Adhesion I

by Clive H. Hare
Coating System Design Inc.

Previous articles in this series have reviewed the molecular morphology of coating films and the effects of physiochemical structure on cohesive behavior. A paint film without a substrate, however, is hardly a paint film. Discussing the mechanical properties of paint films without considering the substrate and the forces that hold the films in place is equally meaningless. The mechanical stresses and abuses of service are directed against the forces of adhesion as much as they are directed against the forces that hold the film together.

This article will consider adhesion and the techniques for optimizing it.

The Nature of Adhesion

Paint film adhesion is generally considered a molecular phenomenon.[1] Beyond this concept, numerous theories have been put forward, but no single theory explains all associated phenomena. Theories include the weak boundary layer concept of Bickerman[2], the electrostatic theory of Derjaguin[3,4], the molecular diffusion theory of Voyutski[5,6], and adsorption theories such as Schornhorn's[7] and Guerra's.[8] As will be discussed below, bulk phase considerations include the absorption and entanglement of the paint film into the porosity of the substrate, which is sometimes termed "mechanical adhesion." This type of adhesion, also referred to as "lock and key" adhesion, will be discussed in more detail next month.

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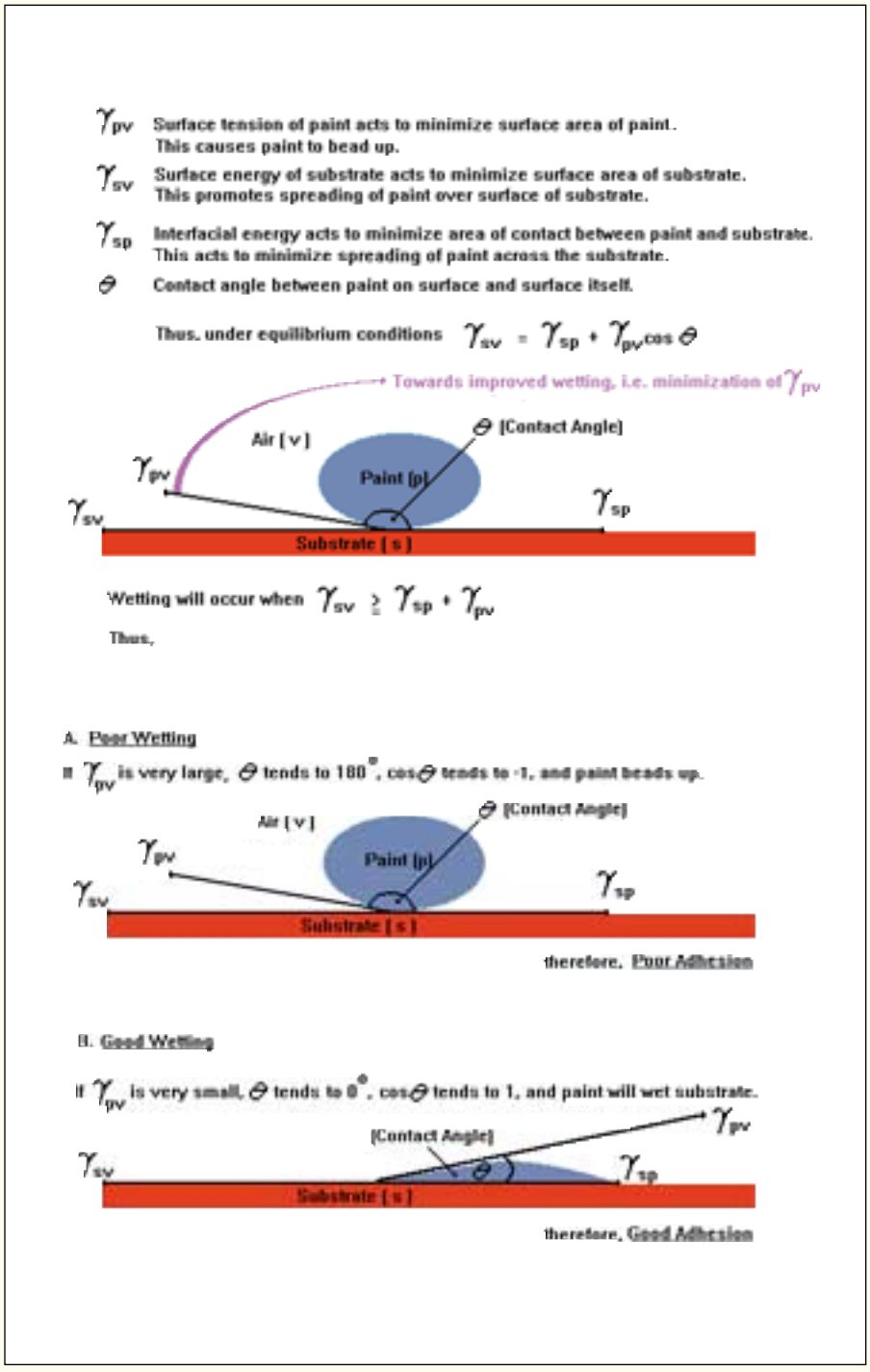


