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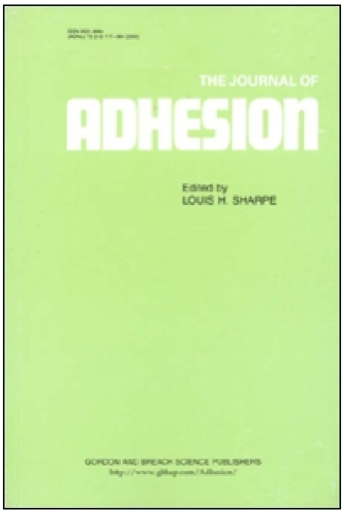

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Chemical Aspects of Adhesion Between Metals and Polymers

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Long Abstract

Chemical Aspects of Adhesion Between Metals and Polymers†

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The present paper considers the binding forces between organic molecules and metal surfaces, especially those covered with an oxide layer. Furthermore, the adherence of low molecular weight organic compounds onto polymers is discussed by comparison with textile dyeing procedures. The results of this analysis allows the molecular design of new adhesion promoters and proposes some modified techniques of metal surface pretreatment.

KEY WORDS Adhesion; adhesion promotors; adsorption; chemical bond; molecular design; textile dyeing.

INTRODUCTION

On exposure to air the surface of most metals will be coated by an oxide layer. The structure of an adhesive joint between two of these metals in a first approximation can then be described as a sequence of five layers, *i.e.* metal 1, oxide 1, adhesive, oxide 2, metal 2 (Figure 1). Typical adhesives for the joining of metals are organic polymers which in many cases—as with phenolic and epoxy

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† This is the long abstract of a paper presented orally at the Tenth Annual Meeting of The Adhesion Society, Inc., Williamsburg, Virginia, U.S.A., February 22–27, 1986.

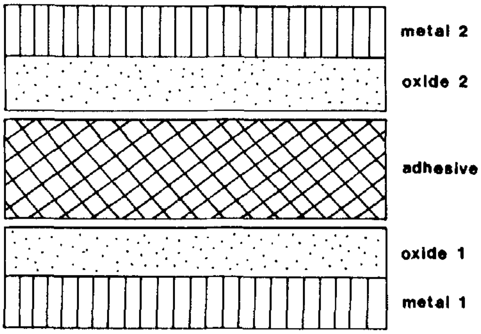

FIGURE 1 Schematic of an adhesive joint between two metals.

resins—are produced only during the joining procedure. The strength and the mechanical properties of an adhesive joint as depicted in Figure 1 will depend on the strength and mechanical properties of the polymer, the mechanical properties of the oxide layer and the adhesive forces between metal and oxide as well as those between oxide and polymer. In the following it will be assumed that the polymer meets the mechanical qualifications, and the mechanical properties of the oxide layer are supposed to be tolerable because of its small depth.

DISCUSSION

Chemical aspects of adhesion between metals and polymers can only be discussed in the dimensions of atoms, molecules, or crystal lattice spacings and, furthermore, the different binding forces between atoms, ions and molecules should be considered. In comparison to these dimensions (0.1–1 nm) glue lines in adhesive joints between metals usually have dimensions of 0.1–5 mm.

i) Chemical Structures: The chemical structure of solids like metals or oxides is described as a three-dimensional lattice structure of either positively charged ions and freely mobile electrons or of oppositely charged ions. In comparison to these the chemical building blocks of polymers are molecules which stick together in the solid state only by intermolecular forces. Although the strength of intermolecular forces is lower than that of metallic, ionic or covalent bonds by one or two orders of magnitude, cooperative effects of a great number of intermolecular bonds give rise to the high cohesion of polymers.

ii) Adhesion Between Metals and Oxides: If the lattice spacings of the oxide formed on exposure of the metal to air are similar to those of the metal, the oxide will strongly adhere to the metal protecting it from further oxidation, provided the oxide is stable under environmental conditions. This is the case with copper, lead, tin, nickel and also with the less noble metals chromium, zinc and aluminum. The chemical bonds between the oxide and the metal in these examples can be described as a small boundary layer of oxide with increasing amounts of metal followed by metal with decreasing amounts of oxide (Figure 2). On the other hand, iron on exposure to air and humidity forms the well-known rust which does not adhere to the metal surface. Hence, for joining iron by adhesives the pretreatment of the metal surface should be in such a way as to avoid the formation of rust.

iii) Adhesion Between Organic Molecules and Metal Oxides: The fact that the chemical structure of organic molecules differs fundamentally from that of solids like oxides raises the question about possible binding forces between molecules and oxides. From the experience with adsorption chromatography for the separation and purification of organic compounds it can be

