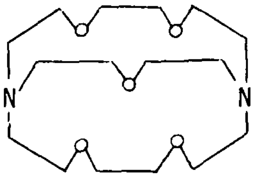
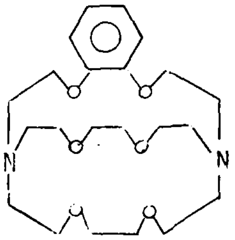
10.1.5.4) Chemicals

Diaminodiphenyl sulfone (Eporal)	(See Tables 1 & 2 For Structure)	Ciba Geigy
4,4'-Methylene-bis-(2-methylanthranilate)	"	Sherwin Williams
1,5-Diaminonaphthalene	"	Aldrich Chemical
3-Amino-1,2,4-triazole	"	Aldrich Chemical
Benzotriazole (Cobratec 99)	"	Sherwin Williams
Tolyltriazole (Cobratec TT-100)	"	Sherwin Williams
Pyridine	"	Aldrich Chemical
2,6-Diaminopyridine	"	Pfaltz & Bauer
8-Hydroxyquinoline	"	Aldrich Chemical
Acridine	"	Aldrich Chemical
3,6-Diaminoacridine	"	Aldrich Chemical
3,6-Bis-(dimethylamine)-acridine	"	Aldrich Chemical
2-Amino-4-morpholino-s-triazine	"	Pfaltz & Bauer
2,4-Diamino-s-triazine	"	Pfaltz & Bauer
2-Amino-4-cyclohexylamino-s-triazine	"	ICN Pharmaceuticals
2-Amino-4-anilino-s-triazine	"	ICN Pharmaceuticals
2-Amino-4-(4-chloroanilino)-s-triazine	"	ICN Pharmaceuticals
2,4-Diamino-6-chloro-s-triazine	"	Aldrich Chemical
2,4-Diamino-6-heptadecyl-s-triazine	"	ICN Pharmaceuticals
2,4-Diamino-6-acetyl-s-triazine (Acetoguanamine)	"	Aldrich Chemical
2,4-Diamino-6-stearyl-s-triazine (stearoguanamine)	"	ICN Pharmaceuticals
2,4-Diamino-6-(2'undecylimidazole-(1'))-ethyl-s-triazine	"	Shikoku Chemicals

Name	Description	Source a)
2,4-Diamino-6-phenyl-s-triazine (Benzoguanamine)	(See Tables 1 & 2 For Structure)	Pfaltz & Bauer
Melamine	"	Aldrich Chemical
Diallylmelamine	"	Pfaltz & Bauer
2,4,6-Tri-(2-pyridyl)-s-triazine	"	Aldrich Chemical
2,4,6-Triphenoxy-s-triazine	"	Aldrich Chemical
Biguanide	"	Pfaltz & Bauer
N-Cyclohexylbiguanide hydrochloride	"	Pfaltz & Bauer
N-B-Phenethylbiguanide hydrochloride	"	Pfaltz & Bauer
4-Chlorophenylbiguanide monohydrate	"	ICN Pharmaceuticals
Imidazole	"	Aldrich Chemical
2-Methylimidazole	"	Shikoku Chemical
1-Cyanoethyl-2-methylimidazole	"	Shikoku Chemical
1-Cyanoethyl-2-ethyl-4-methylimidazole	"	Shikoku Chemical
2-Undecylimidazole	"	Shikoku Chemical
1-Benzyl-2-methylimidazole	"	Shikoku Chemical
2-Phenylimidazole	"	Shikoku Chemical
Benzimidazole	"	Aldrich Chemical
2-(5-Ethyl-2-pyridyl)-benzimidazole	"	Sherwin Williams
Guanidine	"	Aceto Chemical
1,1,3,3-Tetramethylguanidine	"	Pfaltz & Bauer
Dicyandiamide	"	American Cyanamid
Guanylurea	"	Pfaltz & Bauer
Benzoylguanidine	"	Pfaltz & Bauer
Diphenylguanidine (Vulkacit D)	"	Mobay Chemical
Diorthotolylguanidine (Vulkacit DOTG)	"	Mobay Chemical
Triphenylguanidine	"	Aldrich Shemical
Urea	"	Baker

Name	Description	Source[a)]
Cetyltrimethylammonium bromide	(See Tables 1 & 2 for Structure)	Aldrich Chemical
Triethylenediamine (Dabco)	"	Houndry
Sym-diphenylthiourea	"	Pfaltz & Bauer
Dicyclohexylcarbodiimide	"	Aldrich Chemical
2,5-Dichloroaniline	"	Aldrich Chemical
2-Chloroaniline	"	Aldrich Chemical
3-Chloroaniline	"	Aldrich Chemical
4-Bromoaniline	"	Aldrich Chemical
4-Chloroaniline	"	Aldrich Chemical
Phenylanthranilate	"	Sherwin Williams
Aniline	"	Baker
p-Phenylenediamine	"	Aldrich Chemical
4,4'-Diaminodiphenylether	"	Pfaltz & Bauer
m-Toluidine	"	Aldrich Chemical
p-n-Butylaniline	"	Aldrich Chemical
p-Anisidine	"	Pfaltz & Bauer
p-Toluenesulfonic acid monohydrate		Aldrich Chemical
Ethyl dichlorophosphate	 $C_2H\text{ -O-}\overset{O}{\underset{Cl}{P}}\text{-Cl}$	Aldrich Chemical
Titanium IV butoxide	$[(CH_3)_2CHCH_2O]_4Ti$	Ventron Corporation
Phenylphosphonyl chloride		Ventron Corporation
Phosphorous (V) trichloride	$POCl_3$	Ventron Corporation
Chromium trioxide	CrO_3	Mallinckrodt
Potassium Iodide	KI	Mallinckrodt

Name	Description	Source[a]
Mercuric oxide	HgO	Mallinckrodt
Aluminum chloride	$AlCl_3$	Mallinckrodt
Potassium dichromate	$K_2Cr_2O_7$	Mallinckrodt
Triethyl phosphate	 $(CH_3CH_2O)_3P=O$	Aldrich Chemical
Acetic acid	CH_3COOH	Baker
Hydrochloric acid	HCl	Baker
Copper acetate	$Cu(CH_3COO)_2$	Mallinckrodt
Potassium hydroxide	KOH	Mallinckrodt
Sulfuric acid	H_2SO_4	Baker
Sodium hydroxide	NaOH	Mallinckrodt
Sodium thiosulfate	$Na_2S_2O_3$	Ventron Corporation
Sodium dichromate	$Na_2Cr_2O_7$	Mallinckrodt
Monobenzo-15-crown-5 (2,3-benzo-1,4,7,10,13-pentaoxacyclopentadecane)		E. Merek & Company
18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane		Aldrich Chemical
Dicyclohexyl-18-crown-6 (2,3,11,12-Dicyclohexyl-1,4,7,10,13,16-hexaoxacyclooctadecane)		Aldrich Chemical
Dibenzo-18-crown-6 (2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene)		E. Merck & Company

Name	Description	Source a)
Kryptofix 221 (4,7,13,16,21-Pentaoxa-1,10-diazobicyclo-8,5,5-tricosane)		E. Merck & Company
Kryptofix 222B (5,6-Benzo-4,7,13,16,21,24-hexaoxa-1,10-dizobicyclo-8,8,8-hexacosane)		E. Merck & Company

a) Source used. Other suppliers may be available.

9.2) SYNTHESIS OF MATERIALS

9.2.1) Inhibitors

9.2.1.1 Preparation of Diphenylcarbodiimide

Mercuric oxide (47.6 g, 0.22 moles) was suspended in 300 ml. of methylene chloride in a three neck 500 ml round bottom flask. Diphenylthiourea (45.6 g, 0.20 moles) was added slowly over a 30 minute period. The mixture was heated to reflux for 15 minutes, filtered through celite (Johns Manville filtering aid) and dried by gravity filtration through magnesium sulfate. The ethylene dichloride was evaporated on a steam bath under a stream of dry nitrogen. The carbodiimide was vacuum distilled at 120°C and 0.2 mm mercury to give an 18 g yield (47%).

9.2.1.2) Preparation of 1-(4-Bromophenyl)-2,3-Diphenylguanidine

A mixture of diphenylcarbodiimide (11.4 g, 59 m moles) in 200 ml of methylene chloride was cooled to 0°C. Aluminum chloride (7.8 g, 59 m moles) was added while the mixture was kept at 0°C. A solution consisting of 9.3 g 4-bromoaniline (54 m moles) in 50 ml of methylene chloride was slowly added while agitation was continued. After 10 minutes, the mixture was made basic with sodium hydroxide-water solution, the methylene chloride layer was removed using a separatory funnel and filtered through magnesium sulfate. The methylene chloride was evaporated on a steam bath to give a viscous amber liquid. Dilute HCl was added and the mixture boiled. The white solid which formed was added to 1500 ml of distilled water, heated to boiling, and filtered hot. The solution was boiled down to 500 ml and cooled to 5°C. The separated solid was filtered and dried at 120°F to give an 8.5 g yield (43%) of white crystals.

9.2.1.3) Preparation of Melamine Dichromate (Compound 25)

Concentrated hydrochloric acid (8.3 g, 0.10 moles) was added to a mixture of melamine (12.6 g, 0.10 mole) in 200 ml distilled water. The mixture was agitated for 15 minutes. A solution of chromium trioxide (10.5 g, 0.105 moles)in 50 ml of distilled water was slowly added to the melamine hydrochloride salt with rapid agitation to form yellow crystals. The solution was cooled to 40°F and filtered. The crystals were dissolved in boiling water, the solution was hot filtered, cooled to 40°F, and filtered to give an 86% yield of orange crystals.

1,2,3-Triphenylguanidine dichromate was prepared as indicated for melamine dichromate except the hydrochloride salt solution was cooled to 5°C before addition of the chromium trioxide.

9.2.1.4) Preparation of 2-Phenylimidazole Dichromate (Compound #15)

A solution of sodium dichromate (3.15 g, 12.0 m moles) in 50 ml of distilled water was added slowly with agitation to a mixture of 2,4-diamino-s-triazine (1.95 g, 23.5 m moles), concentrated hydrochloric acid (1.95 g, 23.5 m moles), and 200 ml of distilled water. Orange crystals formed immediately after addition of sodium dichromate solution. The solution was cooled to 40°F overnight, filtered, and recrystallized in boiling water to give 3.2 g yield (63%) of a red orange crystalline product.

9.2.1.5) Preparation of Crown Ether Chromate Complex

Potassium dichromate (0.33 g, 1.2 m moles) was slowly added to a solution of Kryptofix 222B (5,6-benzo-4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-8,8,8-hexacosane) (1.0 g, 2.4 m moles) in 10 ml dimethylformamide with a dry nitrogen blanket and agitation. The mixture was stirred until all potassium dichromate has gone into solution and formed the complex.

9.2.1.6) Preparation of Potassium Alizarinate Crown Ether Complex

A stirred suspension of alizarin (2.4 g, 0.10 m moles), in 100 ml of methanol was treated with 0.66 g potassium hydroxide (0.66 g, 10.0 meq.) dissolved in 50 ml of methanol. 18-Crown-6 (1,4,7,10,13,16-hexacyclo octadecane) (4.0 g, 11 m moles) was added and the mixture heated on a steam bath for 15 minutes, hot filtered, and the methanol was evaporated on a rotary evaporator to give a purple solid.

9.2.1.7) Attempted Preparation Chromium VI-Containing Epoxide Resin

A solution of chromium trioxide in water was added dropwise to a solution of EPON 828 in acetone to give a green precipitate indicating oxidation of Cr^{+6}.

9.2.1.8) Attempted Preparation of Phosphate Group-Containing Epoxide Resin

p-Toluenesulfonic acid and triethylphosphate were added to a solution of EPON 1001 in acetone. The mixture was refluxed for seven hours. Infrared spectrophotometry showed no evidence of reaction.

9.2.2) Formulation and Preparation Of Model Diphenolic Adducts Of Epon 828

A. Formulations:

	Concentration (Parts By Weight				
Ingredients*	Model #4	Model #4	Model #5	Model #6	Model #7
Epon 828	100.0	100.0	100.0	100.0	100.0
Hycar CTBN	-	-	-	-	20.0
Resorcinol	18.0	-	-	-	-
Hydroquinone	-	16.4	-	-	-
Bisphenol A	-	-	34.0	-	-
Bisphenol S	-	-	-	37.3	-
TPP Catalyst	0.25	0.25	0.25	0.1	0.25

*See Section 10.1) for description of ingredients.

B. Methods of Preparation (3 Pound Batch)

Adducts with resorcinol, hydroquinone and bisphenol A were prepared in like manner as follows: Charge Epon 828 to an open one-half gallon insulated metal or glass reaction vessel capable of quick cooling. Insert a suitable bow-tie or screw type stirrer into the center of the resin so that the blade is about one-half inch from the bottom of the vessel. Under a fume hood, begin heating the resin, using slow stirring to keep the addition of air to a minimum. When the resin reaches approximately 100°C, add the diphenol and continue stirring until all is dissolved and the mixture is relatively free from air bubbles. At 110-115°C, add the catalyst and allow the temperature to rise at about 1-2°C per minute while maintaining good circulation of the mixture by adjusting the stirrer speed with increasing pot temperature. When the mixture reaches 140-150°C an exothermic reaction may occur and the mixture should be controlled to a maximum of 165-180°C, then cooled to 150°C and the heating continued for at least 30-60 minutes. While the mixture is warm, pour onto a sheet of polyethylene coated kraft paper or teflon to cool. The adduct may be broken up into smaller sections and stored at ambient temperature.

Adducts with bisphenol A and Hycar CTBN were prepared as follows: Charge Epon 828 and CTBN as described above and heat the mixture to 110-115°C. Add the catalyst and heat for 30 minutes at 110-125°C, during which period the color of the mixture will change from amber to deep red. Add bisphenol A and react as described for the other adducts, then pour, cool and store.

Adducts with bisphenol S were prepared as follows: Charge 95% of the Epon 828 to the reaction vessel and heat with stirring to 70-80°C. Add the catalyst, in this case TPPEI (see Appendix description) which has been pulverized and mill ground into the remaining 5% Epon 828, and continue heating to 85-90°C until the catalyst has completely dissolved. Add 1/3 of the bisphenol S and raise the temperature at 1-2°C per minute until the first increment has dissolved (about 135-145°C). Add the second increment (1/3 by weight) and continue heating at 150-160°C until dissolved. Finally add the third increment of bisphenol S, heat at 150-170°C until dissolved and then for an additional 30-60 minutes at 150-160°C. Pour, cool and store.

Note: This adduct was initially prepared by reaction in butyl cellosolve, however, this prevented the preparation of void-free castings for bulk property measurements.

9.3) FORMULATION

The primer vehicles evaluated in this program were prepared using combination of resins, hardeners, catalysts and modifiers dissolved in suitable solvent systems, all of which are listed in Section 10.1 of this Appendix. Specific ingredient ratios are discussed throughout the body of this report with further reference to various tables which follow this Appendix. Generally, all vehicles examined were prepared by charging the correct weight of solid ingredients to a paint can, adding the solvent and agitating the mixture on a paint shaker until all of the solids were completely dissolved. When necessary, the solution was filtered through a 100 mesh stainless steel screen to remove dirt or minute polymer gels. No account was made for losses resulting from the filter step since such losses were negligible. All vehicles were 20% solids except Models 8 and 9 which were approximately 10%. BR-127 Primer (10% solids) was removed from cold storage, the chromate pigment separated by filtration and the filtrate (vehicle solution) returned to storage for later use in control tests. No dyes or additives were used to modify this vehicle.

In preparing the pigmented primers, a standard method was used, whereas the pigment was ground in a procelain pebble mill for 16-20 hours, washed three times, and "let down" with a solution containing the remaining ingredients. The standard formulation for a primer containing 0.11 pigment/binder ratio was:

Mill grind -	Adduct or solid resin	100 pbw
	Methylethyl ketone (MEK)	100
	Diacetone alcohol (DAA)	50
	Pigment (inorganic)	100
		350
Wash solution -	MEK	500
	DAA	500
		1000
Let down solution -	additional adduct(s), resins, hardener, catalyst and additives	800
	MEK	4350
	Tetrahydrofuran (THF)	2700
	DAA	800
		8650

% Non-volatiles - 10.0

When incorporating pigments in the BR-127 filtrate, the pigments were roller milled into 40% of the filtrate for 16 hours and then washed with the remaining 60%. It is recognized that the resin/hardener/catalyst system was milled simultaneously and deviates from the actual manner in which BR-127 (or any other primer of this type, for that matter) is made. However, mill grinds were considered acceptable when comparing them with grinds in other vehicles. Also, the reactivity of the vehicle as measured by MEK resistance and scratch hardness after bake, did not appear to change, as a result of the out-time or grinding action during the milling procedure.

All primers were refrigerated within four hours after final blending and normally not used if allowed to stand at room temperature longer than 48 hours.

9.4) TEST METHODS

9.4.1) Inhibitors

9.4.1.1) Chromium VI Titration Method

I. Preparation of Standards

A. Preparation of sodium thiosulfate solution ($Na_2S_2O_3$).
1. Charge 15.8 gr. $Na_2S_2O_3$ to a liter volumetric flask.
2. Add DI water to 1 liter on flask. Dissolve by shaking. This makes an approximately 0.1 N solution.

B. Standard Solution
1. Charge the following to a 500 ml Erlenmeyer flask.

DI Water	200 gm
H_2SO_4 (36N)	62 gm
$Na_2Cr_2O_7$	18 gm

Mix well with stirring.

C. Preparation of Starch Solution -0.2%.
1. Bring 1000 ml of distilled water to boiling.
2. Add starch slowly with stirring.

D. Method of Standardizing $Na_2S_2O_3$ Solution (run in duplicate).
1. Pipette 10 ml of diluted solution into Erlenmeyer flask containing 50 ml of DI H_2O.
2. Add one gm potassium iodide, 12.5 ml of 10% sulfuric acid (dilute concentrated H_2SO_4, nine parts DI H_2O to one part H_2SO_4).
3. Titrate with approximately 0.1N $Na_2S_2O_3$ to green, then add approximately one ml of 0.2% starch solution.
4. Titrate this solution with $Na_2S_2O_3$ to a faint blue color. Record ml $Na_2S_2O_3$ used to neutralize.

II. Sample Titration

Chromium VI analysis - Weigh 0.15 to 0.20 g of organic chromate salt into an Erlenmeyer flask. Add 10 ml of DI water H_2SO_4 solution at the ratio shown in IB above.

Titrate as in method ID above. Determine Chromium VI content as follows:

$$\%\ Cr^{+6} = \frac{(V\ S_2O_3^{=})\ (N\ S_2O_3^{=})\ (52)}{3X\ (\text{Sample weight in grams})\ (10)}$$

Stoichiometry of reaction:

$$Cr_2O_7^{=} + 14\ H^{+} + 6I^{-} \longrightarrow 3I^{2} + 2\ Cr^{+3} + 7\ H_2O$$

$$I_3^{-} + 2\ S_2O_3^{=} \longrightarrow 3I^{-} + S_4O_6^{=}$$

9.4.1.2) Solubilities of Organic Chromate Salts

A saturated solution of the organic chromate salt was made with 50 ml of the appropriate solvent at 150°F, cooled to 25°C and allowed to equilibrate overnight. A 10.0 ml aliquot was removed with a pipette and evaporated in a tared beaker and weighed back to determine the solubility in grams/ 10 ml of solvent at 25°C. The result multiplied by 10 gave the solubility in grams/ 100 ml of solvent at 25°C.

9.4.2) Bulk Properties Tests

9.4.2.1) Tensile Test

The bulk tensile properties were determined per ASTM D 638-64T(10). Manufacture of the 1/8" thick blanks required development of a special technique. The resin system and the novolac curing agent were melted together at 90-100°C. At this stage, the mixture had approximately 30 minutes stability before it became unworkable. Deletion of the TPPEI catalyst reduced this working life to about 10 minutes. This shortened work life precluded any deaeration of the molten system. In addition, the high viscosity of the systems required the high temperature. Consequently, the TPPEI catalyst was milled into an equal amount of EPON 828 to reduce its particle size and reduce the time necessary to intimately mix it into the molten resin. Therefore, the catalyst was quickly mixed into the resin system and then the entire mixture quickly poured into a cool, release surface to stop the reaction. The resulting intermediate product, in most instances, except models number 1 and 3, was a friable solid.

This material was ground in a mortar and pestle and passed through a 60 mesh sieve. This was done to eliminate the larger voids in the resin system. The sieved powder was then placed in an open mold and sintered, under vacuum, at 120°C. This sintering process tended to eliminate smaller voids before the powder coalesced. Upon coalescence, the mold was removed from the vacuum oven and placed in a circulating air oven for cure. In all instances except Model #7, a void-free casting resulted. The heterophase particle precipitation in Model #7 resulted in an opague casting.

This sintering process was not possible with Models #1 and #3. The intermediate, pre-powdered stage of Model #1 (the phenoxy-DEN 438 resin system) was a very tough material which could not be powdered even at -55°C (dry ice). Both a mortar and pestle and a Wiley Mill were tried with powdered dry ice with no success. Model #3 (the EPON 828-DEN 438 resin system) was liquid at temperatures enough below the cure temperature that it was degassed as a fluid. The cured castings of Model #3 were also transparent and void-free.

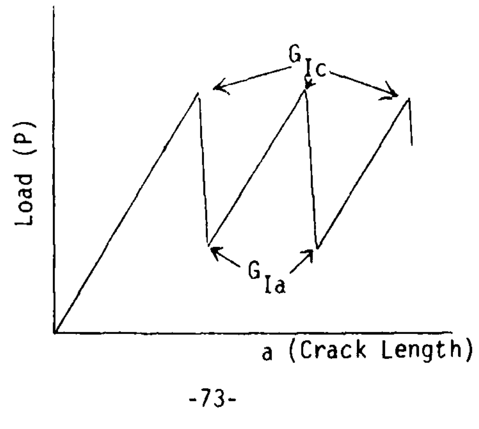
9.4.2.2) Crack Toughness Test

There are two test methods available for the determination of this parameter; cantilevered and tapered cantilevered beams[35]. The former requires measurement of the crack length as the torque moment changes as the crack progresses (i.e. - the beam has variable compliance.) The measurement of the crack length adds a significant amount of uncertainty to the measurements in some systems. The latter method uses a tapered, constant compliance beam and the crack toughness can be determined from the load and beam geometric factor alone. This latter method was chosen as it offered the greatest accuracy for the variable types of systems to be used.

Two types of beams are available for use.[33] The first is machined out of a sizeable blank of the cured bulk materials. The second uses metal beams bonded together with the material of interest. The second method was chosen for economic reasons. The beams must be machined to a complex curve to have constant compliance. This was beyond the economic scope of the contract. The metal beams (2024-T351 aluminum) had a less complex curve (Figure 12) due to the material's higher modulus, which could be more easily machined and could generally be re-used.

The test specimens were manufactured by placing -60 mesh powder, produced as in Section 5.0, onto both halves of the beam and sintering under vacuum. The two halves were then assembled using shrink tape and cured, ultimately at 350°F. The bondline thickness was shimmed to 10 mils. This was done since the bondline thickness affects crack toughness as pointed out by Bascom[33]. He found that the crack toughness decreased significantly at low thicknesses when testing rubber heterophase systems. He hypothesized that this was due to the fact that the specific volume of resin is necessary for complete development of the toughening effect of the rubber particle. At the lower bond line thicknesses, this required volume is not available.