Fig. 1 - Paint film wetting–vector quantities at equilibrium
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It is likely that all of the above effects may play some part in paint film adhesion. On some substrates, such as paper, wood, and concrete, the mechanical effects may be substantial. On metals, glass, and plastic, however, molecular bonding effects predominate. When molecular bonding predominates, it results from chemical linkages (primary valency bonds) between reactive species on binder and substrate or molecular associations (secondary valency bonding) between the two. Such forces are operative only across very limited distances. For adhesion of any kind, the coating and the substrate must approach each other extremely closely. Separation must be no greater than approximately 5Å units (1Å=10^{-10} meter), which are molecular dimensions about 3 times the diameter of the oxygen atom. These attracting forces also diminish at the sixth power of the distance between attracting moieties. (That is, if the distance doubles, the force is diminished by a factor of 64 [2^6].) To achieve this level of approach, the coating must wet the substrate. The coating must spread across the substrate, either spontaneously or with the aid of the forces of application. It must not bead up or draw back from the surface after application.

Wetting

Wetting and its relevance to adhesion have been discussed comprehensively by a number of authorities, including Zisman[9] and Adamson.[10] Reference 11 is a good introduction to the subject. Wetting is an effect of surface energy that depends on the relative surface free energies, or surface tension, of the coating and the substrate. For any given coating and substrate model, the coating will wet the substrate only when the interfacial energetics are appropriate.

All surfaces have surface free energy (also known as surface tension). Molecules at the surface of a liquid tend to orient themselves to minimize the surface area of the liquid. The phenomenon is more visually recognizable in liquids than in solids. In liquids, surface tension is demonstrated in the spherical shape that is naturally assumed by the unrestricted volumes or drops of liquid. Here, the surface tension of the liquid constricts the surface of the drop to the smallest surface area possible that will contain the liquid volume. Solids also have surface free energy, however, and will minimize their own surface area by spreading liquids across this surface. This tendency is opposed by the surface tension of the liquid (such as a paint) that is applied to the surface and by the interfacial free energy that minimizes the area of the interface between the paint and the substrate.

Contact of the paint (p) with the substrate (s) is represented in Fig. 1. Here, γ_{sv} is the surface free energy of the substrate in air (expressed as v [vapor]), γ_{pv} is the surface tension of the paint in air, and γ_{sp} is the interfacial tension between the paint and the substrate. Treating the energetics as vector quantities, at equilibrium these forces may be represented by Young's equation:

$$\gamma_{sv}=\gamma_{sp} + \gamma_{pv}\cos\text{Ø}.$$

Theta (Ø) is the contact angle between the liquid on the surface and the surface itself (Fig. 1). If the coating is to completely wet the substrate, i.e., if the liquid is not to bead up at all, then the contact angle Ø must equal 0 (i.e., cosØ= 1). Wetting will occur, therefore, when $\gamma_{sv} \geq \gamma_{pv} + \gamma_{sp}$.

The surface energy of the substrate (γ_{sv}) should never be lower than the surface energy of the paint being applied (γ_{pv}). On clean met-

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als, the surface free energy of the metal oxide film is normally very high (several hundred dynes/cm). It is not usually a problem for coatings with relatively low surface energies (20-70 dynes/cm) to wet such substrates. On certain low-energy plastics, however, surface energies may range from 15 to 20 dynes/cm. (The inherently low surface energy of fluoropolymers is utilized in non-stick cookware applications).

