



# Adhesion Aspects of Polymeric Coatings

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## PREFACE

This volume chronicles the proceedings of the Symposium on Adhesion Aspects of Polymeric Coatings held under the auspices of the Electrochemical Society in Minneapolis, MN, May 10-15, 1981. This event was cosponsored by the Dielectric and Insulation, and Electrothermics and Metallurgy Divisions.

Polymeric coatings are used for a number of purposes, e.g., decorative, protective, functional (as dielectrics or insulators) and a special application of polymeric (organic) coatings is their use as lithographic materials for making integrated circuit elements. Irrespective of the purpose of the coating, it must adhere well to the underlying substrate. So the need to understand the factors which influence adhesion of organic coatings and the ways to attain desired adhesion is quite manifest.

This Symposium was designed to bring together scientists and technologists interested in the adhesion aspects of polymeric coatings, to provide a forum for discussion of latest findings, and to provide an opportunity for cross-pollination of ideas. The technical program contained a total of 46 papers by authors from various corners of the world. The program comprised both invited overviews and contributed original research papers, as this blend is the best way to present the state of knowledge of a topic. The invited speakers were selected so as to represent widely differing disciplines and interests and they hailed from various academic and industrial research laboratories. If the level of attendance and comments from the attendees are any measure of the success of a symposium, then this event was a grand success and the objectives set forth were amply fulfilled.

The technical program was divided into seven sessions, but for the purpose of this proceedings volume, the papers have been somewhat rearranged so as to group them in a more logical manner. Although the original program contained 46 papers, for a variety of reasons, some of these are not included in this volume. Furthermore, it should be added that this volume contains some papers which were not presented and these were specifically com-



missioned by the Editor. Also, it should be emphasized that all papers were reviewed by qualified reviewers and as a result most of these were sent back to the authors for suitable revision and some of these were not accepted at all. So this volume contains a net total of 36 papers by 67 authors and the papers are divided into six parts as follows: Part I. General Overviews; Part II. Factors Influencing Adhesion; Part III. Bond Durability; Part IV. Adhesion Promotion via Coupling Agents; Part V. Resist Adhesion; and Part VI. Adhesion Measurement. The topics covered include: acid-base interactions and their role in adhesion; role of surface topography in coating adhesion; use of modern surface analysis techniques in determining the locus of failure; various factors which influence adhesion of coatings; role of internal strain in coating adhesion; adhesion of plasma-polymerized coatings; investigation of polymer-metal interactions; factors influencing bond durability and ways to enhance it; adhesion of organic coatings and its loss due to corrosion; use of silanes and other coupling agents to promote adhesion; various aspects of resist adhesion; and a number of techniques for adhesion measurement of coatings.

Even a cursory look at the Table of Contents will convince that there is a great deal of interest and activity taking place in understanding and controlling adhesion of organic coatings. One of the perennial problems concerning adhesion of coatings has been the precise determination of the locus of failure, and the availability of sophisticated surface analytical tools has been extremely helpful in this regard. Furthermore, these techniques have proved a boon in understanding coating-substrate interactions. The interest in developing better coupling agents for improving adhesion of organic coatings is amply manifested by the papers covered in this volume. Another important problem deals with the durability of the bond against the deleterious effect of moisture and other fissiparous elements and a number of papers deal specifically with this aspect. It should be added that the factors influencing photoresist adhesion can be quite different from those that dictate the mechanical adhesion of organic coatings, and in this volume both of these topics are discussed.

This volume should be a useful source of information to both the seasoned researcher (as a reference) and the neophyte (as a guide) interested in adhesion aspects of organic coatings. It should be emphasized here that the Editor had hoped to include written discussion at the end of each paper or Part, but, unfortunately, in spite of constant reminding, the number of written questions received did not warrant undertaking such endeavor. However, it should be recorded that there were many enlightening formal (in the auditorium) and informal discussions throughout the symposium.

Acknowledgments. First of all I am thankful to the appropriate officials of both Divisions for sponsoring this event, and to the appropriate management of IBM Corporation for permitting me to organize this Symposium and to edit this volume. Also I should take this opportunity to thank the reviewers for their fine and valuable comments. On a personal side I would like to acknowledge the cooperation and assistance of my wife, Usha, and am thankful to my kids (Anita, Rajesh, Nisha and Seema) for rendering home environment conducive to work. Special thanks are due to Mr. Jim Busis of Plenum Publishing Corp. for his continued interest in this project. Last, but not least, I must acknowledge the enthusiasm, cooperation, and contribution of the authors.

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**Part I**  
**General Overviews**



## ACID BASE INTERACTIONS BETWEEN OXIDE SURFACES AND POLAR ORGANIC COMPOUNDS

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A model for the hydrated oxide layer present on all metals, glasses and other "oxide" surfaces, first presented in 1967<sup>1</sup> described how these surfaces could interact with polar organic compounds by a combination of dispersion forces plus acid-base forces. The free energy change and relative probabilities for the acid-base interactions can be calculated from two (derived) equations which involve the arithmetic difference between the isoelectric point of the surface and the  $pK_a$  of the polar groups in the organic phase. The present paper shows how these equations can be used to interpret a wide range of adhesion, flotation, surfactant adsorption and water displacement data.