The crack toughness was determined in opening Mode I in both the critical (G_{Ic}) and arrest (G_{Ia}) locations. These are defined on the Load (P) vs. crack length (a) curve by those loads at which cracking initiates and arrests. This is shown on the following curve:



9.4.3) Primer and Adhesive Tests

9.4.3.1 Thickness Guage Verification

Definition of the true primer thickness was important to the progress of this work. To this end sprayed panels were prepared and the primer thickness measured using various techniques including the Dermitron (eddy current method), a micrometer on known thickness foil, chem-milled primer films, and weight-density methods.

For correlations between the Dermitron and the micrometer, the same panels that were measured using the Dermitron thickness tester were then placed in a 30% caustic bath and maintained at approximately 90°C until the metal was dissolved. The remaining film was carefully rinsed, blotted, dried at 180°F and measured for thickness using a Starrett stage micrometer. For direct micrometer measurements, 2 x 2 in. pieces of 0.003 in. aluminum foil were fastened to a stiffener plate and sprayed to various thicknesses, baked and measured with the micrometer. Weight-density panels were dried and weighed prior to coating. The coated panels were then baked, re-weighed and the film thickness determined from the pre-measured density of the resin. The table below shows an acceptable correlation between methods and justified confidence in the Dermitron Gauge which was used for the majority of the primer thickness measurements.

Average(*) Coating Thickness (mils)

Dermitron	Chem-Mill	Foil	Weight-Density
0.10	-	-	0.09
0.20	-	0.40	0.22
0.25	-	0.46	-
0.26	-	-	0.25
0.27	0.52	-	0.27
0.29	-	-	0.22
0.31	-	-	0.30
0.39	-	0.83	-
0.40	-	-	0.38
0.42	0.45	-	-
0.46	-	-	0.42
0.47	-	-	0.43
0.50	-	0.95	-
0.51	0.45	-	0.54
0.52	-	-	0.54
0.61	0.60	-	-
0.56	-	1.2	-
0.78	-	1.1	0.8
0.87	0.91	-	-
0.98	0.97	-	-
1.00	-	-	1.05
1.38	-	-	1.40
1.46	-	1.54	-
1.52	1.52	-	-
1.87	-	-	1.93
1.95	-	1.94	-

* 5 readings

9.4.3.2) MEK (Methyl Ethyl Ketone) Resistance Test

This test was used to measure the degree of cure of primer coated panels. The coating was rubbed hard by hand, back and forth rapidly, using an industrial wiper cloth (i.e. Kimwipe) which had been saturated with methyl ethyl ketone (MEK). The coating was rated for MEK resistance as follows:

None - < 5 double rubs
Poor - 5-24 double rubs
Fair - 25-50 double rubs
Good - > 50 double rubs (film marred)
Excellent- > 50 double rubs (film unaffected)

9.4.3.3) Pencil Scratch Hardness Test

A set of Eagle Turquoise drawing pencils ranging in hardness from 1 - 8H were prepared by stripping away the wood approximately 3/8 inch without damaging the lead. The lead tip was squared by moving it across 600 grit paper in a verticle manner. Primer coated test panels were placed securely in a horizontal position and pencils of increasing hardness pushed across the panel surface at a 45° angle until one was found which cut or scratched the coating. The number of that pencil was used to express the hardness.

9.4.3.4) Solvent Resistance Test

Three primer coated test panels were tested for pencil hardness at 75°F and then immersed for 7 days in selected solvents. The containers were air tight. After the immersion cycle the panels were removed, lightly wiped dry and allowed to stand at 75°F, 50% relative humdity for at least 1 hour and re-tested for pencil hardness.

9.4.3.5) Moisture Equilibrium Test

This test is designed to measure the degree of moisture absorbtion of primer and paints by spray or dip coating a pre-weighed metal panel, curing and exposing the panel to high humidity or total immersion in deionized water. The two-fold advantage of the test was the ability to (1) test rapidly and (2) to measure the effect of thin film cures on systems applied from solvent.

Three 4 x 6.25 x 0.02 inch 2024-T3 bare aluminum panels were used for each test primer. A 3/32 inch diameter hole was drilled in one corner where the panel was to be subjected to high humidity by hanging. The panels were scribed for reference and all frayed aluminum scraped away from the edges. The panels were then vapor degreased in trichloroethane and etched with standard dichromate-acid solution (other surface treatments may be used). Panels were then desiccated, weighed to the nearest 0.1 mg and the thickness measured (nearest 0.1 mil). The panels were then spray coated with the test primers to a dry film thickness of approximately 2.5-5.0 mils per side using controlled flash techniques to build up bubble-free coatings. The panels were then cured and the total film thickness and weight calculated.

The cured coated panels were then immersed in a 120°F deionized water bath by inserting in slotted PVC racks which held the panels 0.5 inches apart. Periodically the panels were removed to a room temperature D.I. water tray and each weighed to determine the weight gain. Prior to weighing, the panels were blotted dry twice between a folded paper towel and two metal platens, the top platen applying a 0.02 psi pressure. The panel was then weighed within 30 seconds and the % weight gain determined.

9.4.3.6) MMCD Peel Lay-up, Cure and Test

2024-T3 Clad aluminum skins, 0.020 inches thick, 5 x 14 inch dimensions were degreased and etched for 12-15 minutes in a 150-160°F solution consisting of the following:

Deionized H_2O	1 l.
Sodium dichromate ($Na_2Cr_2O_7 \cdot 2\ H_2O$)	60 g/l of H_2O
Sulfuric acid, conc.	300 g/l of H_2O
Bare Aluminum, 2024 Alloy	1.5 g/l

After tap water rinsing and drying at 120-140°F, the panels were then anodized at 10 ± 1 volts for 20-25 minutes in a 65-85°F solution consisting of the following:

Deionized H_2O	3.78 l
Phosphoric acid H_3PO_4, 75%	454 g

After tap water rinsing, drying at 160°F (maximum) and checking the quality of the anodic coating, panels were primed within 8-24 hours.

<u>Spray Technique</u> - In this and other tests where the primers were applied by hand spraying, the following conditions were used with modifications as required:

Spray gun	Devilbiss JGA-502
Gun settings	Air: 3-1/2 turns open Fluid: 4 turns open
Air pressure	30 psi
Distance	6 - 8 inches

<u>Lay-Up Technique</u> - After baking the primed panels, they were assembled with a matched sheet of 0.063 inch thick aluminum of the same alloy but which had been etched with the dichromate-acid solution only. Between the skins was inserted a matched strip of .045-.060 psf EA 9628 adhesive containing a knitted nylon fabric. A 3 inch long, 1-mil Mylar starter strip was inserted over the adhesive along the width of one end of the assembly. Two of these assemblies were then stacked together, four stacks placed 1/2 inch apart on a 1/2 inch caul plate and a 0.5 x 5 x 14 inch aluminum pressure plate placed over each stack. The caul plate containing the four stacks was covered with bleeder, bagging and sealing material to form a vacuum bag assembly to which approximately 25 inches of mercury vacuum was applied.

<u>Curing Schedule</u> - The vacuum bagged assembly(s) was placed in an electric autoclave and the chamber pressurized to approximately 25 psi. At this point, the bags were checked for leaks and then vented to the atmosphere. The autoclave was then pressurized to 50 psi and programmed for a heat rise of 60 minutes to 250° + 5°F

followed by the applicable cure time. Cool down was approximately 30 minutes to 140°F after which the chamber was de-pressurized and the assemblies removed.

Testing of Specimens - The cured 5 x 14 inch assembly was trimmed and cut into four 1 x 14 inch specimens. The average bondline thickness was measured and each specimen tested on an Instron Tester with a drum assembly as prescribed by ASTM D 1781. Calculations were for 1-inch wide specimens.

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TABLE 1. ORGANIC CHROMATE SALTS

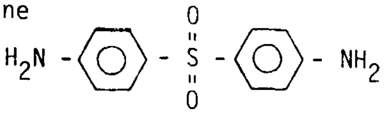
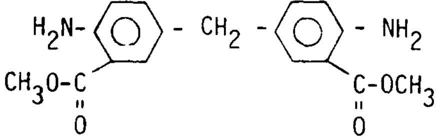
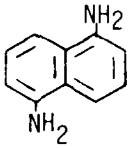
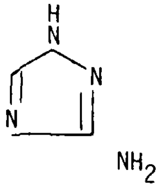
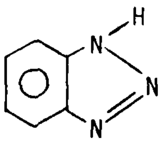
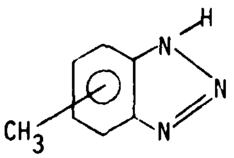
Compound Number	Base Compound	Base Structure	Synthesis Comments	Storage Stability
I. Primary Aromatic Amines				
1	Diaminodiphenyl sulfone		Oxidation During Reaction	-
2	4-4'-Methylene-bis-(2-methylanthranilate)		Oxidation	-
3	1,5-Diaminonapthalene		Oxidation	-
II. Triazoles				
4	3-amino-1,2,4-triazole		No Chromate Salt Formed	-
5	Benzotriazole		Orange Solid	Stable Very Strong Oxidizing Agent
6	Tolyltriazole		Red Oil	Unstable

TABLE 1. Continued

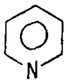
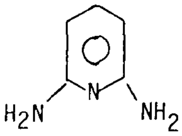
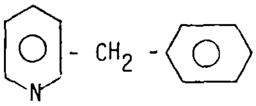
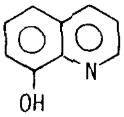
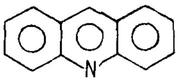
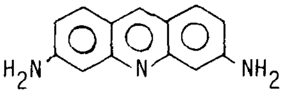
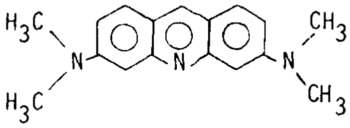
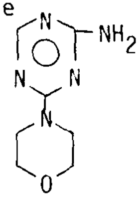
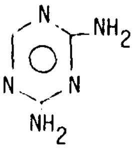
Compound Number	Base Compound	Base Structure	Synthesis Comments	Storage Stability
III. Pyridines				
7	Pyridine		Red Solid	Unstable
8	2,6-Diaminopyridine		Oxidation	-
9	2-Benzylpyridine		Red Oil	Unstable
10	8-Hydroxyquinoline		Oxidation	-
IV. Acridines				
11	Acridine		Orange Solid	Stable
12	3,6-Diaminoacridine		Yellow Solid	Stable
13	3,6-Bis-(dimethylamine)-acridine		No Salt Formed	-
V. 2 & 2,4-Diamino-s-triazines				
14	2-Amino-4-morpholino-s-triazine		Red Oil	Unstable
15	2,4-Diamino-s-triazine		Red Solid	Stable

TABLE 1. Continued

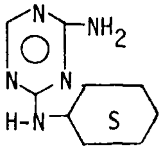
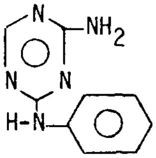
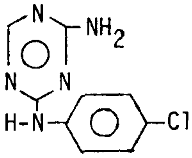
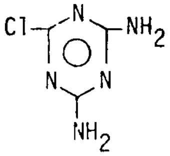
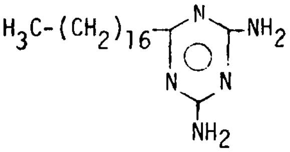
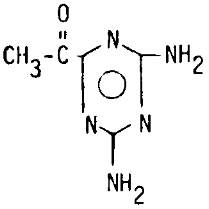
Compound Number	Base Compound	Base Structure	Synthesis Comments	Storage Stability
16	2-Amino-4-cyclohexylamino-s-triazine		No Salt Formed	-
17	2-Amino-4-anilino-s-triazine		Orange Solid	Stable
18	2-Amino-4-(chloroanilino)-s-triazine		Orange Solid	Stable
VI. Guanamines				
19	2,4-Diamino-6-chloro-s-triazine		No Salt Formed	-
20	2,4-Diamino-6-heptadecyl-s-triazine		Yellow Solid	Very Photosensitive
21	2,4-Diamino-6-acetyl-s-triazine (Acetoguanamine)		Red Solid	Photosensitive

TABLE 1. Continued

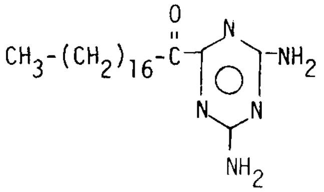
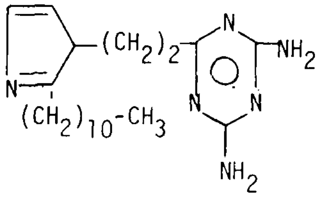
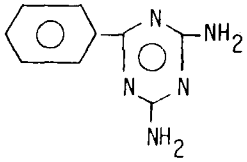
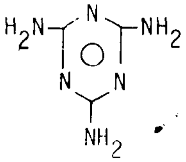
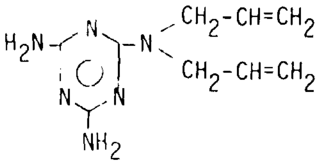
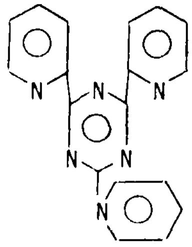
Compound Number	Base Compound	Base Structure	Synthesis Comments	Storage Stability
22	2,4-Diamino-6-stearyl-s-triazine (Stearoguanamine)		Orange Solid	Very Photosensitive
23	2,4-Diamino-6-(2'-undecylimidazole-(1'))-ethyl-s-triazine		Yellow Solid	Photosensitive
24	2,4-Diamino-6-phenyl-s-triazine (Benzoguanamine)		Yellow Solid	Photosensitive
VII. 2,4,6-s-triazines				
25	Melamine		Red Solid	Stable
26	Diallylmelamine		Red Solid	Unstable
27	2,4,6-Tri-(2-pyridyl)-s-triazine		Red Solid	Photosensitive

TABLE 1. Continued

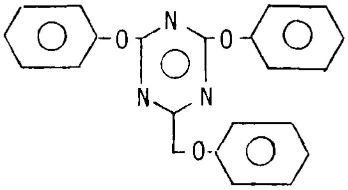
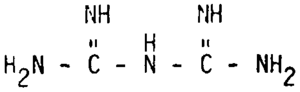
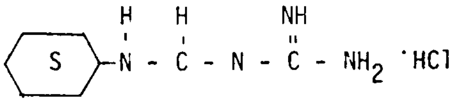
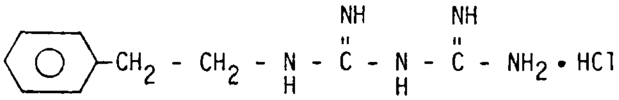
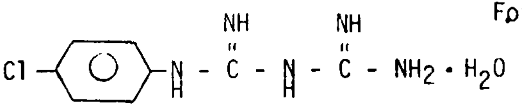
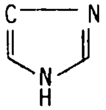
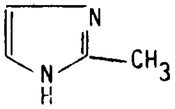
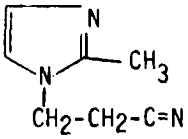
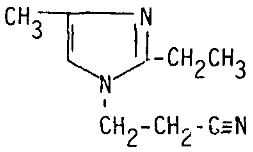
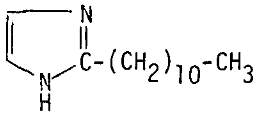
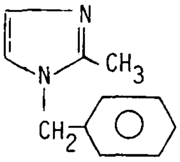
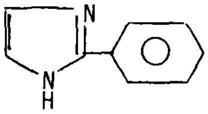
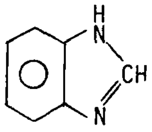
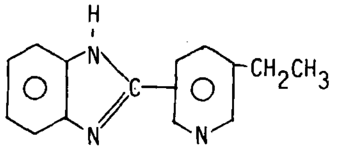
Compound Number	Base Compound	Base Structure	Synthesis Comments	Storage Stability
28	2,4,6-Triphenoxy-s-triazine		No Salt Formed	-
VIII. Biguanide				
29	Biguanide	 $H_2N-\overset{\overset{NH}{\parallel}}{C}-\overset{H}{N}-\overset{\overset{NH}{\parallel}}{C}-NH_2$	No Salt Formed	-
30	N-Cyclohexylbiguanide hydrochloride		No Salt Formed	-
31	N-B-Phenethylbiguanide hydrochloride		Oxidation	-
32	4-Chlorophenylbiguanide monohydrate		No Salt Formed	-
IX. Imidazoles				
33	Imidazole		No Salt Formed	-
34	2-Methylimidazole		No Salt Formed	-
35	1-Cyanoethyl-2-methylimidazole		No Salt Formed	-

TABLE 1. Continued

Compound Number	Base Compound	Base Structure	Synthesis Comments	Storage Stability
36	1 Cyanoethyl-2-ethyl-4-methylimidazole		No Salt Formed	-
37	2-Undecylimidazole		No Salt Formed	-
38	1-Benzyl-2-methylimidazole		Dark Red Oil	Unstable
39	2-Phenylimidazole		Orange Solid	Photosensitive
40	Benzimidazole		Orange Solid	Stable
41	2-(5-Ethyl-2-pyridyl)-benzimidazole		Oxidation	-

X. Guanidines

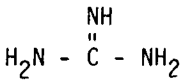
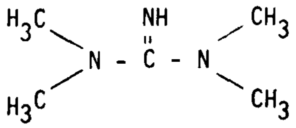
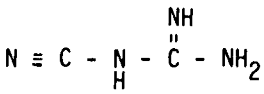
Compound Number	Base Compound	Base Structure	Synthesis Comments	Storage Stability
42	Guanidine	 $\mathrm{H_2N-\overset{NH}{\overset{\parallel}{C}}-NH_2}$	Red Solid	Stable
43	1,1,3,3-tetramethylguanidine		No Salt Formed	-
44	Dicyandiamide	 $\mathrm{N\equiv C-\underset{H}{N}-\overset{NH}{\overset{\parallel}{C}}-NH_2}$	No Salt Formed	-

TABLE 1. Continued

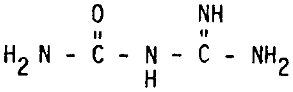
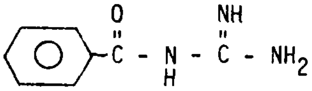
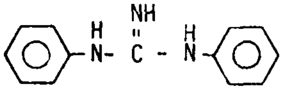
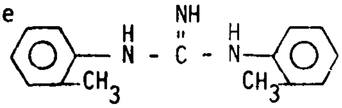
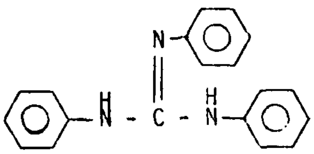
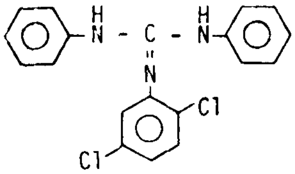
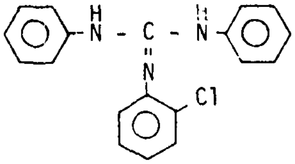
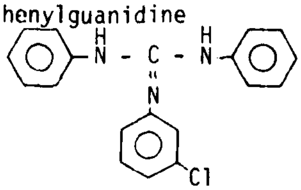
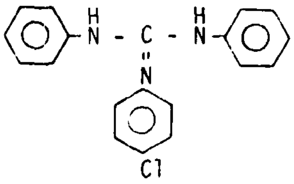
Compound Number	Base Compound	Base Structure	Synthesis Comments	Storage Stability
45	Guanylurea		Red Solid	Stable
46	Benzoylguanidine		Orange Solid	Slightly Photosensitive
47	Diphenylguanidine		Red Solid	Unstable To Heat
48	Diorthotolyl guanidine		Red Solid	Unstable To Heat
49	Triphenylguanidine		Yellow Solid	Stable
50	1-(2,5-Dichlorophenyl)-2,3-diphenylguanidine		Red Soild	Unstable To Heat
51	1-(2-Chlorophenyl)-2,3-diphenylguanidine		Red Soild	Unstable To Heat
52	1-(3-Chlorophenyl)-2,3-diphenylguanidine		Yellow Solid Low Yield	Stable
53	1-(4-Chlorophenyl)-2,3-diphenylguanidine		Yellow Soild	Stable

TABLE 1. Continued

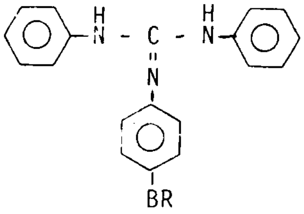
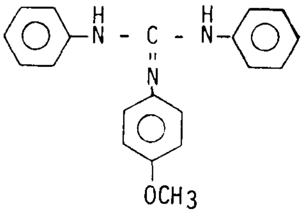
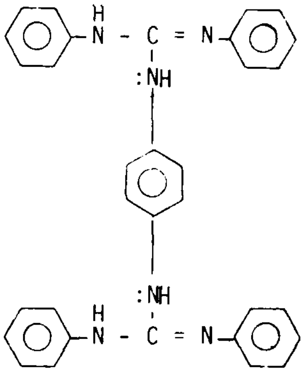
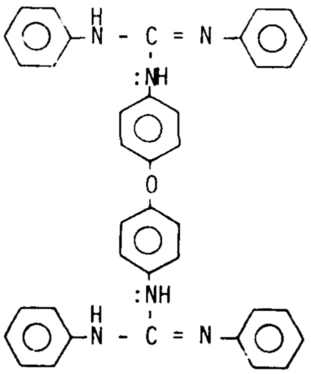
Compound Number	Base Compound	Base Structure	Synthesis Comments	Storage Stability
54	1-(4-Bromophenyl)-2,3-diphenylguanidine		Yellow Solid	Stable
55	1-(4-Methoxyphenyl)-2,3-diphenylguanidine		Oxidation	-
56	1,1'-Bis-(2,3-diphenylguanidine)-4-aminoaniline		Red Solid Oxidatively Unstable	-
57	1,1'-Bis-(2,3-diphenylguanidine)-4,4'-diphenylether		Oxidation	-

TABLE 1. Continued

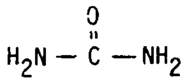
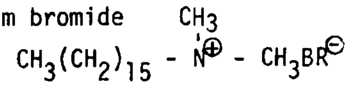
Compound Number	Base Compound	Base Structure	Synthesis Comments	Storage Stability
XI. Miscellaneous				
58	Urea	 $H_2N-\overset{O}{\overset{\parallel}{C}}-NH_2$	No Salt Formed	-
59	Cetyltrimethylammonium bromide	 $CH_3(CH_2)_{15}-\overset{CH_3}{\overset{\vert}{N^{\oplus}}}-CH_3BR^{\ominus}$	Red Solid	Photosensitive
60	Triethylenediamine (Dabco)		No Salt Formed	-

TABLE 2. SYNTHESIS OF SUBSTITUTED GUANIDINES

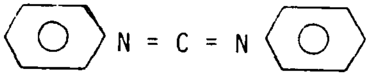
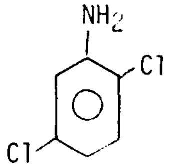
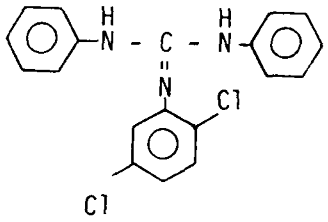
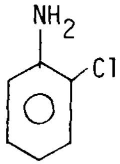
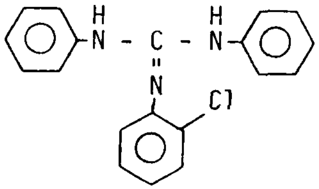
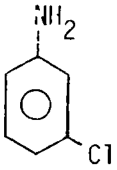
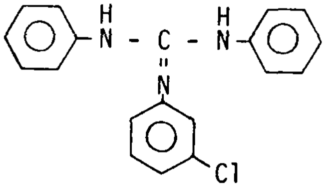
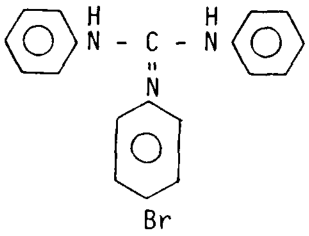
Carbodiimide	Aniline	Substituted Guanidine	Synthesis Comments
 Diphenylcarbodiimide (DPC)	 2,5-Dichloroaniline		$AlCl_3$ Catalysis 17% Yield White Crystals
Diphenylcarbodiimide (DPC)	 2-Chloroaniline		$AlCl_3$ Catalysis 21% Yield White Crystals
Diphenylcarbodiimide (DPC)	 3-Chloroaniline		$AlCl_3$ Catalysis 32% Yeild White Crystals
Diphenylcarbodiimide (DPC)	 4-Bromoaniline		$AlCl_3$ Catalysis 43% Yield White Crystals