Even some low surface energy coatings may not wet these plastics properly and will have problems with adhesion. Adhesion problems can occur on polyolefins and fluoropolymers or surfaces that have been contaminated with oils or other hydrocarbon impurities, silicone, or fluorochemical fluids because these contaminants reduce the surface energy of the substrate. A monomolecular layer of oils and silicone fluids will prevent the paint film from wetting the substrate. Because of their low energy, these materials will spread themselves readily over high energy surfaces, lowering the surface energy of the surface from several hundred dynes/cm to less than 20 dynes/cm. These substances must be carefully removed to ensure good adhesion of subsequently applied coatings. The effect of such minute quantities of hydrocarbon oils and dimethyl silicone fluids on the wettability of all kinds of surfaces is the foundation for their use as lubricants.

Adhesion to High Energy Surfaces

The key to obtaining good adhesion to metals and other high energy surfaces is, therefore, to ensure that the true substrate is presented to the paint. Usually this involves the removal of foreign materials that interfere with adhesion. These materials include oils and other contamination that reduce surface energy and loose materials that restrict access of the paint to all areas of the substrate. The positive consequences of surface renewal are magnified when it can be done simultaneously with the expansion of the real surface area of the substrate, compared to the apparent planar area. This result occurs with scarification techniques such as sanding and abrasive blasting. In air, thin oxide and hydroxide films will reform almost instantly on most structurally important metal substrates. Unlike rust, these films are well bonded to the metal and will serve as reactive sites that attract polar and chemically reactive groups on the polymer binder of the paint. Molecular associations between the substrate and the paint can then occur on these sites.

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Good surface preparation will also remove damaging contamination, such as soluble salts and other hydrophilic species. If coated, hydrophilic species will reduce adhesion and may reduce corrosion protection. This phenomenon will be discussed in a later column.

Adhesion to Low Energy Surfaces

Low Energy Plastic Surfaces

On low energy, highly crystalline plastics, cleaning will have little or no effect. The removal of mold release residues and machining lubricants from high energy plastics, such as epoxies, phenolics, and acrylics, may result in better adhesion of low energy paint films. Cleaning polyethylene, polypropylene, and polytetrafluoroethylene, however, will only bare a substrate that is inherently low energy and, therefore, cannot be wetted by coatings. Techniques for improving the ability of these widely used plastics to be coated involve surface treatments that change the chemistry of the surface by oxidation.[12]

These techniques were traditionally achieved with oxidizing agents such as chromic acid. Because of the costs and difficulties associated with waste disposal, these traditional procedures, which were effective, are now being replaced by other oxidizing methodologies. New approaches include treatments using propane torches, corona discharge techniques in which the surface is oxidized in an electrically generated field of ionized air or oxygen, and even ultraviolet-generated free radical attack on the plastic surface. In one important technique, free radicals are generated in the surface of the plastic by abstracting hydrogen atoms with electrically excited rare gases. This technique, known as CASING (crosslinking by activated species of inert gases), is now used extensively. These oxidative techniques generate polar groups, such as ethers and hydroxyls, on the surface of the nonpolar plastic. The polar groups increase the surface energy of the solid and provide sites for subsequent primary valency-bonded adhesion with coating systems bearing complementary functionalities (i.e., isocyanate groups).

In some cases, low energy substrates (such as polypropylene) are copolymerized with amorphous, rubber-like materials to improve their ability to be painted. Even here, the immediate surface of the extruded plastic may remain highly crystalline.[13] For subsequent adhesion, this surface skin must be penetrated by the solvent system of the primer, which may then more easily swell the rubber-rich layers beneath the immediate surface. Thin coats of chlorinated polyolefin- (CPO) based "wash primers" are commonly used to help the paint system adhere to these surfaces. It has been postulated that adhesion is affected by diffusion of solvents of the CPO pretreatment through the crystalline skin and into the more susceptible rubber domains. The CPO binder is carried with the solvent, which results in a "mechanical interweaving" of primer and substrate[14] (Fig. 2).