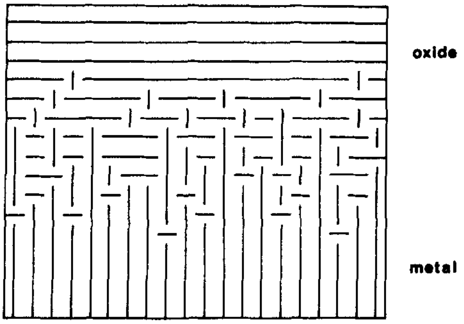

FIGURE 2 Schematic of a bond between metal and oxide.

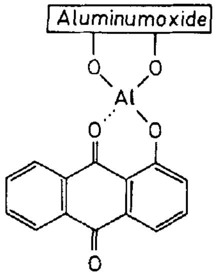

FIGURE 3 Irreversible complex formation of alizarin on aluminum oxide.

concluded that the adherence between oxides and molecules depends on the nature and the 'activity' of the oxide and highly on the structure and the functional groups of the molecules. Thus, compounds with hydroxy and amino groups with the ability to form hydrogen bonds are adsorbed much better than, for example, esters, ethers or hydrocarbons. Some compounds, especially those with chelating properties like hydroxy anthraquinones, even form irreversible adsorbates on aluminum oxide (Figure 3).

Aluminum oxides which are produced on the metal surface by phosphoric acid anodization (PAA) or chromic acid anodization (CAA) were found to be of rather low adsorption activity[1] as compared to aluminum oxide used in adsorption chromatography. Thus, further efforts should be made to enhance the adsorption activity of oxides on metal surfaces. As preliminary investigations indicate, this seems to be possible in the case of aluminum by precipitation of aluminum hydroxide on to the oxide surface.

iv) Adhesion Between Organic Molecules and Polymers: Only a limited number of polymers used as adhesives meets the requirement for good adsorption on oxides and, in practice, adhesion promoters and primers are applied. They are expected to bind just as well to the metal (oxide) as to the polymer. For that reason and as a result of investigations of joint failures which frequently show that the failure occurs in the adhesive very near to the interface,[2] the 'adhesion' and possible binding forces between molecules and polymers have to be considered. Information on this problem can be best received form textile dyeing procedures.

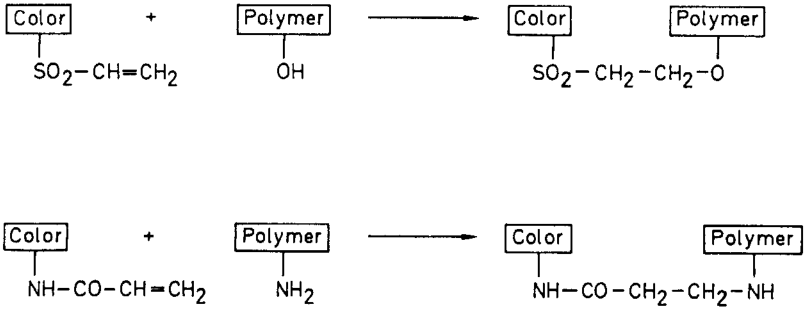

FIGURE 4 Formation of covalent bonds between reactive dyes and polymers.

The chemical diversity of fibrous polymers from synthetic or natural sources used in the manufacture of fabrics has led to the development of a variety of dyes and a variety of dyeing methods. In virtually all dyeing processes a water resistant 'adhesion' between dye and polymer is achieved. The chemical bonds between dyes and polymers formed in these processes range from van der Waals forces (disperse dyes for polyesters) to covalent bonds (reactive dyes for cotton and polyamides) including hydrogen bonds (substantive dyes), ionic bonds (ion exchange dyes for wool and silk) and complex formation (mordant dyes). The formation of covalent bonds between reactive dyes and polymers (Figure 4) suggests the applicability of a similar reaction principle also to adhesion promotors, provided that the polymer contains hydroxy or amino groups which is the case with phenolic and epoxy resins.

CONCLUSION

High adhesive forces between organic molecules and metal oxides as well as between organic molecules and polymers are well known. For the molecular design of bifunctional compounds with high affinity to metal oxides on the one hand and with the ability to form strong bonds to polymers on the other, structural requirements can be deduced from results in adsorption chromatography and from textile dyeing techniques. Compounds of this type, however, can only serve as adhesion promotors and still call for a joining polymer to fill the glue line in adhesive joints.

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