TABLE 2. Continued

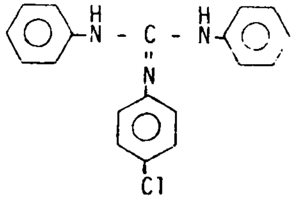
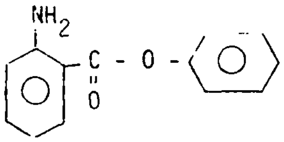
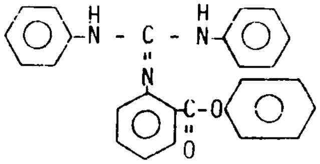
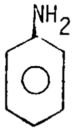
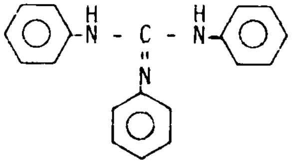
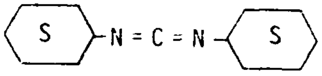
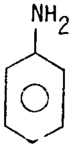
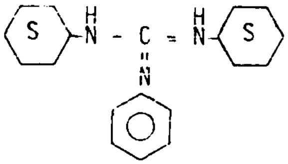
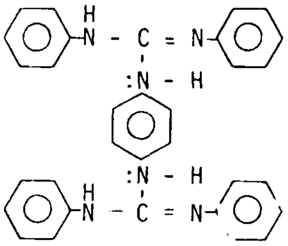
Carbodiimide	Aniline	Substituted Guanidine	Synthesis Comments
Diphenylcarbodiimide (DPC)	 4-Chloroaniline		$AlCl_3$ Catalysis 46% Yield White Crystals
Diphenylcarbodiimide (DPC)	 Phenylanthranilate		No Catalysis No Reaction
Diphenylcarbodiimide (DPC)	 Aniline		No Catalysis Low Yield White Crystals
 Dicyclohexylcarbodiimide	 Aniline		Acid Catalysis No Reaction
Diphenylcarbodiimide (DPC)	 p-Phenylenediamine		No Catalysis 50% Yield White Crystals

TABLE 2. Continued

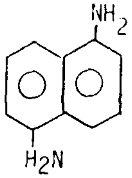
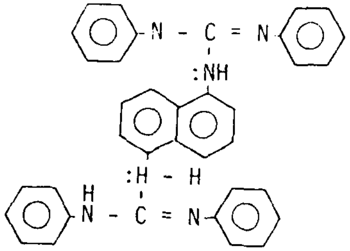
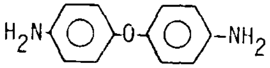
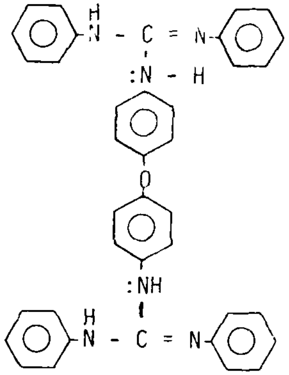
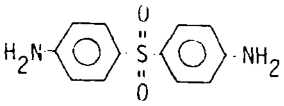
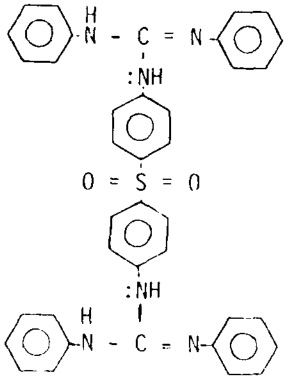
Carbodiimide	Aniline	Substituted Guanidine	Synthesis Comments
Diphenylcarbodiimide (DPC)	 1,5-Diaminonaphthalene		No Catalysis No Reaction
Dipnenylcarbodiimide (DPC)	 Diaminodiphenylether		No Catalysis Needed 35% Yield White Crystals
Diphenylcarbodiimide (DPC)	 Diaminodiphenyl sulfone		No Catalysis No Reaction

TABLE 2. Continued

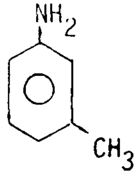
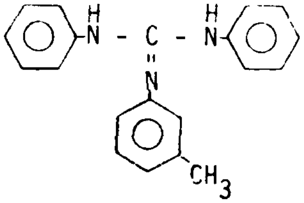
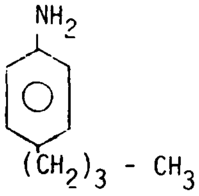
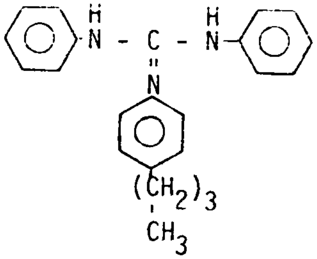
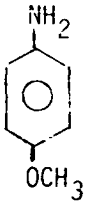
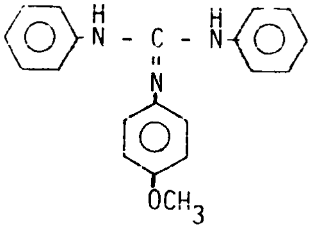
Carbodiimide	Aniline	Substituted Guanidine	Synthesis Comments
Diphenylcarbodiimide (DPC)	 m-Toluidine		No Catalysis No Desired Product
Diphenylcarbodiimide (DPC)	 n-Butylaniline		$AlCl_3$ Catalysis No Desired Product
Diphenylcarbodiimide (DPC)	 p-Anisidine		No Catalysis No Desired Product

TABLE 3. RELATIVE BASICITY OF AMINES

	Compound	pKa
Increasing Basicity ↓	2,5-Dichloroaniline	-
	2-Chloroaniline	2.65
	3-Chloroaniline	3.46
	4-Bromoaniline	3.86
	4-Chloroaniline	4.15
	Aniline	4.63
	4-Aminoaniline	-
	1,5-Diaminonaphthalene	-
	3-Methylaniline	4.73
	n-Butylaniline	5.12
	4-Methoxyaniline	5.34

TABLE 4. DSC Results for Organic Chromate Salts[1)]

Compound Number	Storage Compound	Melt Temperature[2)]			Decomposition Temp.[3)]		
		Initial	Maximum	Final	Initial	Maximum	Final
	A. Stable Salts						
49	1,2,3-Triphenylguanidine dichromate	-	-	-	164	170	174
42	Guanidine dichromate	155	159	161	168	-	-
25	Melamine dichromate	-	-	-	164	173	183
45	Guanylurea dichromate	-	-	-	177	178	179
15	2,4-Diamino-s-triazine dichromate	142	147	154	209	215	218
11	Acridine dichromate	-	-	-	206	213	216
17	2-Amino-4-anilino-s-triazine dichromate	-	-	-	176	180	184
18	2-Amino-4-(4-chloroanilino)-s-triazine-dichromate	-	-	-	191	199	204
40	Benzimidazole dichromate	-	-	-	169	183	193
53	1-(4-Chlorophenyl)-2,3-diphenylguanidine dichromate	-	-	-	199	203	207
54	1-(4-Bromophenyl)-2,3-diphenylguanidine dichromate	-	-	-	193	195	199
	B. Unstable Salts - Photosensitive During Storage and Heat Sensitive						
24	2,4-Diamino-6-phenyl-s-triazine dichromate (Benzoguanamine)	97	115	131	189	-	-
21	2,4-Diamino-6-acetyl-s-triazine dichromate (Acetoguanamine)	-	-	-	222	230	237
22	2,4-Diamino-6-stearyl-s-triazine dichromate (Stearoguanamine)	97	114	119	127	129	132
27	2,4,6-Tri-(2-pyridyl)-s-triazine dichromate	71	74	75	114	117	120
23	2,4-Diamino-6-(2'undecylimidazole-(1'))-ethyl-s-triazine dichromate	-	-	-	140	145	152

Table 4. (Continued)

Compound Number	Storage Compound	Melt Temperature[2)]			Decomposition Temp.[3)]		
		Initial	Maximum	Final	Initial	Maximum	Final
39	2-Phenylimidazole dichromate	72	89	95	135	138	146
46	Benzoylguanidine dichromate	-	-	-	158	-	-
48	Diorthotolylguanidine dichromate[4)]	107	111	114	-	-	-

1) Perkin Elmer Model 1B Differential Scanning Calorimeter

DSC parameters

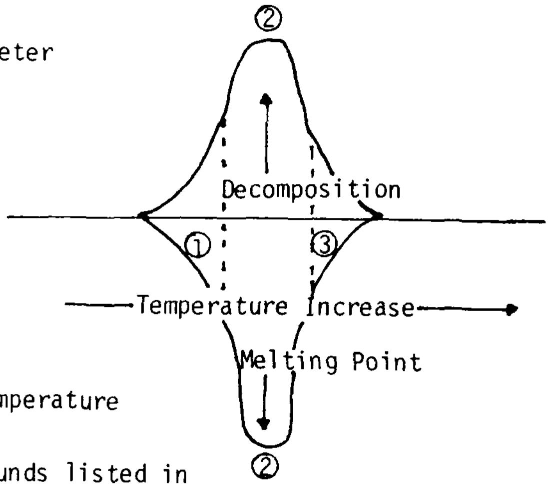
Scan Rate = 10°C/min.

Sample Size = 5 mg

Slope = 450

Range = 16

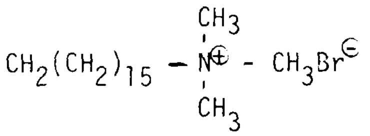
2) & 3)



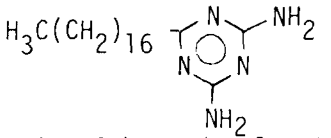
① Initial
② Maximum
③ Final Temperature

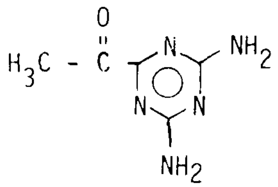
4) Heat sensitive. All other compounds listed in unstable salts section are photosensitive.

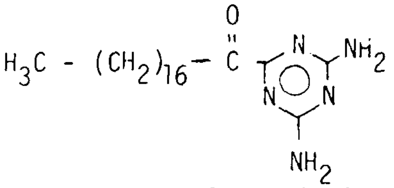
TABLE 5. Photosensitive Dichromate Salts

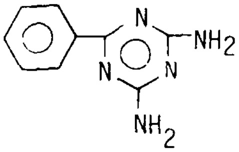

$CH_2(CH_2)_{15}-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}-CH_3Br^{\ominus}$

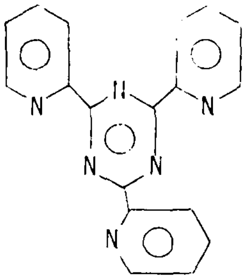
Cetyltrimethylammonium bromide

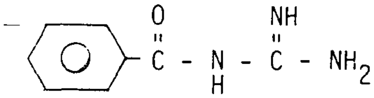

2,4-Diamino-6-heptadecyl-s-triazine

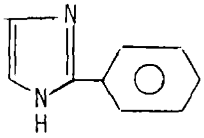

2,4-Diamino-6-acetyl-s-triazine (acetoguanamine)


2,4-Diamino-6-stearyl-s-triazine (stearoguanamine)


2,4-Diamino-6-phenyl-s-triazine (benzoguanamine)


2,4,6-Tri-(2-pyridyl)-s-triazine


Benzoylguanidine


2-Phenylimidazole

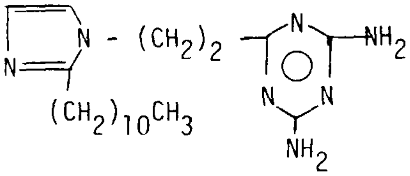

2,4-Diamino-6-(2'undecylimidazole-1')-ethyl-s-triazine

TABLE 6. CROWN ETHER COMPLEXES AS CORROSION INHIBITORS

Crown	Crown Radius A	Complexing Agent	Cation Radius Å	Complex[1] Stability in Dimethyl Formamide	Complex Stability in Primer Vehicle[2]	Scribe[3] Failure Time, Hrs.
None	-	-	-	-	Good	94
None-Strontium Chromate Control	-	-	-	-	Good	306
Dicyclohexyl-18-crown-6	1.15-1.60	$K_2Cr_2O_7$	1.33	Stable	Oxidation-Turns Green	90[7]
Dicyclohexyl-18-crown-6	1.15-1.60	$K_2Cr_2O_7$	1.33	Stable	Turns Green Shortly After Addition of Complex	350
Dibenzo-18-crown-6	1.15-1.60	$K_2Cr_2O_7$	1.33	Stable	Darkens with Time & Precipitate Forms	600
18-Crown-6	1.15-1.60	$K_2Cr_2O_7$	1.33	Stable	Slowly Darkens with Time	408
18-Crown-6	1.15-1.60	Potassium Alizarinate	1.33	Stable	Stable	240
Monobenzo-15-crown-5	0.85-1.10	$K_2Cr_2O_7$	1.33	Oxidation Turned Green	Crystals Formed Immediately	-
Monobenzo-15-crown-5	0.85-1.10	$Cu(CH_3CO_2)_2$	0.95	Stable	Precipitate Formed After Several Days	72
Monobenzo-15-crown-5	0.85-1.10	$CoCrO_4$	0.70	No Complex Formed	-	
Kryptofix 221[4]	1.15	$K_2Cr_2O_7$	1.33	Unstable[5]	-	-
Kryptofix 222B[6]	1.45	$K_2Cr_2O_7$	1.33	Stable	Slowly darkens with time. Storage in dark improves stability.	192

1) Complexes prepared in dimethylformamide. Stability of solution noted.
2) Used #201 Primer Vehicle without pigment.
3) 5% salt fog and 100% relative humidity at 95°F, on dichromate etched 2024-T3 Bare Aluminum panels. All panels primed immediately after addition of the complex to the primer model vehicle except as noted in 7). Panels flashed 30 minutes at 75°F and baked 1 hour at 250°F.
4) 4,7,13,16,21-Pentaoxa - 1,10-diazobicyclo-8,5,5-tricosane; E. Merck & Co.
5) Complex formed very slowly and the entire reaction mixture turned cloudy and dark in 10 minutes.
6) 5,6-Benzo -4,7,13,16,21,24-hexaoxa - 1,10-diazobicyclo - 8,8,8 - hexacosane; E. Merck & Co.
7) Panel primed after 3 days storage at 0°F of the complex-primer model vehicle mixture.

TABLE 7. Pigment Suspension with Organic Titanates[1][2]

	1	2	3	4	5	6
Solvent	90-					
Solids without Pigment	9-					
Pigment	1-					
ETDP-234[3]		0.25				
TTR-27[4]			0.25			
TTPO-12[5]				0.25		
TTOPI-41B[6]					0.25	
GTDOPP-1385[7]						0.25
Time to Settle, Hrs.	16	16	16	16	16	16

1) Primer Model Vehicle #201 with 10% strontium chromate based on solids.
2) Ken-React$^{(R)}$ - Supplied by Kenrich Petrochemicals, Inc., Bayonne,NJ.
3) Di-cumylphenoxy, ethylene, isostearoyl titanate
4) Isopropyl, triricinoyl titanate
5) Isopropyl, tri(dioctylphosphate) titanate
6) Tetraisopropyl, di(dioctylphosphito) titanate
7) Titanium di(dioctylpyrophosphate) oxyacetate

TABLE 8. Pigment Suspension With Gel Type Thickeners[1)]

	% Additive in Total Solids	Pigment Settling Time, Hours	Ease of Breaking Pigment Cake[2)]
Control[3)]	None	21	60
Thixatrol ST[4)]	0.5	< 17	30
Thixatrol ST	5.0	< 17	13
Thixatrol GST[4)]	0.8	41	21
Thixatrol GST	5.0	41	40
MPA-MS[4)]	1.0	21	39
MPA-MS	5.0	< 17	12
MPA-1078X[4)]	0.7	41	25
MPA-1078X	5.0	< 17	20
TenLo 70[5)]	0.04	< 17	40
TenLo 70	0.4	< 17	39

1) Primer Model Vehicle #201 with 10% strontium chromate based on primer solids.

2) Indicates the number of inversions required to break pigment cake. Primer was stored 7 days before cake breaking experiment.

3) No suspending agent.

4) National Lead.

5) Diamond Shamrock.

TABLE 9. PROPERTIES OF ORGANIC CHROMATE INHIBITORS

Cmpd. No.	Organic Base	Chromate Salt Structure 1)	% Cr^{+6} in Solid 2) 3)	% Cr^{+6} Theor.	H_2O Solubility 4) g/ 100 ml @ 75°F	MEK Solubility 4) g/ 100 ml @ 75°F	Pigment 5) Stability	Primer Solution Stability @-10°F	MEK Wipe 6) 7) 8) Resistance of Baked Primer Film
5	Benzotriazole dichromate	$B_2H_2Cr_2O_7$	22.9	22.8	-	Very Soluble	Stable	Violent decomposition when pigment is added to primer	-
11	Acridine dichromate	$B_2H_2Cr_2O_7$	18.1	18.1	0.02	0.02	Stable	Stable	Good
12	3,6-Diaminoacridine dichromate	$B_2H_2Cr_2O_7$	16.7	16.4	0.02	0.02	Stable	Turned very dark	Good
15	2,4-Diamino-s-triazine dichromate	$B_2H_2Cr_2O_7$	22.5	23.7	0.99	0	Stable	Turned from orange to brown	Good
17	2-Amino-4-anilino-s-triazine dichromate	$B_2H_2Cr_2O_7$	17.0	17.6	0.20	0.42	Stable	Turned from orange to brown	Fair
18	2-Amino-4-(4-chloroanilino)-s-triazine dichromate	$B_2H_2Cr_2O_7$	15.6	15.8	0.07	0.45	Stable	Turned from orange to brown	Good
21	2,4-Diamino-6-acetyl-s-triazine dichromate (Acetoguanamine)	$B_2H_2Cr_2O_7$	22.5	19.8	0.60	0	Slowly turns from orange to green in light	Stable	Good

TABLE 9. Continued

Cmpd. No.	Organic Base	Chromate Salt Structure[1]	Cr^{+6} in Solid[2][3]	Cr^{+6} Theor.	H_2O Solubility[4] g/100 ml @ 75°F	MEK Solubility[4] g/100 ml @ 75°F	Pigment[5] Stability	Primer Solution Stability @-10°F	MEK Wipe[6][7][8] Resistance of Baked Primer Film
22	2,4-Diamino-6-stearyl-s-triazine dichromate (Stearoguanamine)	$B_2H_2Cr_2O_7$	12.0	10.7	0	0	Turns Green Rapidly	-	-
23	2,4-Diamino-6-(2'- undecylimidazole (1'))-ethyl-s-triazine dichromate	$B_2H_2Cr_2O_7$	16.2	18.1	0	.01	Slowly turns from orange to green in light	Condensate gells during ball milling	-
24	2,4-Diamino-6-phenyl-s-triazine dichromate (Benzoguanamine)	$B_2H_2Cr_2O_7$	16.7	16.4	0.30	0	Slowly turns from orange to green in light	Stable	Fair
25	Melamine dichromate	$B_2H_2Cr_2O_7$	21.6	22.1	0.23	0	Stable	Stable	Good
27	2,4,6-Tri-(2-pyridyl)-s-triazine dichromate	$BH_2Cr_2O_7$	18.8	19.5	0.07	0	Slowly turns from orange to green in light	Turns from orange to brown	Good
39	2-phenylimidazole	$B_2H_2Cr_2O_7$	19.7	20.6	0.82	0.01	Slowly turns from orange to green in light	Turns dark	Fair

TABLE 9. Continued

Cmpd. No.	Organic Base	Chromate Salt Structure 1)	% Cr^{+6} in Solid 2)3)	% Cr^{+6} Theor.	H_2O Solubility 4) g/ 100 ml @ 75°F	MEK Solubility 4) g/ 100 ml @ 75°F	Pigment 5) Stability	Primer Solution Stability @-10°F	MEK Wipe 6)7)8) Resistance of Baked Primer Film
40	Benzimidazole dichromate	$B_2H_2Cr_2O_7$	23.4	22.9	0.25	0.02	Stable	Slowly turns from orange to brown	Good
42	Guanidine dichromate	$B_2H_2Cr_2O_7$	26.0	30.9	33.4 at 68°F	26.0	Stable	Stable	Fair
45	Guanylurea dichromate	$B_2H_2Cr_2O_7$	24.7	24.6	2.9	0	Stable	Stable	Good
46	Benzoylguanidine	$B_2H_2Cr_2O_7$	14.8	19.1	0.26	0.18	Slowly turns from orange to green in light	Turns green	-
48	Diorthotolyl-guanidine dichromate	$B_2H_2Cr_2O_7$	15.7	15.0	0.41	17.7	Stable	Turns dark	Fair
49	Triphenylguanidine dichromate	$B_2H_2Cr_2O_7$	13.1	13.1	0.13	0.97	Stable	Turns dark	Fair to Poor
52	1-(3-chlorophenyl)-2,3-diphenylguanidine dichromate	$B_2H_2Cr_2O_7$	4.4	12.1	- 10)	- 10)	Stable	- 10)	- 10)

TABLE 9. Continued

Cmpd. No.	Organic Base	Chromate Salt Structure[1]	Cr^{+6} in Solid[2][3]	Cr^{+6} Theor.	H_2O Solubility[4] g/100 ml @ 75 F	MEK Solubility[4] g/100 ml @ 75°F	Pigment[5] Stability	Primer Solution Stability 0-10 F	MEK Wipe[6][7][8] Resistance of Baked Primer Film
53	1-(4-Cholorphenyl) 2,3-diphenylguanidine dichromate	$B_2H_2Cr_2O_7$	11.1	12.1	0.02	0	Stable	Pigment appears to agglomerate	Good
54	1-(4-Bromophenyl)-2,3-diphenylguanidine dichromate	$B_2H_2Cr_2O_7$	9.4	10.9	0.02	0.03	Stable	Pigment appears to agglomerate	Good
-	Organokrome A[9]	Chromium VI containing substituted guanidine	10.5	-	2.5	Appears to dissolve in or react with MEK	Stable	Turns primer somewhat green	Very poor

1) Represents the structure of the salt where B is a molecule of the base which in some cases may contain several basic amine groups. See Appendix for structure.

2) Determined by titration. See Appendix for details.

3) Primer prepared with 0.25% Chromium VI based on solids.

4) See Appendix for method.

5) Stability in diffused light at 75°F.

6) Determine by 40 hard pressure double rubs with a MEK saturated paper wiper.

7) Model #201 primer vehicle prepared at approximately 10% solids with an appropriate amount of inhibitor.

8) Primer film flashed 30 minutes at 75°F and baked one hour at 250°F to give dry film thickness of 0.2 mils.

9) A proprietary product that had been marketed by Pfizer but was withdrawn from the market approximately 4 years ago.

10) Not tested because the %Cr^{+6} content was far below the theoretical Cr content indicating that very little of the amine had been converted to the chromate salt.