## INTRODUCTION

Reference 1 was written for, and presented at, the General Motors Symposium on Interfaces in Sept. 1967. It was primarily a review paper, written to serve as the introductory chapter to the Symposium proceedings, which were later published in 1969. The chapter also contained a new method of estimating acid-base forces at interfaces between polymeric materials and oxide surfaces.

Prior to 1967, most theories of adhesion to metals and oxides assumed complex combinations of dispersion forces plus dipole, induced dipole and other forces. Reference 1 led to the important simplification that the only forces worth considering, in addition to dispersion forces, were hydrogen bonds, and used an acid-base mechanism to predict the relative magnitude of the hydrogen bonds.

Mittal<sup>2</sup> and others have pointed out, correctly, that the Bolger-Michaels approach is limited to Bronsted acid-base interactions, whereas a more general treatment should be based on electron donor-acceptor (Lewis acid-base) interactions. The Bolger-Michaels model was never intended to be a general theory of adhesion. But it has proven to be useful for the specific, and very important, case of adhesion between polar polymers and oxide surfaces, and in explaining why such polymers, can or cannot, retain adhesion to oxide surfaces in the presence of water.

## CHEMICAL COMPOSITION OF METAL AND OXIDE SURFACES

Figure 1 (in Ref. 1) gives a convenient way of representing the hydrated oxide surface of any metal, metal oxide or silicate. The essential features of this model are based on a large number of prior studies of adherend surfaces, and particularly on the prior work of Fowkes<sup>3</sup>, Parks<sup>4</sup> and Zisman and co-workers<sup>5</sup>. The reader is referred to Ref. 1 for complete discussion of prior references. The three basic features of the surface model of Figure 1 are:

1. A metal surface is, in fact, a metal oxide surface. Surface oxide films may be thin for mercury or for noble metals (gold, platinum) but are thick enough (40-80Å or more) for metals and alloys of primary commercial importance (nickel, iron, aluminum, copper, zinc, magnesium, etc.) to eliminate, for purposes of estimating attractive forces, effects due to metal atoms underlying the oxide layer. By knowing the surface chemistry of the metal oxides, one can therefore deal with all the metal, oxide, silicate and ceramic surfaces.

2. While the oxide surface can be dehydrated and dehydrogenated at elevated temperatures, at normal ambient bonding conditions the outermost surface oxygens hydrate to form a high density of hydroxyl groups. Zettlemoyer<sup>6</sup> and others<sup>7,8</sup> have estimated that about one silanol group is present per 50 to 100 Å<sup>2</sup> on the surface of a variety of glasses, silicas, and clays, and that a similar hydroxyl population density exists on aluminum, iron and other oxides.
3. The hydroxyl rich surface adsorbs, and strongly retains, several molecular layers of bound water. When silica powder is washed with water and then dried at 100°C, it retains an adsorbed surface layer of water approximately 100 Å thick, and this water layer cannot be removed completely at temperatures below about 400°C. Studies of aluminum, iron and copper surfaces at ambient temperatures and humidities show up to 20 molecular layers of water present on "dry" surfaces.

The fact that metal surfaces are in fact oxide surfaces, and contain these hydrated polar surface groups, is fortunate from the standpoint of bonding these with polar organic resins. Epoxies and other polar resins require an oxide layer to wet and spread on a metal surface. It is well known that, when a metal is fractured in a moisture-free and oxygen free environment, such that no oxide layer can form, this metallic surface is not then wet by polar organic liquids. When a small amount of oxygen is admitted to the chamber, however, the surface oxidizes, the polar liquid is able to form hydrogen bonds and other forces to the surface, and the liquid droplets spread out and wet the surface.

If all metals, metal oxides and silicates have a similar hydrated, hydroxyl-rich surface, how can we explain the fact that oxides of different metals such as copper, or iron, or silicon differ to such a large degree in their surface interactions with water and with organic coatings and adhesives? In part, these differences are due to geometric factors, since the spacing and regularity of the surface hydroxyl groups can vary from metal to metal. The surfaces may also vary during short periods after exposure to elevated temperature, since the hydroxyl groups can be made to condense and disappear at sufficiently elevated temperatures. Whereas a metal oxidizes almost immediately after exposure to oxygen, the rate of hydroxyl formation is considerably slower via:

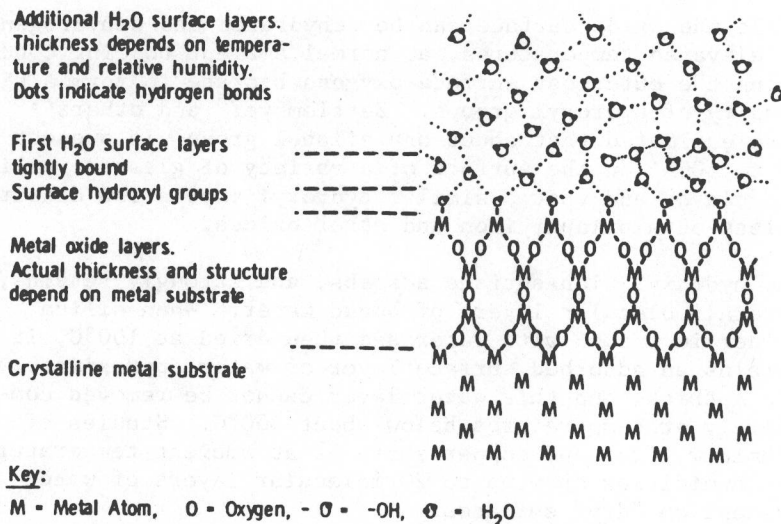
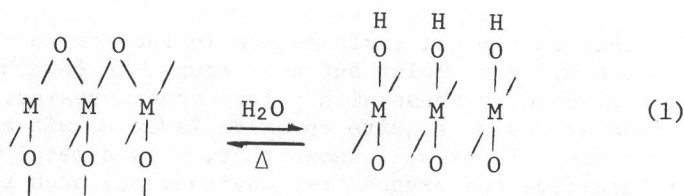


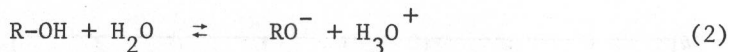
Figure 1. Schematic representation of water and oxide layers on metal surface.



The rate of formation of these hydroxyl groups can be measured from I.R. absorption bands at 2.6 to 2.9  $\mu\text{m}$ , or at slightly longer wavelengths characteristic of hydrogen bonded hydroxyl groups. Within a few hours at ambient conditions, freshly calcined alumina hydrates to yield a surface characteristic of  $\text{Al}(\text{OH})_3$  while  $\text{Fe}_2\text{O}_3$  hydrates to resemble  $\text{FeOOH}$ .

#### ACID-BASE INTERACTIONS OF SURFACE HYDROXYL GROUPS

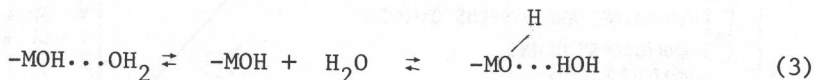
The most important difference between oxides has to do with the "acidity" or "basicity" of the hydroxyl groups shown in Figure 1. The identity of the metal atom M in the surface group, - written as -MOH, influences the activity of the -OH group in the same way an organic radical influences the ionization of an attached -OH group:



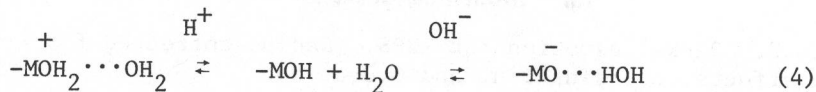
As progressively more electron attracting groups are attached to the oxygen atom, i.e., as R goes from an aliphatic to an aromatic to a carboxylic acid group, the proton is less strongly held and the "acidity", or ability to donate a proton, increases. Similarly, aromatic amines are less "basic" than aliphatic amines because the aromatic nitrogen is less able to attract a proton. Acid or base strength of organic compounds is tabulated in handbooks<sup>9</sup> as pK values, where a low pK value indicates a strong acid and a high pK value indicates a strong base.

#### OXIDE INTERACTIONS WITH WATER

The surface hydroxyl groups of Figure 1 adsorb water molecules via H-bond interactions wherein the surface acts either as the acid (proton donor) or base (proton acceptor).



As the pH in the aqueous phase is altered by electrolyte addition, the surface acquires an ionic charge via



Surface charge can be calculated from zeta potential measurements as a function of pH, using suspensions of the powdered oxide in water. For every oxide, there exists some pH at which the number of positive charges equals the number of negative charges and the zeta potential is zero (Figure 6). This pH value is defined as the IEPs, the isoelectric point of the surface. A low IEPs value indicates an acidic oxide surface. A high IEPs value indicates a basic surface.

Parks<sup>7</sup> has shown that the IEPs for an oxide depends on the valence (Z) and the radius (R) of the cation (Figure 2). IEPs is highest for the divalent (Z=2) metal oxides such as MgO, FeO, NiO; is in the medium pH range for trivalent metal oxides (Z=3) such as Al<sub>2</sub>O<sub>3</sub> or Fe<sub>2</sub>O<sub>3</sub>, and is lowest (most acidic) for metals of valence 4 or higher (e.g., SiO<sub>2</sub>). Oxidation always reduces IEPs, for example, ferric versus ferrous oxide. For the various oxides of molybdenum, as the Mo valence increases from Mo<sub>2</sub>O through Mo<sub>2</sub>O<sub>5</sub> and MoO<sub>3</sub>, IEPs decreases from about 12 down to about 0.5. IEPs is always higher for hydrated than for freshly calcined oxides.