TABLE 10. PROPERTIES OF INORGANIC PIGMENTS[1)]

Pigment	H_2O Solubility g/100 ml, 75°F	Cr^{+6}[2)] In Pigment	Stability In Primer Solution (Model 201 Primer)	Primer[3)] MEK Wipe Resistance	Time To Corrosion[4)] Failure In Salt Spray (Hrs.) (Scribe Panel Tests)
Potassium chromate	62.9 @ 68°F	26.8	Turns a bit Green	Good	300
Magnesium chromate	41	37.1	Stable	Good	190
Nickle chromate	4.0	29.8	Stable	Good	215[5)]
Calcium chromate	2.7	33.3	Stable	Good	500
Strontium chromate	.22	25.5	Stable	Good	350[6)]
Zinc chromate	.20	28.6	Stable	Good	745
Cobalt chromate	.19	29.7	Stable	Good	1240
Barium chromate	3.4×10^{-4} @ 59°F	20.5	Stable	Good	460

1) Model #201 primer vehicle
2) Primers prepared with 0.25 chromium VI based on solids
3) Determined by 40 hard pressure double rubs with a MEK saturated paper wiper.
4) Tested per ASTM B117-64. Primer sprayed at 0.2 mils thickness, flashed 30 minutes at 75°F, and baked 1 hour at 250°F. Used 2024-T3 bare dichromate etched aluminum substrate.
5) Average of 2 values
6) Average of 3 values

TABLE 11. ANTICORROSION PERFORMANCE OF VARIOUS INHIBITORS IN SCRIBE PANEL TESTS 1)2)3)

In Order Of Performance Within Groups

Compound Number 4)	I. Model #201 Primer Vehicle 5)	Average Number Of Tests 6)	Failure Time, Hours 5% Salt Fog at 95°F	Failure Time, Hours Distilled 7) H_2O Fog at 95°F
	A. Inorganic Pigments			
	No pigment control		90	1370
	Cobalt chromate	2	1240/226 8)	5540
	Zinc chromate	2	910/236	3600
	Strontium chromate	3	350/69	4370
	Calcium chromate		500	4340
	Barium chromate		460	5540
	Potassium chromate		300	2040
	Nickle chromate	2	215/63	4780
	Magnesium chromate		190	3000
	Zinc molybdate		170	4780
	Ammonium molybdate		70	190
	B. Organic Amine-Chromate Salts			
42	Guanidine dichromate		1340	2060
-	Organocrome A (Pfizer)		1320	4080
53	1-(4-Chlorophenyl)-2,3-diphenylguanidine dichromate		790	4680
24	2,4-Diamino-6-phenyl-s-triazine dichromate (Benzoguanimine)		650	8980
25	Melamine dichromate	3	645/84	6935
27	2,4,6-Tri-(2-pyridyl)-s-triazine dichromate		460	8160
21	2,4-Diamino-6-acetyl-s-triazine dichromate (Acetoguanamine)		430	4200
15	2,4-Diamino-s-triazine dichromate		360	8590
45	Guanylurea dichromate		360	8590
49	1,2,3-Triphenylguanidine dichromate	2	305/4	2060
17	2-Amino-4-anilino-s-triazine dichromate		260	8160

TABLE 11. Continued

Compound Number	I.	Model #201 Primer Vehicle	Average Number Of Tests	5% Salt Fog at 95°F	Distilled H_2O Fog at 95°F
	B.	Organic Amine-Chromate Salts (Cont'd)			
54		1-(4-Bromophenyl)-2,-diphenyl-guanidine dichromate		260	4700
11		Acridine dichromate		240	3600
39		2-Phenylimidazole dichromate		220	7600
18		2-Amino-4-(4-chloroanilino)-s-triazine dichromate		170	8160
48		Diorthotolylguanidine dichromate		140	4680
40		Benzimidazole dichromate		70	3460
	C.	Miscellaneous Organic Materials			
		Alizarin[4]		360	4780
		Potassium alizarinate-18-crown-6-complex		240	1820
		Isatin (2,3 indolinedione)		140	260
		p-Hydroxybenzophenone		100	1440
		Ethylenediaminetetracetic acid		70	1010
		Picrolonic acid		70	340
		Ethylenediaminetetraceticacid, tetrasodium salt dihydante		70	70
	D.	Organometallic Complexes			
		Tris(2'-hydroxyacetophenono)chromium		240	4200
		Tris(ethylenediamine)chromium(III) sulfate		170	1510
		Chromium(III) 2-ethylhexaonoate		170	5330
		Chromium(III) 2,4-pentanedionate		170	1510
		Cobalt(III) 2,4-pentanedionate		170	1510
		Triphenyl antimony		100	1270
	II.	Model #210 Primer Vehicle[5][7]			
		Cobalt chromate		740	3600
		Strontium chromate		240	2350
	III.	Model #7 Primer Vehicle[5]			
		Strontium chromate		430	4700
		Cobalt chromate		430	1940
		Melamine dichromate		430	5700
		1,2,3-Triphenylguanidine dichromate		240	3960

TABLE 11. Continued

Compound Number	IV. Model #127 Primer Vehicle	Average Number Of Tests	5% Salt Fog at 95°F	Distilled H_2O Fog at 95°F
	Strontium chromate		1870	5010
	Cobalt chromate		1220	5380
	Melamine dichromate		740	5700
	No Pigment		240	1940

1) Model #201 primer vehcile prepared at approximately 10% solids with an appropriate amount of inhibitor to give 0.25% chromium VI based on solids.
2) Primer film flashed 30 minutes at 75°F and baked one hour at 250°F to give a dry film thickness of 0.2 mils.
3) Panels primed shortly after primer preparation.
4) Compound numbers assigned to synthesized organic chromate salts.
5) See Appendix for description of models
6) One test sample unless otherwise indicated.
7) Ball mill mix gelled during ball milling with melamine dichromate and 1,2,3-triphenylguanidine dichromate inhibitors.
8) First number is the mean and second number the standard deviation.

TABLE 12. CHEMICAL PROPERTIES OF DIPHENOLIC ADDUCTS OF EPON 828

Model Adduct	WPE[a) Lot	WPE[a) Theo.	WPE[a) Active	Phenolic OH⁻ [b) (Equiv./100 g)
#4 (Resorcinol)	151-178	580	640	0.000
#4' (Hydroquinone)	151-180	489	502	0.000
#5 (Bisphenol A)	151-44	562	590	0.000
	171-5	562	591	0.000
	171-17	562	601	0.000
	171-36	562	590	0.000
#6 (Bisphenol S)	151-51	578	558	-
	151-173	578	736	0.028
	151-184	578	572	0.016
	151-193	578	640	0.011
#7 (Bisphenol A-Hycar CTBN)	151-47	686	686	0.023
	151-196	686	694	0.005
	171-20	686	659	0.010
	171-41	686	672	0.018
	171-94	686	690	0.000

a) Weight per epoxide.

b) Theoretical 0.000 (100% reaction).

TABLE 13. SCREENING OF DOW EPOXY NOVALAC 438 WITH SEVERAL PHENOLIC RESINS AND CATALYSTS

Phenolic Resin	Catalyst	Solution Compatibility	Dry Film Appearance	Bake Cycle (Hours/°F)			
				1/250		1/250 + 0.5/350	
				MEK Resin	Pencil Hard.	MEK Resis.	Pencil Hard.
SP-6700	C.A. 1)D	Clear	Transparent w/fine particles	Excellent	6H	-	-
	BDMA	"	"	Poor	"	Excellent	6H
	TPPEI	"	"	Poor	"	"	"
BRZ-7541	C.A. 1)D	"	Transparent - some film break	Excellent	"	-	-
	BDMA	"	"	"	"	-	-
	TPPEI	"	"	"	"	-	-
Varcum 4326	C.A. 1)D	"	"	"	"	-	-
	BDMA	"	"	"	"	-	-
	TPPEI	"	"	"	"	-	-
Methylon 75108	C.A. 1)D	"	Transparent, Smooth	"	"	-	-
	BDMA	"	"	Poor	"	Excellent	6H
	TPPEI	"	"	Poor	"	"	"
BRZ 4020	C.A. 1)D	"	"	Excellent	"	-	-
	BDMA	"	"	"	"	-	-
	TPPEI	"	"	"	"	-	-
Varcum 5416	C.A. 1)D	"	"	"	7H	-	-
	BDMA	"	"	"	"	-	-
	TPPEI	"	"	"	> 8H	-	-

Note: See Appendix for description of materials.
1) C.A. = Curing Agent

TABLE 14. EFFECT OF HARDENER VARIATIONS MODEL #2[1)]

Test Category	Phenolic Hardener Variation									Phenolic Hardener Substitution		
System Number	1 (Control)			2			3			4		
Description Of Hard./Cat.[2)]												
Hardener Stoic. (%)	100			90			110			100 (BRZ-7541)		
Catalyst Conc. (phr)	1.16			1.16			1.16			1.16		
Cure Cycle[3)]	A	B	C	A	B	C	A	B	C	A	B	C
Casting Properties[4)]												
Appearance	Opaque			Opaque			Opaque			Clear		
Tg (°C)	82	89	95	71	73	98	81	90	101	44	71	75
α(x 10-6 in/in)	61.8	52.5	58.8	60.7	56.1	64.9	62.1	60.9	61.4	35.7	59.7	52.9
Extent Of Cure	I	I	C	I	I	C	I	I	I	I	I	I
Flexure Strength @ 25°C												
Yield, (lb)	-	68	-	37	110	219	23	105	257	-	70 (TPPEI)	
Ultimate (lb)	-	148	-	156	110	316	27	112	257	-	140 (TPPEI)	
Coating Properties (25°C)												
Pencil Hardness	6H	6H	>8H	6H	6H	>8H	6H	6H	>8H	6H	6H	>8H
MEK Resistance[5)]	VP	VP	G	N	VP	G	VP	VP	G	G	E	E

1) Resin System: Epon 1007 - 40 pbw Hardener: Varcum 4326
DEN 438 - 60 pbw Catalyst: Curing Agent D

2) Hardener expressed as % of stoichiometry necessary to react with the total epoxide present. Catalyst expressed as parts per hundred resin (phr).

3) Cure: A (1 hr. @ 250°F); B (2 hr. @ 250°F); C (2 hr. @ 250°F + 1 hr. @ 350°F)

4) See Appendix for preparation of castings.

5) As rubbed hard with a MEK-soaked wiper:

N (none) <5 double rubs	G (Good) 50 double rubs (film marred)
P (poor) 5-24 double rubs	E (Excellent) >50 double rubs (film unaffected)
F (fair) 25-50 double rubs	

TABLE 15. EFFECT OF CATALYST VARIATIONS MODEL #2[1)]

Test Category	Catalyst Variation/Substitution											
System Number	1			2			3			4		
Description Of Hard./Cat.[2)]												
Hardener Stoic. (%)	100			100			100			100		
Catalyst Conc. (phr)	0.58			1.55			1.16 (TPPEI)			1.16 (BDMA)		
Cure Cycle[3)]	A	B	C	A	B	C	A	B	C	A	B	C
Casting Properties[4)]												
Appearance	Opaque			Opaque			Opaque			Opaque		
Tg (°C)	71	73	93	65	79	86	54	64	93	67	67	101
α(x10^{-6} in/in)	57.1	49.1	48.1	58.2	56.1	51.8	54.9	48.0	50.3	54.0	60.5	62.3
Flexure Strength @ 25°C	I	I	I	I	I	C	I	I	I	I	I	C
Yield, (lb)	-	-	-	-	-	-	-	116	-	-	-	-
Ultimate (lb)	-	-	-	-	-	-	-	204	-	-	-	-
Coating Properties (25°C)												
Pencil Hardness	6H	6H	>8H	6H	6H	>8H	7H	7H	>8H	7H	6H	>8H
MEK Resistance[5)]	N	VP	G	VP	P	G	E	E	E	N	P	G

1) Resin System: Epon 1007 - 40 pbw Hardener: Varcum 4326
DEN 438 - 60 pbw Catalyst: Curing Agent D

2) Hardener expressed at % of stoichiometry necessary to react with the total epoxide present. Catalyst expressed as parts per hundred resin (phr).

3) Cure: A (1 hr. @ 250°F); B (2 hr. @ 250°F); C (2 hr. @ 250°F + 1 hr. @ 350°F)

4) See Appendix for preparation of castings.

5) As rubbed hard with a MEK-soaked wiper:
N (none) <5 double rubs
P (poor) 5-24 double rubs
F (fair) 25-50 double rubs
G (Good) >50 double rubs (film marred)
E (Excellent) >50 double rubs (film unaffected)

TABLE 16. COMPARISON OF OTHER COMMERCIAL PHENOLIC HARDENERS FOR MODEL #2 1)

System Number	1			2			3		
Description 2)									
Hardener (44.0 phr)	Methylon 75108			Resinox P-97 (as solid)			BRJ-473 (as solid)		
Catalyst Conc. (phr)	2.7 (H_3PO_4)			None			None		
Cure Cycle 3)	A	B	C	A	B	C	A	B	C
Coating Properties									
Pencil Hardness	3H	4H	>8H	5H	6H	>8H	6H	6H	>8H
MEK Resistance	N	N	E	P	G	E	N	N	VP

1) Resin System: Epon 1007 - 40 pbw
DEN 438 - 60 pbw
2) Hardener expressed at % of stoichiometry necessary to react with the total epoxide present. Catalyst expressed as parts per hundred resin (phr)
3) Cure: A (1 hr. @ 250°F); B (2 hr. @ 250°F); C (2 hr. @ 250°F + 1 hr. @ 350°F)
4) See Appendix for description and source of materials.

TABLE 17. COMPARISON OF COATING AND ADHESIVE PROPERTIES FOR MODIFICATIONS TO MODEL #2 1)

System Number	1	2	3	4	5	6
Hardener	V-4326	V-4326	BRZ-7541	BRZ-7541	Resinox P-97	Resinox P-97
Hardener Stoichiometry ( )	100	100	100	100	-	-
Catalyst	C.A. D	TPPEI	C.A. D	TPPEI	None	TPPEI
Catalyst Concentration (phr)	1.16	1.16	1.16	1.16	-	1.16
Coating Properties						
Pencil Hardness Bake A 2)	4H	6H	6H	6H	4H	6H
Bake B	6H	6H	6H	7H	6H	6H
Bake C	>8H	>8H	>8H	>8H	>8H	>8H
MEK resistance Bake A	N	E	P	F	VP	VP
Bake B	VP	E	F	G	F	P
Bake C	G	E	E	E	E	E
Adhesive Properties3)						
MMCD Peel @ 75°F (in-lb/in)						
0.2 mil coating						
Unbaked	66.1	64.1	74.6	72.9	62.8	64.8
(Failure) 4)	(98C/5AP)	(95C/5PM)	(100C)	(100C)	(95C/5PM)	(95C/5PM)
Bake A	9.0	7.0	59.4	0.5	25.6	1.0
(Failure)	(95PM/5c)	(80PM/20CP)	(60C/40CP)	(100PM)	(70C/30PM)	(100PM)
0.4 mil coating						
Unbaked	44.6	65.4	74.4	73.5	62.6	64.0
(Failure)	(60C/40PM)	(80C/20PM)	(95C/8PM)	(100C)	(95C/5PM)	(95C/5PM)
Bake A	1.0	2.5	52.1	1.0	2.0	1.0
(Failure)	(100PM)	(100CP)	(80C/20AP)	(100PM)	(95PM/5CP)	(100PM)

1) Epon 1007 - 40 pbw
DEN 438 - 60 pbw

2) Bake: A - 1 hour @ 250°F
B - 2 hours @ 250°F
C - 2 hours @ 250°F + 1 hour @ 350°F

3) With EA 9628 cured 1 hour @ 250°F on phosphate anodized 2024-T3 clad alum.

4) Failure mode Key (%)
AP - Adhesively from primer
C - Cohesive
CP - Cohesive in primer
PM - Primer from metal

TABLE 18. MODEL PRIMER VEHICLE CURABILITY, HARDNESS AND MEK RESISTANCE

Model Number	Description	Epoxide Consumption,% After Bake (Mins./°F) 10/ 150	15/ 250	30/ 250	+30/ 350	Pencil Hardness	MEK Resistance After 350°F Bake
1	Phenoxy	0	70	75	80	2H	None
2	Epon 1007	0	58	75	87	3H	Fair-Good
3	Epon 828	0	88	93	96	3-7H	Outstanding
4	Resorcinol	0	83	87	90	1H	None
5	BPA	0	52	70	94	2H	Fair
6	BPS	0	64	81	98	2H	None
7	BPA-Rubber	0	59	75	94	FH	None
10	EA 9628 (Sol'n.)	0	5	13	87	2H	Good

TABLE 19. EFFECT OF CATALYST TYPE AND CONCENTRATION ON COMPLETENESS OF CURE

System	pbw
Epon 1007	40
DEN 438	60
Varcum 4326	38.7
Catalyst	0.4 → 1.2
PC-1344	0 → 1.4[1]

Catalyst	C.A. "D"		TPPEI					
Concentration (pbw)	1.2	1.2	0.4	0.4	1.2	1.2	1.2	1.2
PC-1344 (pbw)	0	0	0	0	0	0	1.4	1.4
Cure Cycle[2]	A	B	A	B	A	B	A	B
Cure Complete (TMA)[3]	No	Yes	No	Yes	No	Yes	No	Yes
Tg (°C)	89	95	92	95	88	92	93	96
MEK Wipe Resistance[4]	P	G	E	E	G	E	-	-

1) Anti-foaming agent (Monsanto)
2) Cure Cycle: A - 2 hours @ 250°F
B - 2 hours @ 250°F plus 1 hour @ 350°F
3) Cure Complete: No - probe penetrates sample giving "S" shaped curve.
Yes - no probe penetration, expansion curve above Tg is linear.
4) MEK Wipe Resistance: P - coating survives more than 5 but less than 25 wipes with MEK soaked wiper.
G - coating survived 50 wipes but was marred.
E - coating survived 50 wipes and was not marred.

TABLE 20. EFFECT OF TPPEI CONCENTRATION ON COATING PROPERTIES OF MODEL #2 VEHICLE

Model Resin System	pbw
Epon 1007	40
DEN 438	60
Varcum 4326	38.7
TPPEI Catalyst	Various

System	A		B		C		D	
Catalyst Conc.(Wt.)								
phn (Hardener)	0		1.0		2.0		3.0	
phe (Epoxy)	0		0.65		1.29		1.94	
Phr (Total Resin)	0		0.39		0.77		1.16	
Bake Cycle	PH	MR	PH	MR	PH	MR	PH	MR
1 Hr. @ 250°F	<H	N	6H	G	8H	VG	8H	G
2 Hr. @ 250°F	<H	N	>8H	E	>8H	VG	>8H	G
2 Hr. @ 250°F + 1 Hr. @ 350°F	3H	N	>8H	E	>8H	E	>8H	VG

Film Thickness - 0.5 mil
PH - Pencil Harndess, scratch test
MR - MEK Resistance, as rubbed hard with solvent-soaked wiper
N (None) - <5 double rubs
P (Poor) - 5-24 double rubs
F (Fair) - 25-50 double rubs
G (Good) - >50 double rubs (film marred)
E-(Excellent) - >50 double rubs (film uneffected)

TABLE 21. FORMULATION OF MODEL PRIMERS

	Model Number									
Ingredient (pbw)[1]	1	2	3	4	4'	5	6	7	8	9
Phenoxy PAHJ	40	-	-	-	-	-	-	-	-	-
Epon 1007	-	40	-	-	-	-	-	-	-	-
Epon 828	-	-	40	-	-	-	-	-	-	-
DEN 438	60	60	60	-	-	-	-	-	-	-
Resorcinol-Epon 828 Adduct	-	-	-	100	-	-	-	-	-	-
Hydroquinone-Epon 828 Adduct	-	-	-	-	100	-	-	-	-	-
Bisphenol A-Epon 828 Adduct	-	-	-	-	-	100	-	-	-	-
Bisphenol S-Epon 828 Adduct	-	-	-	-	-	-	100	-	-	-
Hycar CTBN-BPA-Epon 828 Adduct	-	-	-	-	-	-	-	100	-	-
Eponol 55B40	-	-	-	-	-	-	-	-	100	-
Butvar 76	-	-	-	-	-	-	-	-	-	100
Varcum 4326	35.0	38.7	57.0	19.0	21.0	18.0	19.0	16.0	-	-
Cymel 245-8	-	-	-	-	-	-	-	-	8.7	-
Resinox P-97	-	-	-	-	-	-	-	-	-	92.7
Phosphoric Acid, 85%	-	-	-	-	-	-	-	-	-	74.3
TPPEI	0.7	0.77	1.14	0.38	0.42	0.36	0.38	0.32	-	-
SR-82	1.35	1.35	1.57	1.19	1.21	1.18	1.19	1.16	-	-
Chinoline Yellow SS	0.14	0.14	0.16	0.10	0.12	0.10	0.10	0.10	0.11	-
Methyl Ethyl Ketone	299	308	350	263	273	262	263	256	207	401
Tetrahydrofuran	163	168	191	144	149	142	144	140	101	-
Diacetone Alcohol	82	84	95	72	75	71	72	70	50	-
Cellosolve Acetate	-	-	-	-	-	-	-	-	44	-
Toluene	-	-	-	-	-	-	-	-	7	-
n-Butyl Alcohol	-	-	-	-	-	-	-	-	-	937
Ethyl Alcohol	-	-	-	-	-	-	-	-	-	376
Non-volatiles	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	10.5	10.6

1) See Appendix for description and source of materials.

TABLE 22. MODEL MMCD PEEL STRENGTH WITH EA 9628 FILM (R.T. TESTS)

		Nominal 0.2 Mil Coating					Nominal 0.4 Mil Coating				
		Unbaked			Baked 1)		Unbaked			Baked	
Model Number	Description	Actual Thick.	Peel @ 75°F (in-lb/in)	% 2) Failure	Peel @ 75°F (in-lb/in)	% Failure	Actual Thick.	Peel @ 75°F (in-lb/in)	Failure	Peel @ 75°F (in-lb/in)	Failure
-	Unprimed Control	-	-	-	74	90C 10A	-	-	-	-	-
1	Phenoxy	0.40	63	100C	56	80C 20AP	0.60	58	90C 10PM	7	100AP
2	Epon 1007	0.30	68	100C	27	90PM 10C	0.50	70	100C	3	100PM
3	Epon 828	0.30	70	100C	2	100AP	0.60	68	100C	2	100AP
4	Resorcinol Adduct	0.20	75	100C	35	60C 40AP	0.40	82	100C	38	60C 40P
5	BPA Adduct	0.24	75	100C	65	100C	0.46	78	100C	63	100C
6	BPS Adduct	0.30	78	100C	35	100C	0.60	75	100C	33	B/R 100C
7	BPA-Rubber Adduct	0.25	72	100C	73	100C	0.48	80	100C	67	100C
8	Phenoxy-Melamine Formaldehyde	0.18	47	90C 10CP	0	100AP	0.30	37	80C 20CP	0	100AP
9A	Vinyl Butyral-Phenolic	0.20	5	95CP 5C	73	B/R 80C 20AP	0.40	2	95PM 5CP	12	95PM 5C
9B	Vinyl Butryal-Phenolic (Acid Catalyzed)	0.10	2	B/R 50CP 50PM	2	95PM 5CP	0.20	0	100PM	2	100PM
0	EA 9628 Solution	0.30	70	100C	68	100C	0.60	67	100C	38	70C 30AP

1) 1 hr. @ 250°F except
Model 8 (30 min. @ 350°F and
Model 9A and B (30 Min. @ 300°F)

2) Failure Mode Key:
AP - Adhesively from Primer
C - Cohesive
CP - Cohesive In Primer
PM = Primer From Metal
B/R - Break and run

3) Catalyst: Curing Agent D

4) Surface Preparation - phosphate anodize

TABLE 23. MODEL MMCD PEEL STRENGTH WITH EA 9628 FILM (-67 F TESTS)

		Nominal 0.2 Mil Coating					Nominal 0.4 Mil Coating				
		Unbaked			Baked1)		Unbaked			Baked	
Model Number	Description	Actual Thick.	Peel @-67°F (in-lb/in)	2) Failure	Peel @-67°F (in-lb/in)	Failure	Actual Thick.	Peel @-67°F (in-lb/in)	Failure	Peel @-67°F (in-lb/in)	Failure
-	Unprimed Control	-	-	-	62	80C 20A	-	-	-	-	-
1	Phenoxy	0.40	22	95PM 5C	16	80PM 20C	0.60	17	95PM 5CP	Not Tested	Not Tested
2	Epon 1007	0.30	40	50C 50PM	7	95PM 5CP	0.50	46	70C 30PM	Not Tested	Not Tested
3	Epon 828	0.30	49	80CP 20PM	Not Tested	Not Tested	0.60	28	40C 60PM	Not Tested	Not Tested
4	Resorcinol Adduct	0.20	63	80C 20PM	36	80PM 20CP	0.40	36	95PM 5C	41	90CP 10PM
5	BPA Adduct	0.24	61	80C 20PM	40	70PM 30C	0.46	39	70PM 30C	27	95PM 10PM
6	BPS Adduct	0.30	63	95C 5PM	12	95PM 5C	0.60	37	70C 30PM	7	90PM 10C
7	BPA-Rubber Adduct	0.25	54	70C 30PM	43	50C 50PM	0.48	60	60C 40PM	49	90PM 10C
8	Phenoxy-Melamine Formaldehyde	0.18	45	40C 60CP	Not Tested	Not Tested	0.30	37	80CP 20PM B/R	Not Tested	Not Tested
9A	Vinyl Butyral Phenolic	0.20	Not Tested	Not Tested	4	100AP	0.40	Not Tested	Not Tested	Not Tested	Not Tested
9B	Vinyl Butyral Phenolic (Acid Catalyzed)	0.10	Not Tested	Not Tested	Not Tested	Not Tested	0.20	Not Tested	Not Tested	Not Tested	Not Tested
0	EA 9628 Solution	0.30	64	80C 20PM	57	70C 30PM	0.60	61	70C 30PM	41	60C 40PM

1) 1 hr. @ 250°F except
Model 8 (30 Min. @ 350°F) and
Model 9A and B (30 Min. @ 300°F)

2) Failure Mode Key:
AP - Adhesively from Primer
C - Cohesive
CP - Cohesive In Primer
PM - Primer From Metal
B/R - Break And Run

3) Catalyst: Curing Agent D

4) Surface Preparation - Phosphate Anodize

TABLE 24. MODEL MMCD PEEL STRENGTH AT 75°F WITH EA 9628 FILM

Model Number	Description	Nominal 0.2 Mil Coating				Nominal 0.4 Mil Coating			
		Unbaked		Baked[1]		Unbaked		Baked[1]	
		Peel Strength (in-lb/in)	Failure[2]	Peel Strength (in-lb/in)	Failure %	Peel Strength (in-lb/in)	Failure %	Peel Strength (in-lb/in)	Failure %
-	Unprimed Control			71	85C				
1	Phenoxy	62	100C	6	90PM 10CP	13	90PM 10C	3	100CP
2	Epon 1007	68	95C 5PM	4	100CP	53	70C 30PM	3	100CP
3	Epon 828	70	95C 5PM	0	100AP	15	20PM 20C	0	100AP
4	Resorcinol Adduct	72	100C	64	80C 30CP	71	100C	23	50C 50CP
4'	Hydroquinone	70	100C	53	40C 60CP	75	100C	61	80C 30CP
5	BPA Adduct	73	95C 5PM	65	80C 20AP	80	100C	67	80C 20AP
6	BPS Adduct	64	100C	57	85C 5AP	70	100C	48	50C 20AP
7	BPA-Rubber Adduct	76	100C	65	100C	80	100C	67	100C

1) 1 hour at 250°F
2) Failure Mode Key: AP - Adhesively from primer
C - Cohesive
CP - Cohesive in primer
PM - Primer from metal
3) Catalyst: TPPEI
4) Surface Preparation: Phosphate Anodize

TABLE 25. MODEL MMCD PEEL STRENGTH AT -67°F WITH EA 9628 FILM

		Nominal 0.2 Mil Coating				Nominal 0.4 Mil Coating			
		Unbaked		Baked 1)		Unbaked		Baked 1)	
Model Number	Description	Peel Strength (in-lb/in)	Failure 2)	Peel Strength (in-lb/in)	Failure %	Peel Strength (in-lb/in)	Failure %	Peel Strength (in-lb/in)	Failure %
-	Unprimed Control	Not Tested	-	58	70C 30A	Not Tested	-	Not Tested	-
1	Phenoxy	25	20C 80CP	Not Tested	-	Not Tested	-	Not Tested	-
2	Epon 1007	49	70C 30PM	Not Tested	-	36	40C 60PM	Not Tested	-
3	Epon 828	44	30C 70PM	Not Tested	-	Not Tested	-	Not Tested	-
4	Resorcinol Adduct	45	50C 50PM	16	20C 80PM	28	20C 80PM	Not Tested	-
4'	Hydroquinone	50	80C 40PM	17	20C 80PM	42	70C 20PM	15	100PM
5	BPA Adduct	30	10C 90PM	16	10C 90PM	67	80C 20PM	13	100PM
6	BPS Adduct	29	50C 50PM	22	40C 60PM	52	50C 50PM	8	5C 95PM
7	BPA-Rubber Adduct	62	80C 20PM	34	60C 40PM	68	90C 10PM	51	20C 80PM

1) 1 hour at 250°F

2) Failure Mode Key:
AP - Adhesively from primer
C - Cohesive
CP - Cohesive from primer
PM - Primer from metal

3) Catalyst: TPPEI

4) Surface Preparation: Phosphate Anodize

TABLE 26. EFFECT OF MODEL VEHICLE PRIMER THICKNESS ON EA 9628 MMCD PEEL STRENGTH (IN-LB/IN), 75°F TEST

Model Number	Description	Thickness, Mils										
		0.05	0.15	0.2	0.3	0.4	0.5	0.6	0.8	1.0	1.4	1.9
1	Phenoxy	-	74	-	74	-	33	-	-	-	-	-
2	Epon 1007	-	77	-	67	-	69	-	-	-	-	-
3	Epon 828	-	0	-	0	-	0	-	-	-	-	-
4	Resorcinol Adduct	76	70	64	62	71	62	-	-	61	-	-
4'	Hydroquinone	77	-	65	-	73	-	-	70	73	-	-
5	BPA Adduct	-	-	-	67	-	70	-	-	-	44	-
6	BPS Adduct	73	76	67	71	71	68	70	32	-	-	-
7	BPA-Rubber Adduct	-	-	-	69	-	69	-	-	-	-	62
-	Unprimed Control	77	-	-	-	-	-	-	-	-	-	-

Primer Bake: 1 hour at 250°F
Adhesive Cure Cycle: 1 hour at 250°F plus 1 hour at 350°F
Catalyst: TPPEI
Surface Preparation: Phosphoric Anodize

TABLE 27. EFFECT OF MODEL VEHICLE PRIMER THICKNESS ON EA 9628 MMCD PEEL STRENGTH (in-LB/IN, -67°F TEST

Thickness, mils:		0.05	0.15	0.2	0.3	0.4	0.5	0.6	0.8	1.0	1.4	1.9
Model No.	Description											
1	Phenoxy	34	21	21	10	5						
2	EPON 1007	54	46	-	23	-	16					
3	EPON 828	55	0									
4	Resorcinol Adduct	64	46	20	-	13	-	5				
4'	Hydroquinone Adduct	66	-	-	34	-	34	22	21	17		
5	BPA Adduct	-	-	-	41	-	33	-	29	16	6	
6	BPS Adduct	53	-	37	21	-	17	8				
7	BPA-Rubber	-	-	-	43	-	43	-	40	37	-	19
-	Unprimed	(48)										

Catalyst: TPPEI
Primer Bake: 1 hour @ 250°F
Adhesive Cure Cycle: 1 hour @ 250°F plus 1 hour @ 350°F
Surface Preparation - Phosphoric Anodize

TABLE 28. MODEL SYSTEMS USED IN BULK PROPERTY DETERMINATION

Model System	1[1]	2	3	4	5	6	7
DEN-438	60	60	60	/	/	/	/
EPON 828	/	/	40	/	/	/	/
EPON 1007	/	40	/	/	/	/	/
PAHJ	40	/	/	/	/	/	/
Hydroquinone/828 Adduct	/	/	/	100	/	/	/
Bis A/828 Adduct	/	/	/	/	100	/	/
Bis S/828 Adduct	/	/	/	/	/	100	/
Bis A/CTBN/828 Adduct	/	/	/	/	/	/	100
Varcum 4326	35	38.7	57	21.3	19	18.7	16
TPPEI	0.7	0.77	1.15	0.43	0.425	0.38	0.32
PC-1344	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Intermediate Form	Tough Solid	Friable Powder	Viscous Liquid	Friable Powder	Friable Powder	Friable Powder	Friable Powder
Processing By Powder Sintering at Reduced Pressure	Very Difficult	Easy	Not Done	Easy	Easy	Difficult	Difficult

[1] All systems are given by weight

TABLE 29. CRITICAL THICKNESS VALUES OF MODEL PRIMER SYSTEMS

Model	Type[1]	Critical[2)3)] Thickness (CT) (mils)
1	Phenoxy-DEN 438	Not Obtained
2	Epon 1007-DEN 438	0.10
3	Epon 828-DEN 438	0.05
4	Hydroquinone-828 Resin	0.55
5	Bisphenol A-828 Resin	0.40
6	Bisphenol S - 828 Resin	0.20
7	Bisphenol A-828-CTBN Resin	1.50

1) See Table 28 for formulation.
2) Determined at -67°F using EA 9628 as the adhesive.
3) Primers were applied at varied thicknesses and the solvent removed by exposing to ambient temperatures for 60 minutes followed by 60 minutes at 250°F. The test panels were then assembled with the adhesive and autoclave cured (vented) 60 minutes at 250°F plus 60 minutes at 350°F and 50 lb/in^2. Phosphate anodized 2024-T3 clad aluminum was used as the adherends.

TABLE 30. TENSILE PROPERTIES1)6) FOR MODEL PRIMER SYSTEMS

Model2) #	Type	Ultimate3)4) Tensile (lb/in^2)	Tensile5) Modulus (lb/in^2)	Elongation @ Failure (%)
1	Phenoxy-DEN 438	——— Not Obtained ———		
2	Epon 1007-DEN 438	10500/1200	476000/14000	3.0/0.7
3	Epon 828-DEN 438	10500/2100	595000/40000	3.9/1.4
4	Hydroquinone-Epon 828 Resin	10500/500	404000/61000	4.0/0.2
5	Bisphenol A-Epon 828 Resin	10600/160	464000/6900	6.2/0.4
6	Bisphenol S-Epon 828 Resin	7000/1200	483000/50000	2.0/0.6
7	Bisphenol A-Epon 828-CTBN Resin	7900/700	440000/9600	4.1/0.8

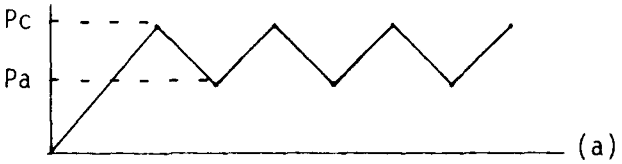
1) As determined by ASTM D638-64T (10)
2) See Table 28 for formulations.
3) All systems were cured for two hours at 250°F followed by one hour at 350°F.
4) All data represent the mean of four test specimens.
5) Initial tangent modulus
6) All data are given as mean ($\bar{x}$)/standard deviation (σx) (n=3)

TABLE 31. CRACK TOUGHNESS PROPERTIES1) OF MODEL PRIMER SYSTEMS

Model2) #	Type	Crack Toughness (lb/in)3)6)	
		G_{Ic} 4)	G_{Ia} 5)
1	Phenoxy-DEN 438	← Not Obtained →	
2	Epon 1007-DEN 438	1.53/0.34	1.04/0.24
3	Epon 828-DEN 438	1.00/0.38	0.59/0.11
4	Hydroquinone-EPON 828 Resin	2.33/0.62	1.37/0.39
5	Bisphenol A-Epon 828 Resin	3.61/0.83	1.66/0.54
6	Bisphenol S-Epon 828 Resin	1.87/0.30	1.18/0.15
7	Bisphenol A-CTBN-Epon 828 Resin	5.50/1.34	3.46/0.94

1) Determined at 75°F using a tapered double cantilevered beam specimen. Adherends were machined aluminum (2024-T351 bare, FPL etch). See Appendix for details of preparation and cure.
2) See Table 28 for formulation.
3) Numbers are data means determined from three specimens each cracked an average of three times.
4) GIa - Arrest Crack Toughness
5) GIc - Critical Crack Toughness

G_{Ia} are determined at the following locations on the load - crack length curve.



6) Data are given in mean ($\bar{x}$) and Standard Deviation (σx) ($n \geq 9$)

TABLE 32. EFFECT OF FORMULATION ON GLASS TRANSITION[1] TEMPERATURE

Model #	Description	Number of Transitions	Transition[2][3] Temperature (°C)	
			#1	#2
1	Phenoxy/DEN 438	2	85	132
2	Epon 1007/DEN 438	2	87	131
3	Epon 828/DEN 438	1	/	123
4	Hydroquinone/Epon 828 Resin	1	/	86
5	Bisphenol A/Epon 828 Resin	1	/	90
6	Bisphenol S/Epon 828 Resin	1	/	115
7	CTBN/Bisphenol A/Epon 828 Resin	1	/	88

1) Transition temperatures were determined using a Perkin-Elmer DSC-2. Approximately 20 mg specimens were cut from the tensile dogbones used in determining the bulk properties. All specimens had been cured two hours at 250°F plus one hour at 350°F prior to test.

2) All values are averages of at least three determinations of the transition temperatures.

3) Transitions were determined as shown in Figure 6.

TABLE 33. PRIMER VEHICLE OPTIMIZATION STUDY SUMMARY

Resin Component (A)	Curing Agent (B)	Catalyst (C)	Ratio By Weight		
			(A)	(B)	(C)
Model #5 Adduct/DEN 438	Varcum 4326	TPPEI	70/30	30	0.6
Model #5 Adduct/DEN 438	Varcum 4326	TPPEI	40/60	42	0.84
Model #5 Adduct/Ciba 0500	Varcum 4326	TPPEI	70/30	41	0.82
Model #5 Adduct/Ciba 0500	Varcum 4326	TPPEI	40/60	64	1.28
Model #5 Adduct	Dicy/V-4326	TPPEI	100	1.8/9.0	0.18
Model #5 Adduct	Dicy	EMI-24	100	3.6	0.5
Model #5 Adduct	MPDA	EMI-24	100	4.6	0.5
Model #5 Adduct	Phosphoric Acid, 85%	None	100	1.0	-
Model #5 Adduct	Gallic Acid	LR082-82	100	7.2	0.34
Model #5 Adduct	Gallic Acid/Melamine	None	100	3.6	1.8
Model #5 Adduct	Varcum 4326	BDMA	100	17	0.34
Model #5 Adduct	Varcum 4326	C.A. "D"	100	17	0.34
Model #5 Adduct	Varcum 4326	DMP-30	100	17	0.34

Note: See Appendix for description of materials.

TABLE 34. MMCD PEEL STRENGTH USING VARIOUS MODIFIED PRIMER VEHICLES (TEST ADHESIVE - EA 9628)

System Number	Description Of Unpigmented Vehicle	Pencil[1)] Hardness (Baked/ Cured)	MEK[2)] Resist. (Baked/ Cured)	MMCD Peel (in-lb/in)					
				0.2 Mils		0.5 Mils		0.8 Mils	
				75°F	-67°F	75°F	-67°F	75°F	-67°F
-	Unprimed Control[3)]	-	-	46	23	58	23	46	23
1	BR-127	6/6	E/E	49	27	29	13	3	-
2	Blank	-	-	-	-	-	-	-	-
3	Model #4 (Resorcinol Adduct)	3/6	N/G	36	23	55	10	55	12
4	Model #4'(Hydroquinone Adduct)	3/6	N/G	53	35	26	16	-	-
5	Model #5 (BPA Adduct)	3/6	N/G	50	34	27	24	-	-
6	Model #5/DEN 438 (70/30)	3/6	G/E	35	1	1	-	-	-
7	Model #5/DEN 438 (40/60)	5/6	E/E	35	5	7	-	-	-
8	Model #5/Ciba 0500 (70/30)	5/6	E/E	62	37	63	13	42	7
9	Model #5/Ciba 0500 (40/60)	5/6	E/E	46	10	27	2	-	-
10	Model #5/Dicy/Varcum 4326	3/6	N/G	31	13	50	2	5	-
11	Model #5/Dicy/EMI-24	5/6	G/G	0	-	55	0	0	-
12	Model #5/MPDA/EMI-24	5/6	G/E	55	35	32	10	-	-
13	Model #5/Phosphoric Acid	3/-	N/-	59	41	66	32	57	31
14	Model #5/Gallic Acid/LR082-82	3/5	N/G	56	40	63	32	56	25
15	Model #5/Gallic Acid/Melamine	< 1/3	N/N	-	-	42	-	-	-
16	Model #5/Varcum 4326/BDMA	4/6	N/G	40	23	52	14	8	-
17	Model #5/Varcum 4326/C.A. "D"	4/6	N/G	47	31	49	19	42	11
18	Model #5/Varcum 4325/DMP-30	5/6	G/E	54	28	60	19	23	-
19	Model #6 (BPS Adduct	4/6	N/E	45	20	4	-	-	-
20	Model #7 (BPA Rubber Adduct)	< 2/4	N/F	60	42	47	32	49	26

1) H Type, on 0.5 mil thick primer.

2) N - None, 0.5 mil thick G - Good
P - Poor E - Excellent
F - Fair

3) Control used during lay-up for each primer thickness set.

TABLE 35. MMCD PEEL STRENGTH OF SELECTED PRIMER VEHICLES (TEST ADHESIVE - EA 9628)

No.	Description Of Unpigmented Vehicle	Pencil[1] Hardenss (Baked/Cured)	MEK[2] Resis. (Baked/Cured)	MMCD Peel Strength (in-lb/in)									
				Primer Thickness, Mils									
				0.10-0.29		0.30-0.45		0.50-0.69		0.70-0.89		0.90-1.09	
				75°F	-67°F	75°F	-67°F	75°F	-67°F	75°F	-67°F	75°F	-67°F
1	BR-127	6/7	E/E	59	39	42	22	22	9	-	-	-	-
3	Model #4 (Resorcinol Adduct)	4/6	N/G	42	26	-	-	38	30	26	5	-	-
4	Model #4'(Hydroquinone Adduct)	4/6	G/E	-	-	46	26	-	-	24	9	25	9
5	Model #5 (BPA Adduct)	3/7	N/E	-	-	48	23	-	-	50	8	19	4
8	Model #5 /Ciba 0500 (70/30)	5/7	E/E	-	-	49	8	18	-	-	-	7	-
14	Model #5 Gallic Acid/LR082-82	3/6	N/G	-	-	57	46	60	36	-	-	56	24
17	Model #5 Varcum 4326/C.A. "D"	3/7	N/E	-	-	60	38	52	23	-	-	50	22
18	Model #5 Varcum 4326/DMP-30	5/7	G/E	-	-	53	24	-	-	18	17	10	4
20	Model #7 (BPA-Rubber Adduct)	1/5	N/G	-	-	49	38	-	-	47	47	45	31
20a	Model #7 /Ciba 0500 (70/30)	5/7	E/E	51	15	-	-	-	-	26	-	18	-
20b	Model #7 /Ciba 0500 (40/60)	5/7	E/E	-	-	6	3	5	-	5	-	-	-
20c	Model #7 Varcum 4326/DMP-30	3/6	F/E	-	-	55	39	16	3	-	-	0	-
20d	Model #7 MPDA/EMI-24	5/7	E/E	-	-	0	0	0	-	-	-	0	-

1) H Type, 0.2-0.5 mils thick coating
2) 0.2-0.5 mils thick coating N - None
P - Poor
F - Fair
G - Good
E - Excellent

3) Unprimed EA 9628 Control: 75°F - 60 in.lb./in.
-67°F - 20 in.lb./in.

TABLE 36. MOISTURE EQUILIBRIUM OF MODEL VEHICLES

Model Number	Description	% Weight Gain In 120°F D.I. H_2O
1	Phenoxy	1.76
2	Epon 1007	1.71
3	Epon 828	1.56
4	Resorcinol Adduct	2.25
5	Hydroquinone Adduct	2.18
6	BPA Adduct	1.81
7	BPS Adduct	2.63
8	BPA-Rubber Adduct	1.78

1) See also Figure 9.

TABLE 37. MOISTURE EQUILIBRIUM OF MODIFIED VEHICLE SYSTEMS

System Number	Description	% Weight Gain In 120°F D.I. H_2O
5	Model #5 (BPA Adduct)	1.88
8	Model #5 (BPA Adduct)/Ciba 0500 (70/30)	2.13
14	Model #5 (BPA Adduct), Gallic Acid/LR022-82	2.76
17	Model #5 (BPA Adduct), Varcum 4325/C.A. "D"	1.85
18	Model #5 (BPA Adduct), Varcum 4325/DMP-30	1.93
20	Model #7 (BPA-Rubber Adduct)	1.90
20a	Model #7 (BPA-Rubber Adduct)/Ciba 0500 (70/30)	2.50
20b	Model #7 (BPA-Rubber Adduct)/Ciba 0500 (40/60)	2.90
20c	Model #7 (BPA-Rubber Adduct),Varcum 4326/DMP 30	1.92
20d	Model #7 (BPA-Rubber Adduct), MPDA/EMI-24	1.99

1) See also Figure 10.

TABLE 38. CRITICAL SURFACE TENSION (γ_C) AND MMCD PEEL STRENGTH[1] VS. THICKNESS OF BR-127 PRIMER

Film Thickness (Mils)	Pencil Hardness		MEK Resistance[2]		γ_c (Dynes/cm)		MMCD Peel Strength (in-lb/in)					
							Run A[5]				Run B	
	A[3]	B[3]	A	B	A	B	@75°F	Fail[4]	@-67°F	Fail.	@75°F	Fail
0.15	3H	-	G	-	-	-	70	95C 5AP	53	95C 5PM	62	95C 5PM
0.20	3H	6H	E	E	31.5	30.8	70	"	35	90C 10PM	59	90C 10PM
0.30	5H	-	E	-	-	-	68	"	41	90C 10PM	-	-
0.40	5H	6H	E	E	31.5	30.8	60	80C 20CP	14	30C 70PM	56	95C 5PM
0.50	5H	-	E	-	-	-	65	60C 40CP	10	20C 80PM	-	-
0.60	-	7H	-	E	-	30.8	-	-	-	-	44	40C 60PM
0.75	7H	7H	E	E	-	30.8	7	50CP 50PM	-	-	33	30C 70PM
0.90	7H	-	E	-	31.5	-	3	100CP	-	-	-	-

1) EA 9628 Film
2) 1 hour at 250°F bake: E - Excellent
G - Good
3) Run Number
4) AP - Adhesively from primer
C - Cohesive
CP - Cohesive in primer
PM - Primer from metal
5) Runs A and B represent initial and repeat tests, respectively.

TABLE 39. RANKING OF PROPERTIES FOR VARIOUS VEHICLE SYSTEMS

System References Key

System Number	Description Of Unpigmented Vehicle
3	Model #4 (Resorcinol Adduct)
4	Model #4'(Hydroquinone Adduct)
5	Model #5 (BPA Adduct)
8	Model #5/Ciba 0500 (70/30)
14	Model #5/Gallic Acid/LR 082-82
17	Model #5/Varcum 4326/C.A. "D"
18	Model #5/Varcum 4326/DMP-30
20	Model #7 (BPA Rubber Adduct)
20a	Model #7/Ciba 0500 (70/30)
20b	Model #7/Ciba 0500 (40/60)
20c	Model #7/Varcum 4326/DMP-30
20d	Model #7/MPDA/EMI-24

(A)

Ten Best MMCD Peel Systems

Rank	Systems
1	20
2	14
3	17
4	20a
5	8
6	5
7	4
8	3
9	20c
10	20b

(B)

Ten Best MEK Resistant Systems

Rank	Systems
1	8
2	20b
3	20a
4	20d
5	18
6	4
7	20c
8	17
9	5
10	14

(C)

Ten Best Pencil Hardness Systems

Rank	Systems
1	20
2	5
3	17
4	20C
5	18
6	20d
7	8
8	20a
9	14
10	20b

(D)

Ten Best Moisture Resistant Systems

Rank	Systems
1	20
2	5
3	17
4	20c
5	18
6	20d
7	8
8	20a
9	14
10	20b

TABLE 40. COMPARATIVE RANKING OF VARIOUS VEHICLE[1] SYSTEMS - ALL CATEGORIES

	Category	Weight %
A.	MMCD Peel	60
B.	MEK Resistance	20
C.	Moisture Resistance	15
D.	Pencil Hardness	5

Rank	System	Points[2]
1	20	75.0
2	17	68.5
3	8	67.0
4	20a	66.0
5	14	59.0
6	5	49.5
7	4	35.5
8	20c	31.0
9	20b	29.5
10	18	25.5
11	20d	24.5
12	3	19.0

1) Table 39
2) Maximum points possible = 100

TABLE 41. 7-DAY AMBIENT EXPOSURE OF VEHICLE COATINGS TO COMMON SOLVENTS (PENCIL HARDNESS TEST)

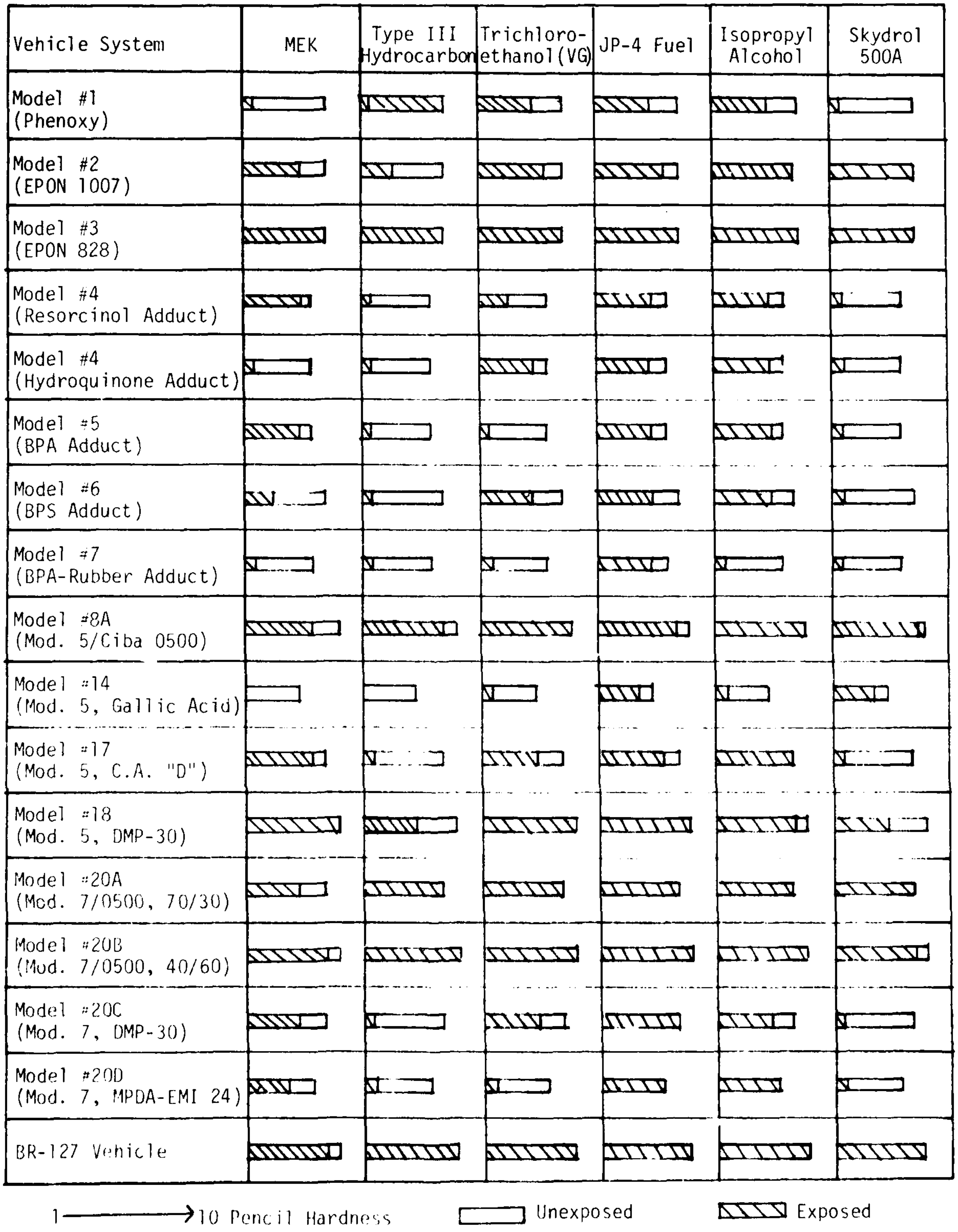


TABLE 42. MMCD PEEL STRENGTH OF SELECTED PRIMER VEHICLES USING IMPROVED PHOSPHATE ANODIZED ALUMINUM (EA 9628 TEST ADHESIVE)

System Ref:	Description Of Unpigmented Vehicle	Catalyst Content phh	Thick. (Mils)	Pencil 1) Hard. (Baked/ Cured)	MEK 2) Resis. (Baked/ Cured)	MMCD (in-lb/in)/	
						R.T.	-67°F
1	BR-127 3)	-	0.3	6/6	E/E	61.3	35.0
5	Model #5 (BPA Adduct)	2.0	0.5	4/6	N/E	44.6	14.0
5A	Model #5 (BPA Adduct)	3.0	0.5	5/6	P/E	55.8	35.0
6A	Model #5/DEN 438 (70/30)	1.5	0.6	6/6	E/E	57.6	9.0
6B	Model #5/DEN 438 (70/30)	1.0	0.4	4/6	N/E	44.6	6.5
6C	Model #5/DEN 438 (70/30)	0.5	0.4	4/6	N/E	24.6	7.5
8A	Model #5/Ciba 0500 (70/30)	1.0	0.4	7/6	E/E	58.8	8.0
14	Model #5, Gallic Acid (100% Stoich.)	4.7	0.5	4/	N/	60.4	43.0
14A	Model #5, Gallic Acid (100% Stoich.)	6.9	0.5	4/5	N/N	58.9	37.5
14B	Model #5, Gallic Acid (133% Stoich.)	5.2	0.5	4/	N/	60.1	37.3
20	Model #7 (BPA-Rubber Adduct)	2.0	0.5	4/6	N/G	49.5	33.8
20-1	Model #7 (BPA-Rubber Adduct)	3.0	0.4	4/6	N/G	52.4	37.8
20-2	Model #7 (BPA-Rubber Adduct)	4.0	0.4	5/5	F/G	4.8	-
20A	Model #7/Ciba 0500 (70/30)	2.0	0.5	7/6	E/E	47.6	11.5
20A-1	Model #7/Ciba 0500 (70/30)	1.0	0.4	6/6	G/E	58.6	6.5
Cont.	EA 9628 Film, Unprimed	-	-	-	-	61.4	56.0

1) H Type

2) N - None
P - Poor
G - Good
E - Excellent

3) Used at lower thickness

TABLE 43. PERFORMANCE RESULTS USED TO OPTIMIZE PRIMER VEHICLES

System	BR-127 Control	8A Hard	20A-1	(X_1)	(X_2)	(X_3)	(X_4)	5	(X_5)	7 Soft	EA 9628
BPA, Equiv./100g w/Epon 828	-	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	-
Hycar CTBN, phr (Epon 828)	-	-	20	40	20	10	-	-	10	20	-
Ciba 0500/Adduct (Wt.)	-	30/70	30/70	30/70	15/85	15/85	15/85	-	-	-	-
TPPEI, phh	-	1.0	1.0	1.0	1.0	1.0	1.0	2.0	2.0	2.0	-
Varcum 4326, phr	-	41	39	37	27	28	29	18	17	15	-
Properties:											
Test Series:[a]	A B	A B	A B	A B	A B	A B	A B	A B	A B	A B	A B
MEK Resis.[b] (Baked[c]/Cured)[d]	E/E E/E	G/E -	F/E F/E	N/G -	N/E F/E	- G/E	G/E G/E	N/E N/E	- F/E	N/G N/E	- -
Pencil Hard.[e] (Baked/Cured)	6/6 6/6	4/6 -	4/6 4/6	4/4 -	4/4 4/6	- 4/6	5/6 4/6	3/6 4/6	- 4/6	3/4 3/4	- -
MMCD Peel, in-lb/in[f]											
@ 75°F 0.2 Mils	61 -	59 -	59 58	18 -	77 67	- 65	58 60	49 57	- 56	48 47	60 63
@ 75°F 0.5 Mils	- 67[g]	50 -	60 50	2 -	66 62	- 60	59 59	52 54	- 52	47 54	- -
@ -67°F 0.2 Mils	44 -	27 -	36 40	- -	14 44	- 39	40 37	30 50	- 44	44 44	55 54
@ -67°F 0.5 Mils	- 33[g]	10 -	21 17	- -	10 23	- 37	29 32	22 30	- 33	34 43	- -

a) Series A bonded at one time, B at another.
b) E - Excellent
F - Fair
G - Good
N - None
P - Poor
c) 1 hour at 250°F bake
d) 1 hour at 250°F bake plus 1 hour at 250°F adhesive cure cycle
e) H - Pencil
f) EA 9628 Adhesive
g) Actual thickness 0.3 mils

TABLE 44. MMCD PEEL, MEK RESISTANCE AND PENCIL HARDNESS PROPERTIES OF OPTIMIZED PRIMER VEHICLES (EA 9628 TEST ADHESIVE)

Bake Cycle (Hr/°F)	Primer Thick. (Mils)	Model 8A (Hard)				Model 22				Model 7 (Soft)				EA 9628 (Unprimed)	
		MR[a]	PH[b]	MMCD (in-lb/in)		MR	PH	MMCD (in-lb/in)		MR	PH	MMCD in-lb/in)		MMCD(in-lb. in)	
				@75°F	@-67°F			@75°F	@-67°F			@75°F	@-67°F	@75°F	@-67°F
None	0.2	-/F	/4	60	55	-/P	/4	63	55	-/N	-/2	63	56	68	61
	0.5	-/G	/5	63	55	-/F	/4	62	58	-/P	-/3	67	61	68	61
	0.8	-/E	/5	27	9	-/G	/5	60	10	-/F	-/4	63	38	68	44
1/250	0.2	F/E	4/6	60	48	N/G	4/5	57	37	N/F	2/4	58	50	58	61
	0.5	G/E	4/6	58	28	P/E	4/6	57	36	N/G	2/4	47	34	68	61
	0.8	G/E	4/6	2	2	F/E	4/6	36	6	N/G	2/4	59	25	68	44

a) MEK Resistance after bake/cure
b) Pencil Hardness after bake/cure
c) Cure: 1 hour at 250°F, 50 psi

TABLE 45. ROOM TEMPERATURE STORAGE OF VARIOUS PRIMER VEHICLES

Vehicle Description	Sol-vent[1]	Month @75°F	Appear-ance	Coat-ability[2]	MEK Resistance[3]		Pencil Hardness	
					Cure A[4]	Cure B	Cure A	Cure B
Model #2[5] (Control)	A	None	Clear	Good	Excellent	Excellent	6H	7H
Model #2 (Control)	A	6	Clear	Fair	Excellent	Excellent	6H	
Model #2 (3 phh catalyst)	A	6	Clear	Fair	Good	Very Good	6H	6H
Model #2 (3 phh C.A. "D")	A	6	Clear	Fair	None	Very Good	6H	6H
Model #4[6]	A	3	Clear	Fair	Very Good	Excellent	6H	6H
Model #6A[7] (Control)	A	0	Clear	Good	Excellent	Excellent	4H	6H
Model #6A (Control)	A	3	Clear	Fair	Excellent	Excellent	6H	6H
Model #8A[8] (Control)	A	0	Clear	Good	Excellent	Excellent	6H	6H
Model #8A (Control)	A	3	Sl. Sed.	Fair	Excellent	Excellent	6H	6H
Model #5[9] (Dicy/EMI-24)	B	3	Clear	Good	Excellent	Excellent	6H	6H
Model #5[10] (MPDA/EMI-24)	A	3	Clear	Good	Excellent	Excellent	6H	6H
Model #5[11] (Gallic Acid)	A	3	Clear	Good	None	Excellent	2H	6H
Model #5 (BDMA Catalyst)	A	3	Clear	Good	Very Good	Excellent	6H	6H
Model #5 (C.A. "D" Cat.)	A	3	Clear	Good	Very Good	Excellent	4H	6H
Model #5 (DMP-30 Cat.)	A	3	Clear	Good	Excellent	Excellent	4H	6H
Model #8[12]	C	9	Clear	-	-	-	-	-
Model #9[13]	D	9	Clear	-	-	-	-	-

1) 20% solids in: A - MEK/THF/DAA C - MEK/Cellosolve Acetate/Toluene
B - MEK/THF/DAA/MOX D - MEK/Ethanol/Butanol

2) Sprayed and baked

3) Methyl ethyl ketone rub

4) Cure A - 1 hour at 250°F; Cure B - 1 hour at 250°F plus 1 hour at 350°F

5) Epon 1007/DEN 438/Varcum 4326/TPPEI Catalyst (2 phh)

6) Resorcinol Adduct/Varcum 4326/TPPEI Catalyst (pphh)

7) Model #5 (BPA Adduct)/DEN 438/Varcum 4326/TPPEI Catalyst (1.5 phh)

8) Model #5 (BPA Adduct/Ciba 0500/Varcum 4326/TPPEI Catalyst (1.5 phh)

9) Model #5 (BPA Adduct/Dicyandiamide/EMI-24 Catalyst (0.5 phr)

10) Model #5 Metaphenylene Diamine/EMI-24 Catalyst (0.5 phr)

11) Model #5 Gallic Acid/TPPEI Catalyst (0.34 phr)

12) Eponol 55/Cymel 245-8

13) Butvar 76/Resinox P-97/Phosphoric Acid Catalyst

TABLE 46. SALT SPRAY SCRIBE CORROSION PERFORMANCE (10 VEHICLES - 6 INHIBITORS)

System Number	Vehicle Description	Failure Range - Hours 1) Strontium Chromate	Cobalt Chromate	Melamine Dichromate	Triphenyl Guanidine Dichromate	Zinc Potassium Chromate	Magnesium Dichromate
1	Phenoxy	400-1250	400-500	500-2000+*	500	-	-
2	Epon 1007	250-1250	400-500	1250*	500	-	-
3	Epon 828	400-750	500-750	500-1250*	500	-	-
4'	Hydroquinone Adduct	1500	500-1250	No Fail*	400-500	-	-
5	BPA Adduct	1250	500-1250	400-1500*	400	500-1250	400
7	BPA-Rubber Adduct	750-2000+*	1250	1500-1750	400	500-1250	400-500
8A	Model 5/Ciba 0500 (70/30)	500-1250	1250-1500	1750-2000+*	400	1500-1750	400
20A-1	Model 7/Ciba 0500 (70/30)	2000-2000+*	500-700	500-1750	400	1500-1750	400
201	Modified EA 9201	1250	400-500	1250-2000+*	250	-	-
127	BR-127	1250-1500	500-2000*	500-2000*	400	-	-

1) Four exposure panels - first and last inspection period to develop 5 corrosion beads (under cut) in scribe.

* Rated best inhibitor for model vehicle based on all criteria after 2000 hours.

TABLE 47. SALT SPRAY SCRIBE CORROSION PERFORMANCE - 2ND TEST SERIES (3 VEHICLES - 4 INHIBITORS)

System Number	Vehicle Description	Cr^{+6} Conc.[2]	Bake Cycle[3]	Failure Range - Hours[1]			
				Strontium Chromate	Cobalt Chromate	Melamine Dichromate	Zinc Pot. Chromate
8A	Model 5/Ciba 0500	2.56	A	Not Tested	Not Tested	1200-1200+	600
			B	Not Tested	Not Tested	1200-1200+	600
		3.84	A	Not Tested	Not Tested	No Failure	1200
			B	Not Tested	Not Tested	No Failure	600
22	Model 22	2.56	A	No Failure	1200-1200+	1200-1200+	600-1200
			B	1200-1200+	1200-1200+	1200	600
		3.84	A	1200-1200+	No Failure	No Failure	1200
			B	600-1200	No Failure	No Failure	600
7	Model 7	2.56	A	Not Tested	Not Tested	No Failure	600
			B	Not Tested	Not Tested	1200	600
		3.84	A	Not Tested	Not Tested	No Failure	600-1200
			B	Not Tested	Not Tested	1200	600-1200
BR-127	BR-127 Stock	3.80[4]	A	1200	-	-	-
			B	1200	-	-	-

1) Two exposure panels - first and last inspection period to develop 5 corrosion beads (undercut) in scribe.
2) PBW inhibitor Cr^{+6} concentration.
3) A - 2 hours @ 250°F B - 0.5 hours @ 250°F + 1 hour @ 350°F.
4) As determined.

TABLE 48. PRELIMINARY EFFECTS OF INHIBITORS ON PRIMER VEHICLE MMCD PEEL PERFORMANCE[1]

		MMCD Peel, in-lb/in at 75°F						
	Chromate:	None	Strontium	Cobalt	Melamine	Triphenyl Guanidine	Zinc Potassium	Magnesium
Vehicle	% Inhibitor[2]	0.00	10.0	8.63	12.25	20.4	10.8	8.54
Model #5	MR[3]	N/E	N/E	N/E	F/E	G/VG	N/E	F/E
	MMCD[4]	47	47	52	48	0	49	42
Model #7	MR	N/G	N/G	N/G	P/E	G/E	N/G	G/E
	MMCD	49	32	50	49	0	52	57
Model #8A	MR	G/E	E/E	E/E	E/E	E/E	E/E	P/E
	MMCD	59	0	18	11	0	0	56
Model #20A-1	MR	P/E	P/E	F/E	G/E	E/E	G/E	F/E
	MMCD	58	38	57	27	0	21	52
Model #201	MR	-	E/E	E/E	E/E	G/E	-	-
	MMCD	-	14	34	0	0	-	-
BR-127	MR	-	-	E/E	-	E/E	-	-
	MMCD	-	-	59	-	0	-	-
Unprimed Control	MR	-	-	-	-	-	-	-
	MMCD	-	-	-	-	-	-	-

[1] EA 9628 cured one hour at 250°F

[2] By weight of vehicle (2.56% Cr^{+6})

[3] MEK Resistance after bake/cure (Primer bake was one hour at 250°F)
E - Excellent
F - Fair
G - Good
N - None
P - Poor

[4] Metal-metal climbing drum peel at 75°F (in-lb/in)

TABLE 49. MMCD PEEL PERFORMANCE VERSUS CIP PRIMER THICKNESS (INHIBITOR Cr^{+6} CONCENTRATION - 2.56%)

	Vehicle:		MMCD Peel @ 75°F (in-lb/in)[1]								
			8A (Hard)			22A			7 (Soft)		
Inhibitor (Wt %)	Primer Thickness (mils)		0.2	0.5	0.8	0.2	0.5	0.8	0.2	0.5	0.8
Zinc Potassium Chromate (10.8)		U[2]	65	64	64	67	67	65	68	68	55
		B	34	3	6	66	66	65	61	54	45
Melamine Dichromate (12.25)		U	67	63	57	62	50	55	67	64	60
		B	59	47	33	52	48	41	59	40	35
Strontium Chromate (10.0)		U	N.T.[3]	N.T.	N.T.	63	66	60	N.T.	N.T.	N.T.
		B	N.T.	N.T.	N.T.	65	62	58	N.T.	N.T.	N.T.
Cobalt Chromate (8.63)		U	N.T.	N.T.	N.T.	66	64	65	N.T.	N.T.	N.T.
		B	N.T.	N.T.	N.T.	68	63	59	N.T.	N.T.	N.T.
Triphenyl Guanidine Dichromate (20.4)		U	N.T.	N.T.	N.T.	58	60	N.T.	N.T.	N.T.	N.T.
		B	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.

1) EA 9628 cured one hour at 250°F, 50 psi. Average of 44 peel specimens - 65.8 σ 4) 8.1 in-lb/in
2) U - Unbaked primer; B - Baked 0.5 hours at 250°F
3) Not Tested
4) σ - standard deviation

TABLE 5C. MMCD PEEL PERFORMANCE VERSUS CIP PRIMER THIKNCESS (INHIBITOR Cr^{+6} CONCENTRATION - 3.84)

Inhibitor Weight	Vehicle		MMCD Peel At 75°F (in-lb/in)[1]											
			8A (Hard)			22A			7 (Soft)			BR-127		
	Primer Thick. (Mils)		0.2	0.5	0.8	0.2	0.5	0.8	0.2	0.5	0.8	0.2	0.5	0.8
Zinc Potassium Chromate (16.2)		U[2]	64	62	61	65	65	64	68	65	64	N.T.[3]	N.T.	N.T.
		B	6	2	2	65	65	65	62	44	47	N.T.	N.T.	N.T.
Melamine Dichromate (18.4)		U	67	51	51	62	43	52	67	61	58	N.T.	N.T.	N.T.
		B	57	40	15	49	42	37	56	35	29	N.T.	N.T.	N.T.
Strontium Chromate (15.0)		U	N.T.	N.T.	N.T.	62	61	60	N.T.	N.T.	N.T.	58	39	28
		B	N.T.	N.T.	N.T.	63	55	47	N.T.	N.T.	N.T.	47	56	48
Cobalt Chromate (12.9)		U	N.T.	N.T.	N.T.	63	63	59	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.
		B	N.T.	N.T.	N.T.	63	59	54	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.

1) EA 9628 cured one hour at 250°F, 50 psi. Average of 44 peel specimens - 65.8 σ 8.1[4] 8.1 in-lb/in
2) U - Unbaked primer; B - Baked 0.5 hours at 250°F
3) Not tested
4) σ - standard deviation

TABLE 51. MMCD PEEL PERFORMANCE VERSUS CIP PRIMER THICKNESS (INHIBITOR Cr^{+6} CONCENTRATION - 3.84)

			MMCD Peel At -67°F (in-lb/in)[1]											
Inhibitor (% Wt)	Vehicle		8A (Hard)			22A			7			BR-127		
	Primer Thick. (Mils)		0.2	0.5	0.8	0.2	0.5	0.8	0.2	0.5	0.8	0.2	0.5	0.8
Zinc Potassium Chromate (16.2)		U[2]	57	53	52	56	54	53	56	55	53	N.T.	N.T.	N.T.
		B	N.T.	N.T.	N.T.	49	38	28	47	36	32	N.T.	N.T.	N.T.
Melamine Dichromate (18.4)		U	N.T.	N.T.	N.T.	N.T.	39	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.
		B	N.T.	N.T.	N.T.	N.T.	15	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.
Strontium Chromate (15.0)		U	N.T.	N.T.	N.T.	N.T.	41	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.
		B	N.T.	N.T.	N.T.	38	25	18	N.T.	N.T.	N.T.	35	24	11
Cobalt Chromate (12.9)		U	N.T.	N.T.	N.T.	N.T.	52	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.
		B	N.T.	N.T.	N.T.	N.T.	20	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.

1) EA 9628 cured one hour at 250°F, 50 psi. Average of 10 peel specimens 57.3 σ[4] 3.8 in-lb/in
2) U - Unbaked primer; B - Baked 0.5 hours at 250°F
3) Not tested
4) σ - standard deviation

TABLE 52. INHIBITOR-VEHICLE STORAGE[1] AT ROOM TEMPERATURE

		Initial Observation		1.5 Months at Room Temperature		
Inhibitor[2]	Vehicle	Vehicle[3] Color	Settling[4] Rate	Vehicle Color	Reconstitution[5]	
Strontium Chromate	Model 5	Clear Yellow	Medium	No Change	Excellent	(E)
	Model 7	Sl. Turbid Yellow	Slow	No Change	Excellent	(E)
	Model 8A	Clear Amber	Fast	No Change	Excellent	(E)
	Model 20A-1	Clear Amber	Slow	No Change	Excellent	(E)
	BR-127	Clear Yellow	Medium	Turbid Yel-White	Poor	(P)
Cobalt Chromate	Model 5	Trubid Brown	Slow	No Change	Fair	(G)
	Model 7	Turbid Brown	Slow	No Change	Fair	(G)
	Model 8A	Clear Gold	Fast	No Change	Excellent	(P)
	Model 20A-1	Turbid Brown	Medium	No Change	Excellent	(P)
	BR-127	Clear Avacado	Fast	Turbid Avacado	Poor	(P)
Melamine Dichromate	Model 5	Clear Lt. Red	Medium	Clear Dark Red	Poor	(P)
	Model 7	Clear Lt. Red	Slow	Clear Dark Red	Poor	(P)
	Model 8A	Clear Lt. Red	Medium	Clear Dark Red	Poor	(P)
	Model 20A-1	Clear Lt. Red	Medium	Clear Dark Red	Poor	(P)
	BR-127	Turbid Olive	Medium	No Change	Poor	(P)
Triphenylguanidine Dichromate	Model 5	Clear Bronze	Soluble	No Change	Soluble	-
	Model 7	Clear Bronze	Soluble	No Change	Soluble	-
	Model 8A	Clear Bronze	Soluble	No Change	Soluble	-
	Model 20A-2	Clear Bronze	Soluble	No Change	Soluble	-
	BR-127	Turbid Olive	Ppts	No Change	Excellent	(G)
Continued						

TABLE 52. Continued

Inhibitor[2]	Vehicle	Initial Observation		1.5 Months At Room Temperature		
		Vehicle[3] Color	Settling[4] Rate	Vehicle Color	Reconstitution[5]	
Zinc Potassium Chromate	Model 5	Clear Yellow	Slow	Turbid Yellow	Fair	(E)
	Model 7	Sl. Turbid Yellow	Slow	Turbid Yellow	Fair	(E)
	Model 8A	Clear Amber	Fast	No Change	Fair	(E)
	Model 20A-1	Clear Amber	Medium	No Change	Excellent	(E)
Magnesium Dichromate	Model 5	Clear Bronze	Soluble	No Change	Soluble	-
	Model 7	Clear Bronze	Soluble	No Change	Soluble	-
	Model 8A	Clear Bronze	Soluble	Sl. Turbid Bronze	Soluble	-
	Model 20A-1	Clear Bronze	Soluble	Sl. Turbid Bronze	Soluble	-

1) glass and tin containers, 10% non-volatiles
2) 2.36% Cr^{+6} concentration
3) supernatant after settling of pigment
4) comparison from 2-48 hours observation
5) ability of pigment to re-disperse in the vehicle after simple agitation;( ) indicates quality of grind.

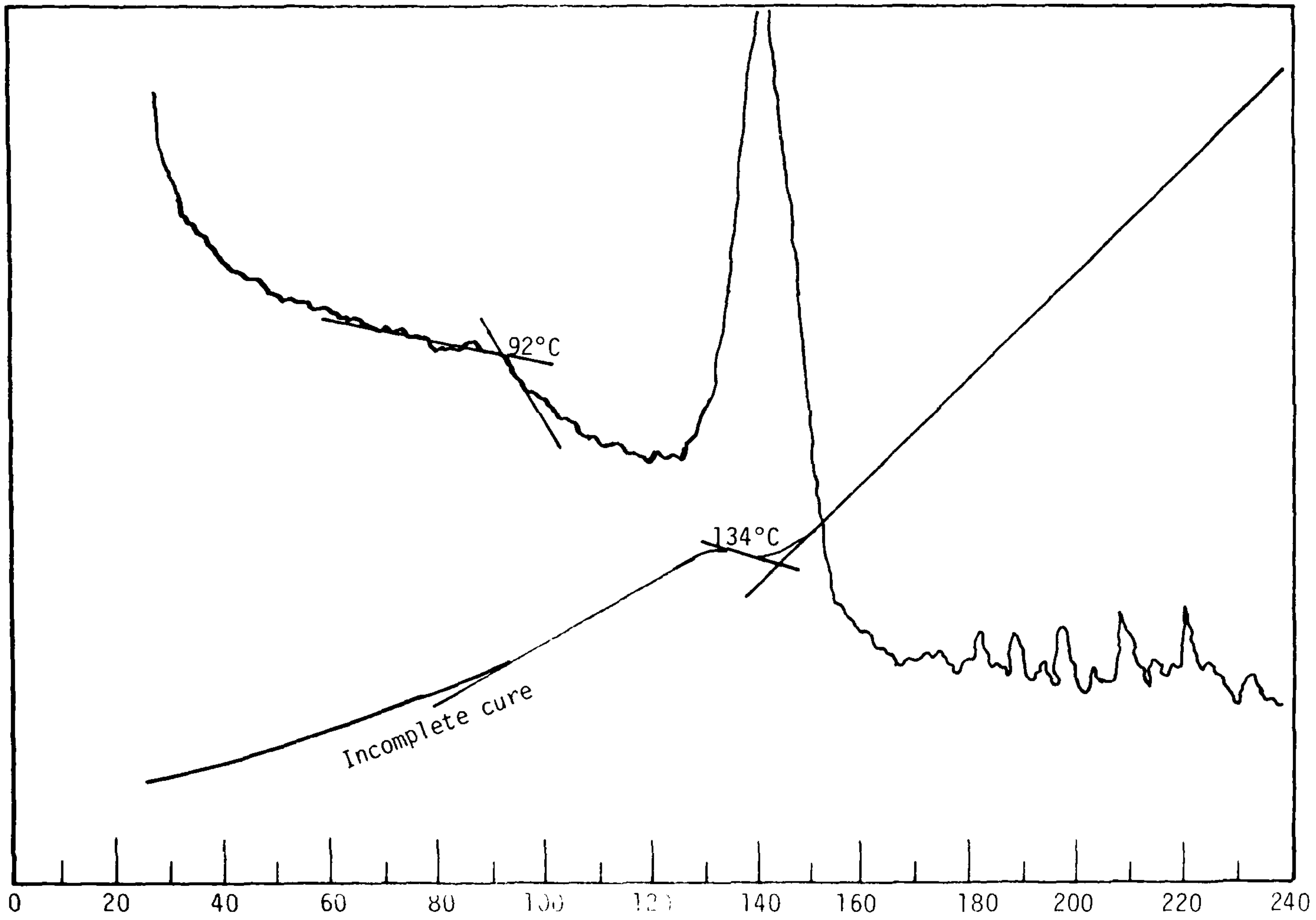


Figure 1. TMA Curve Of Model Number 2 (TPPEI Catalysis, 0.4 pbw) Cured 2 Hours @ 250°F

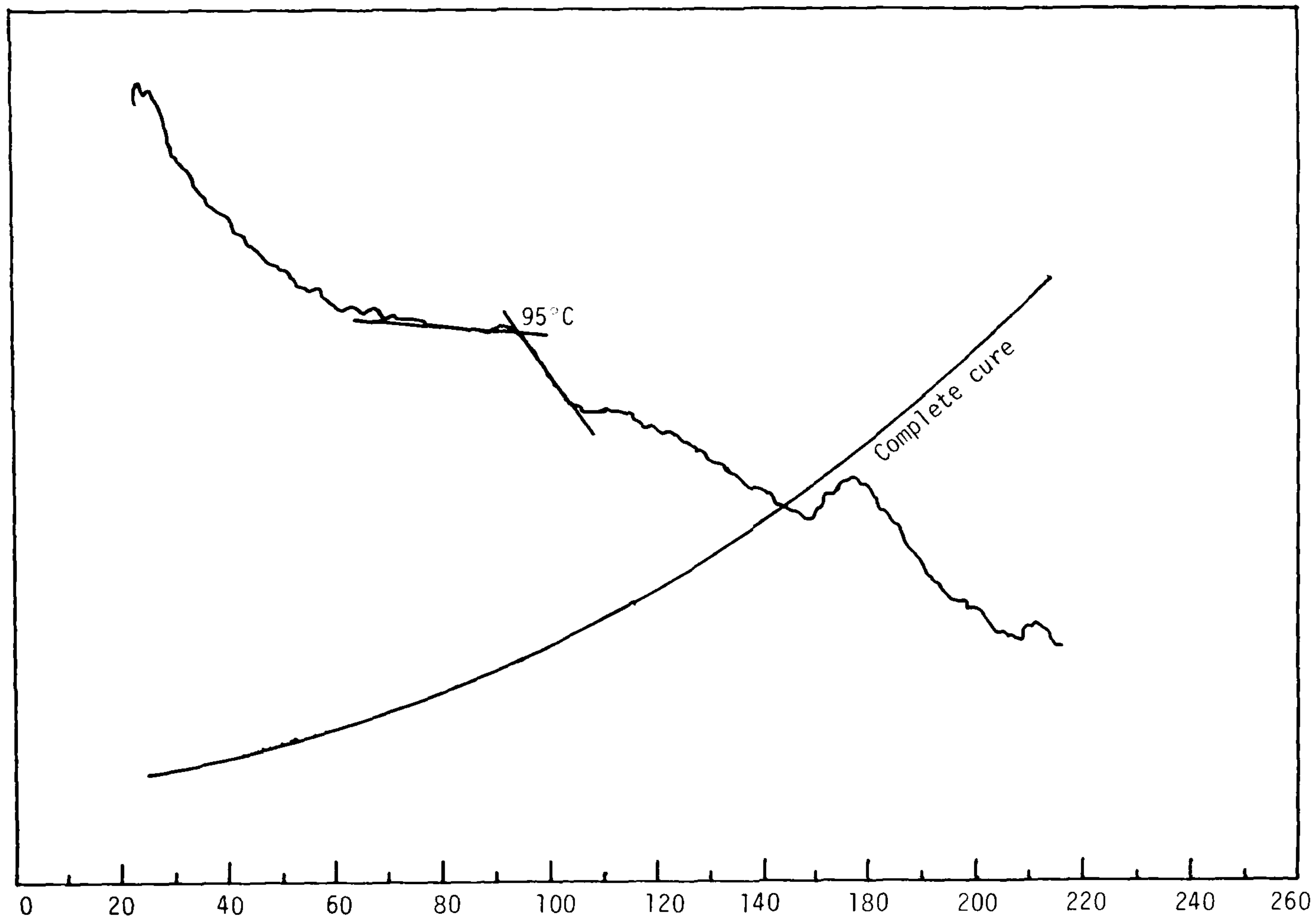


Figure 2. TMA Curve of Model Number 2 (TPPEI Catalysis, 0.4 pbw) Cured 2 Hours @ 250°F + 1 Hour @ 350°F

Figure 3. Effect Of Increasing Primer Thickness On -67°F Peel Strength

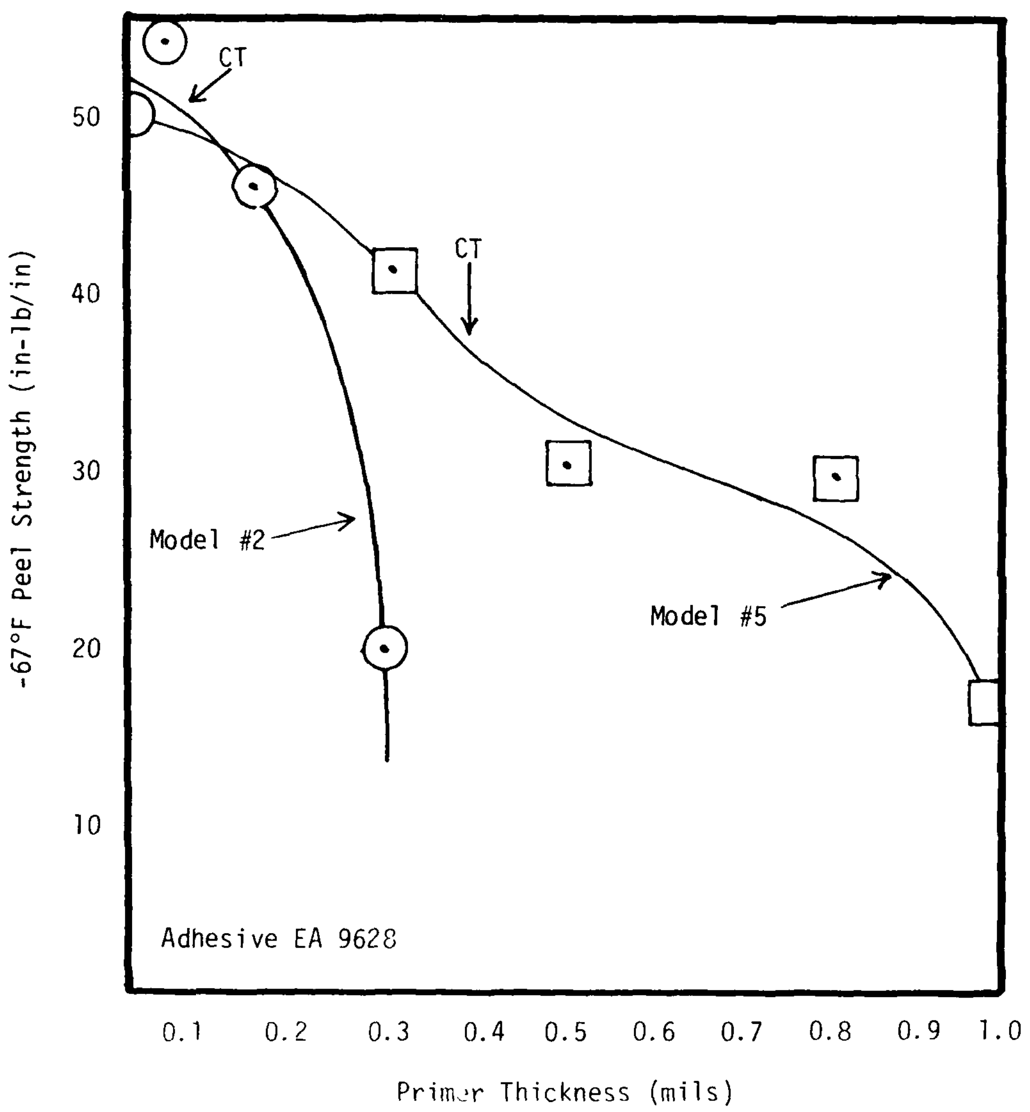


Figure 4. Effect Of Increasing Primer Thickness On -67°F Peel Strength

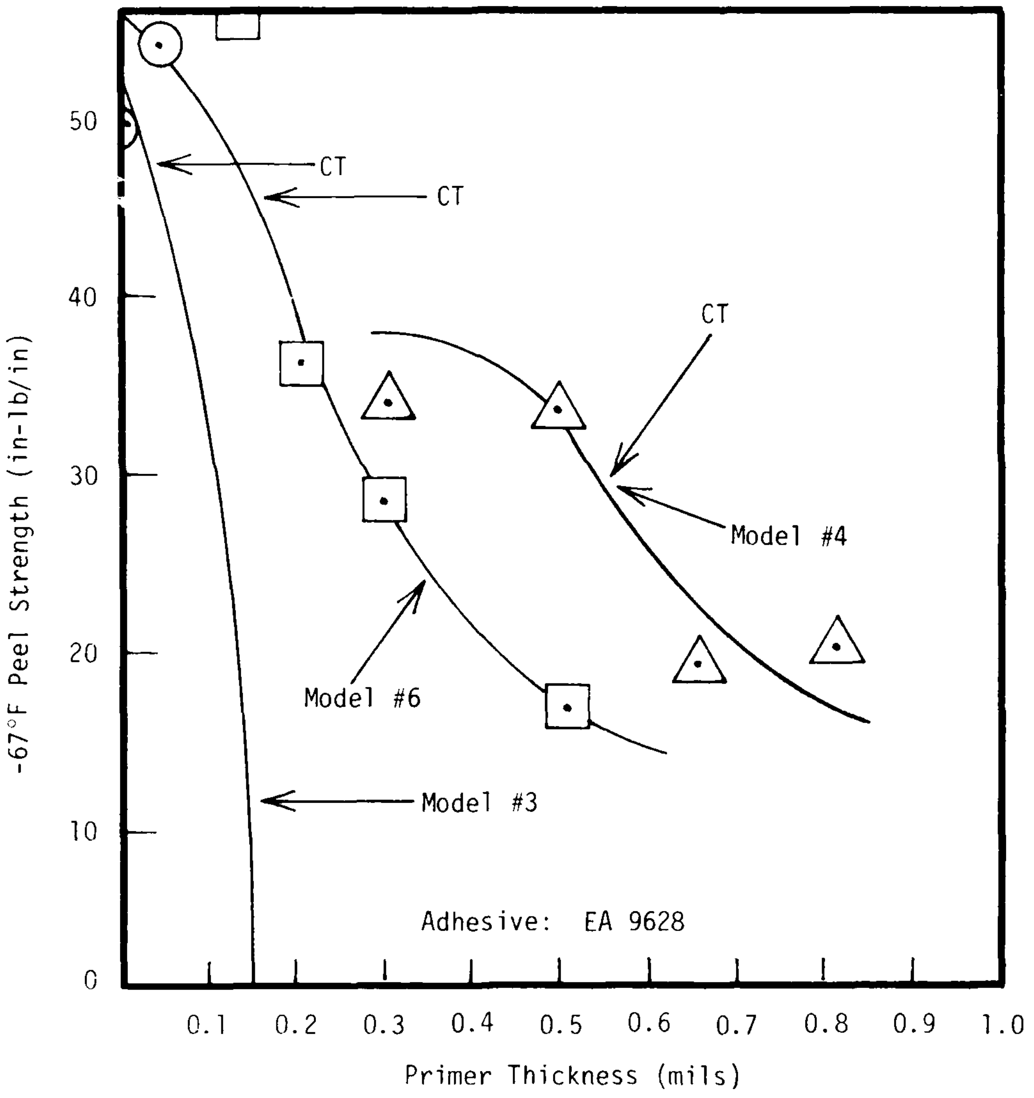
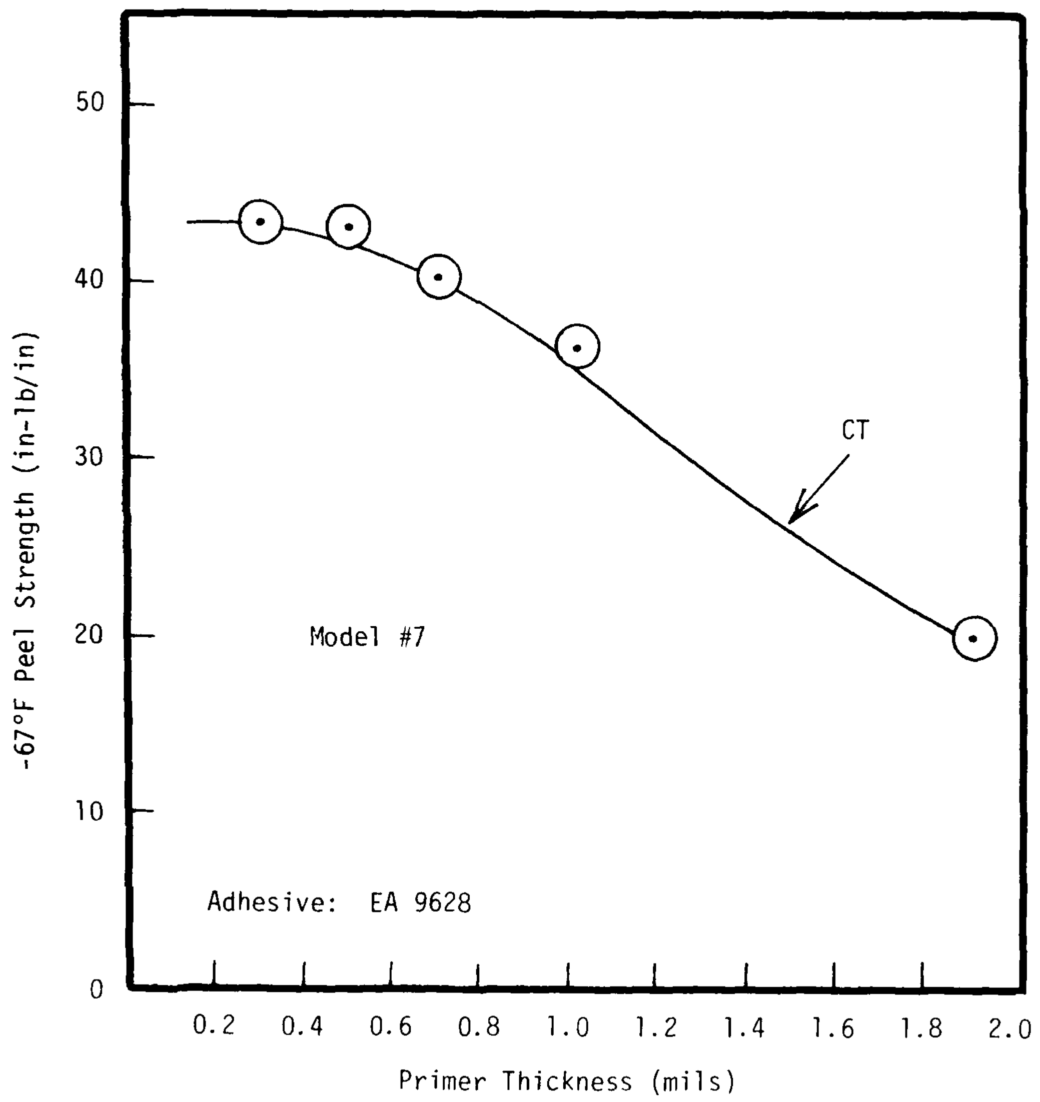


Figure 5. Effect of Increasing Primer Thickness On -67°F Peel Strength



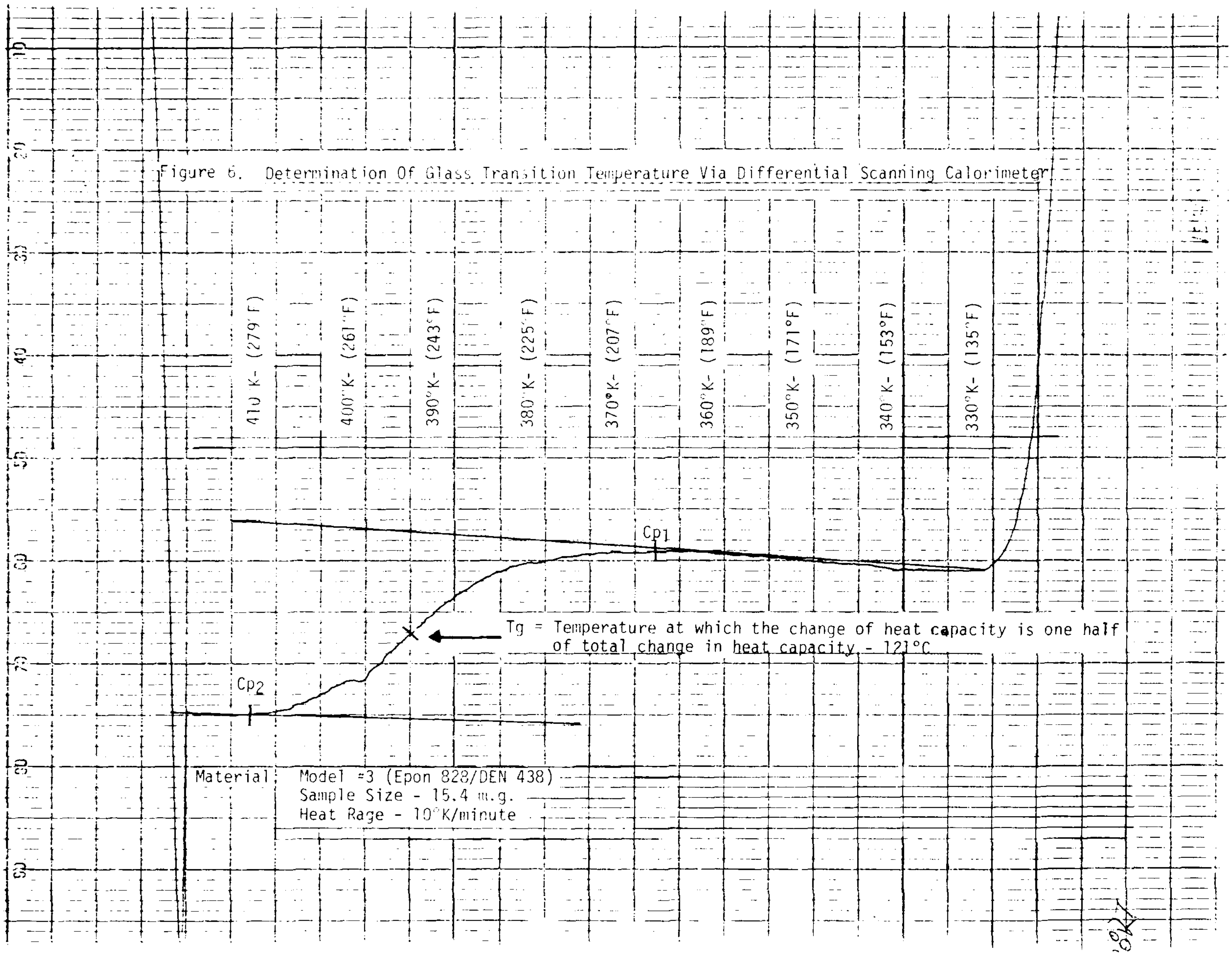


Figure 6. Determination Of Glass Transition Temperature Via Differential Scanning Calorimeter

Tg = Temperature at which the change of heat capacity is one half of total change in heat capacity - 121°C

Material: Model #3 (Epon 828/DEN 438)
Sample Size - 15.4 m.g.
Heat Rage - 10°K/minute

Figure 7. Correlation Of Primer Critical Thickness At -67°F With The Resin Systems Critical Crack Toughness (G_{Ic})

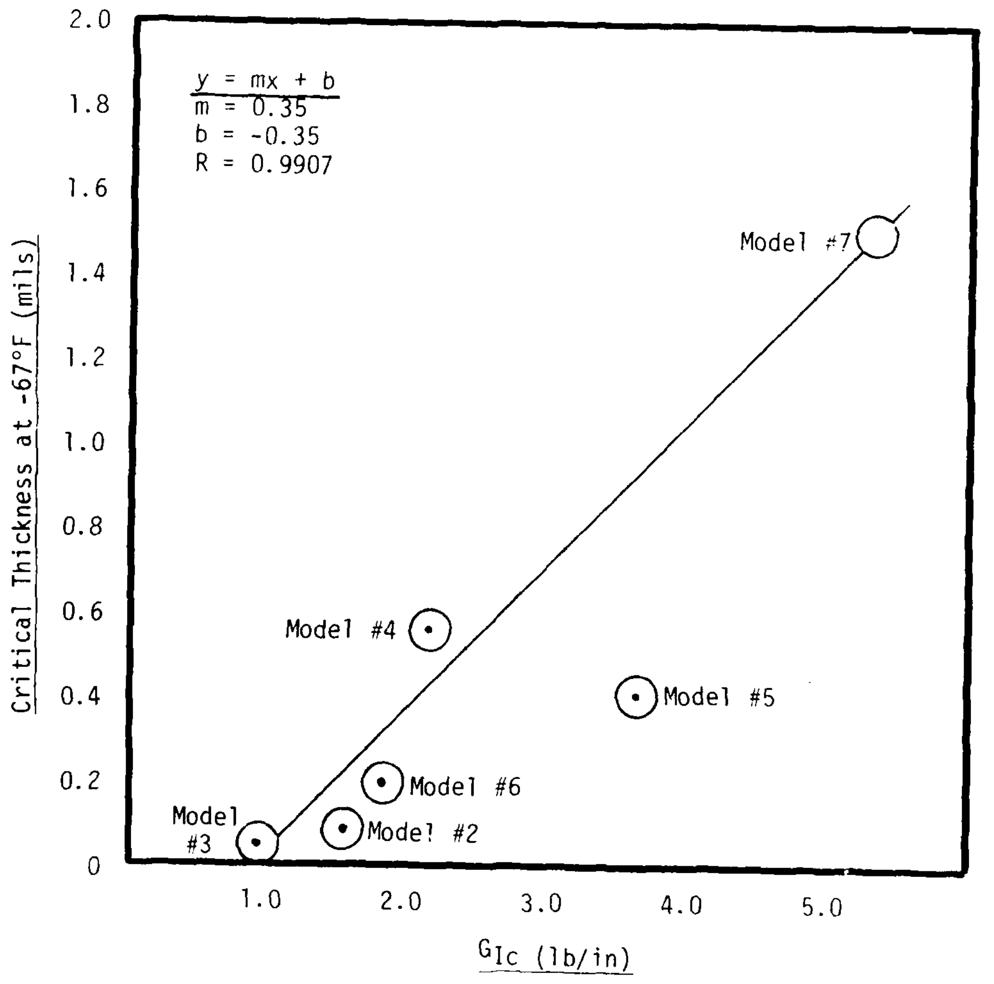


Figure 8. Correlation Of -67°F Critical Thickness Values With G_{Ia}

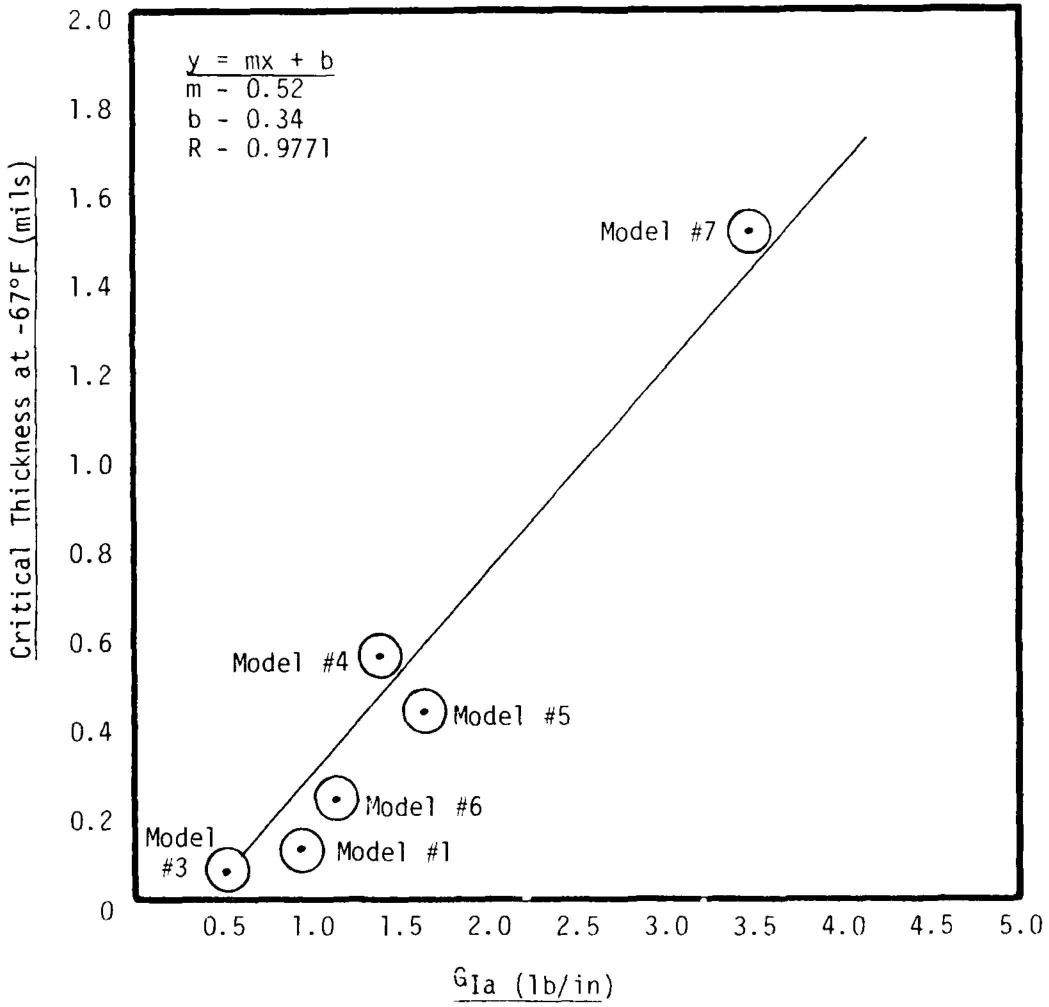


Figure 9. Moisture Equilibrium Panel Test - Model Primer Vehicles

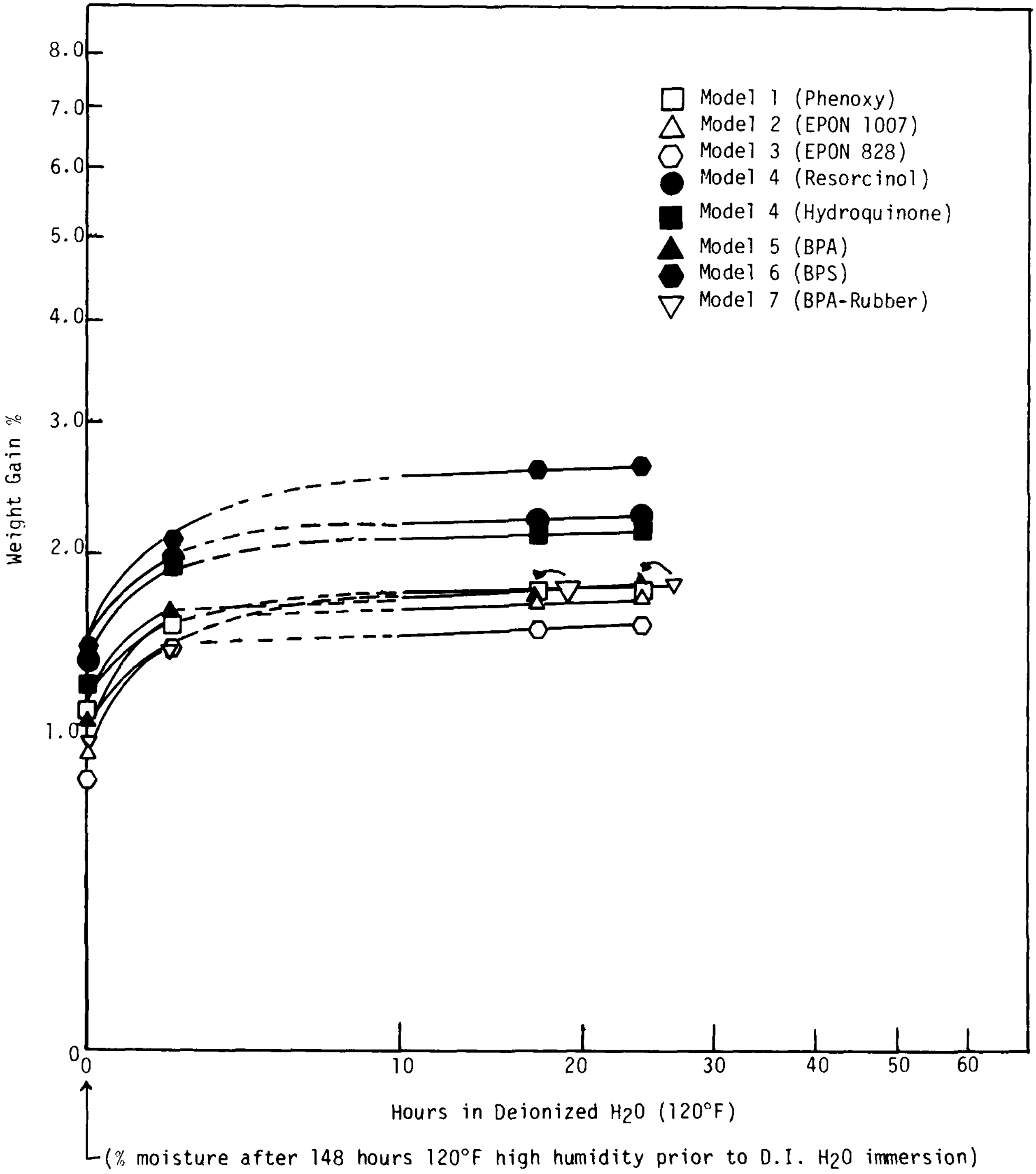


Figure 10. Moisture Equilibrium Panel Test - Primer Vehicle Systems

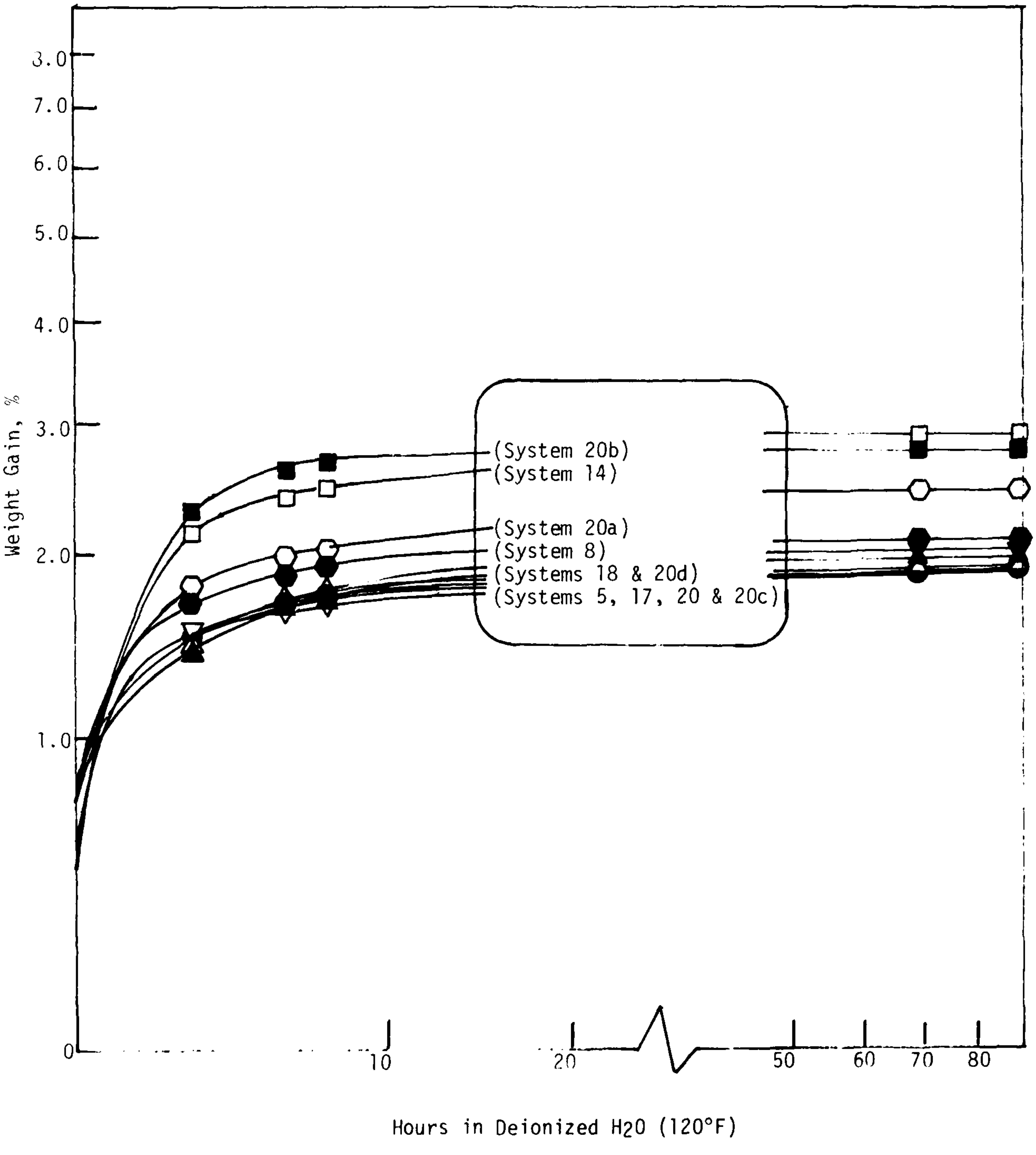
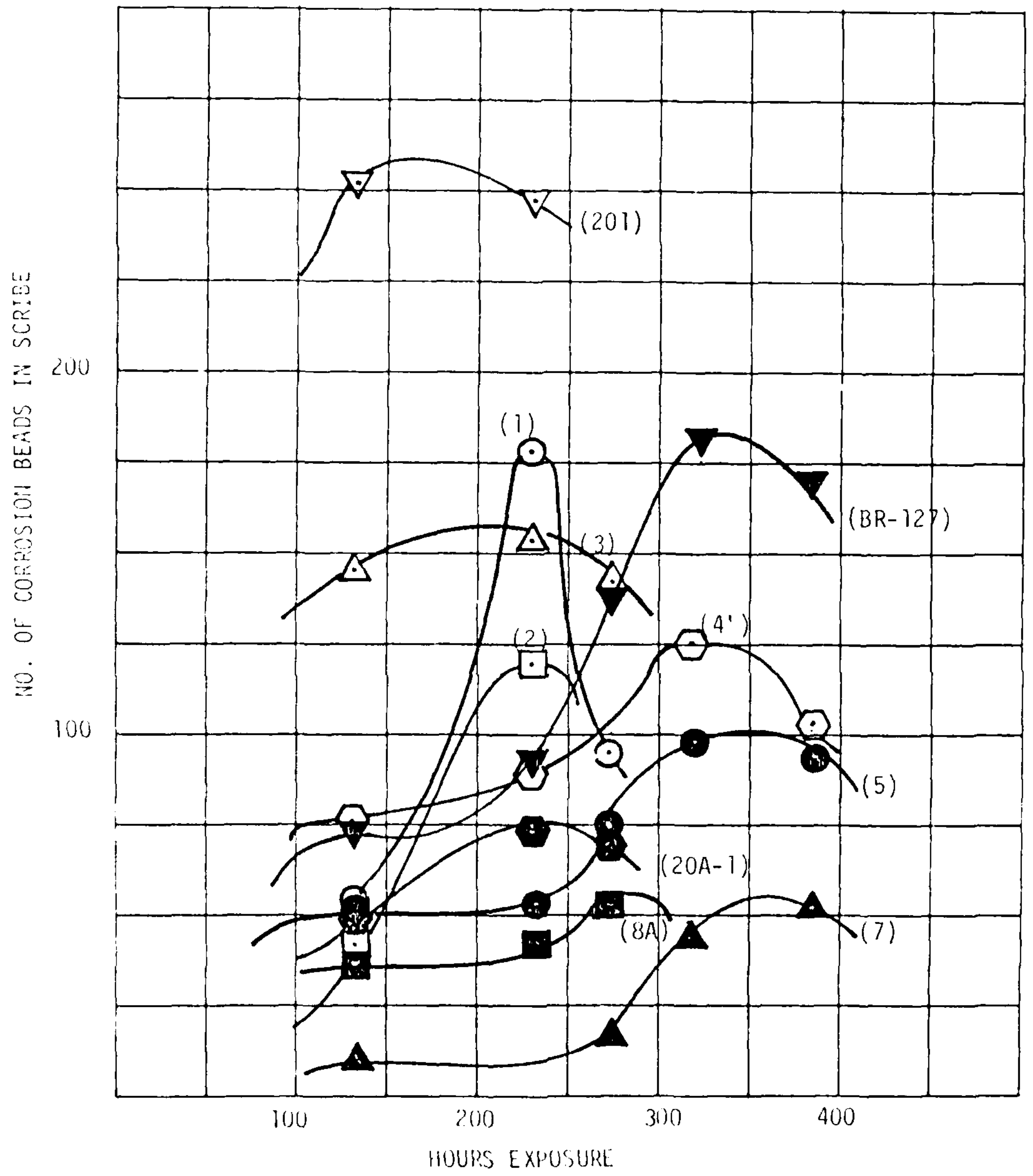
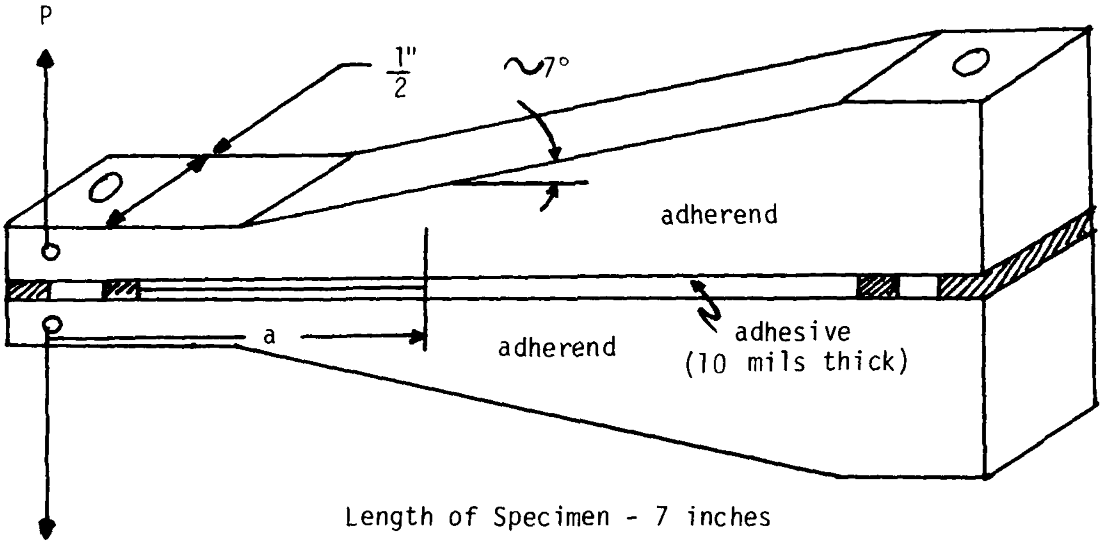


Figure 11. Salt Spray Scribe Test - Unpigmented Primers





Length of Specimen - 7 inches

P = load
M = slope of tapered portion
A = crack length

Figure 12. Contoured Double Cantilever Beam Adhesive specimen (m = 90). Specimen is contoured, in accordance with the m value, which is approximated by a 7° half-angle.

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