Thermoplastic substrates with reduced crystallinity may be coated by carefully selecting a coating with an appropriate solvent system. High boiling solvents that are soluble in the plastic will penetrate the solid. They will reduce the glass transition temperature of the surface layers by expanding the free volume of the surface, allowing more solvent and molecules of the coating resin into the plastic surface. As the solvents are desorbed, the coating, resin, and plastic surface remain locked together, and a type of mechanical bond forms.

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Low Energy Organic Coating Surface

This phenomenon underlies the "solvent weld" effect that ensures intercoat adhesion between successive coats of vinyl- and chlorinated rubber-based coating systems. The trick with some plastics is to use the approach without crazing the plastic surface. Crazing is a fine, random micro-checking that occurs in the surface of high Tg thermoplastics, such as polystyrene and polymethylmethacrylate, as strong solvents from the applied coating film are absorbed into the plastic and subsequently desorbed during drying. The phenomenon is thought to be caused by shrinkage stresses in the surface of the plastic. Presumably, initial solvent release from the surface of the plastic and surface drying entraps solvent residues just below the plastic surface. As this solvent then diffuses through the drier surface layers, the resultant volumetric shrinkage in the lower layers causes stresses that result in cohesive failure of the surface layers.

A similar solvent welding device is often used to improve the intercoat adhesion between successive thermosetting paint films, particularly where long recoat times have elapsed. Here, existing film is relatively insoluble in the solvents of the recoat system. but with judicious selection of a solvent system, some diffusion may occur. Adhesion is probably achieved by the migration of binders from the recoat system along with solvent into the surface layers of the existing film. As the solvent evaporates, the binder of the recoat remains entrapped within the surface of the substrate film. The effect is not unlike that noted above where crystalline plastics are coated. With alkyd and oil thermosets, the effect may be great enough to lift the existing system. (See the paint remover effect noted in the January 1996 *JPCL*, pp. 78-80.) In other cases, the effects may be so slow that the solvent must be applied separately to the coating and be allowed to sit and swell the surface of the existing film before the new film is applied. Excessive delays in recoating hard, coal tar epoxy films have thus been overcome without sweep blasting using applications of n methyl 2- pyrrolidone. The author used a similar technique many years ago, adding methylene chloride to interior latex paints to improve their adhesion to glossy, aged, and well oxidized alkyd films.

Primary Valency Bonding

Chemical adhesion is related to the molecular structure of the paint film binder and the substrate. For primary valency reactions to occur across any interface, both binder and substrate must have mutually reactive functional groups. Metal and metal oxide surfaces, for example, will react with acid groups. Polymers with this type of functionality make good binders for coatings applied to metal. The value of this functionality is exemplified by the adhesion properties of maleic acid-modified vinyl chloroacetate lacquers and by the phosphoric acid-based etch primers. The adhesion of etch primers (a primary valency bond) has been measured to be 6 to 24 times that of a secondary valency bonded primer (12,000 psi [840 kg/cm^2]) as opposed to 500 psi (35 kg/cm^2) for a polystyrene-based system and 2,000 psi (140 kg/cm^2) for a polyvinyl acetate-based system).[15] Vinyl chloroacetate copolymers are so highly cohesive that, when unmodified, they display poor adhesion to metals.

If small amounts of a reactive carboxylic acid (i.e., maleic acid) are interpolymerized into this polymer, however, the resultant vinyl chloroacetate structure is interspersed with pendant acid groups. Although the modification is very

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low (about 1 percent), the acid groups profoundly improve the vinyl binder's adhesion to metal. The metal maleic acid linkages anchor the film to the substrate.

Other examples of primary valency adhesion are as follows. Primary valency linkages may also be achieved in urethane coatings on wood. Here, isocyanate groups react with cellulosic hydroxyls. When acetoacetylated resins are used, there is some evidence of chelation with iron and possibly other metal surfaces.

Primary valency linkages may also be used in adhesion to certain plastics and other coating films. Intercoat adhesion between urethane finish coats and epoxy primers may be facilitated by using the cross interfacial reactions between isocyanates in the finish and the pendant hydroxyls on the epoxy molecules of the primer or unreacted amine groups on the curing agent. In some cases, excess functionality may be used deliberately in a primer to be taken up by complementary groups in the finish. Munger[16] associates the tenacious adhesion of inorganic zinc-rich primers on virgin steel to iron silicate linkages formed between the iron substrate and the silicic acid of the coating binder.

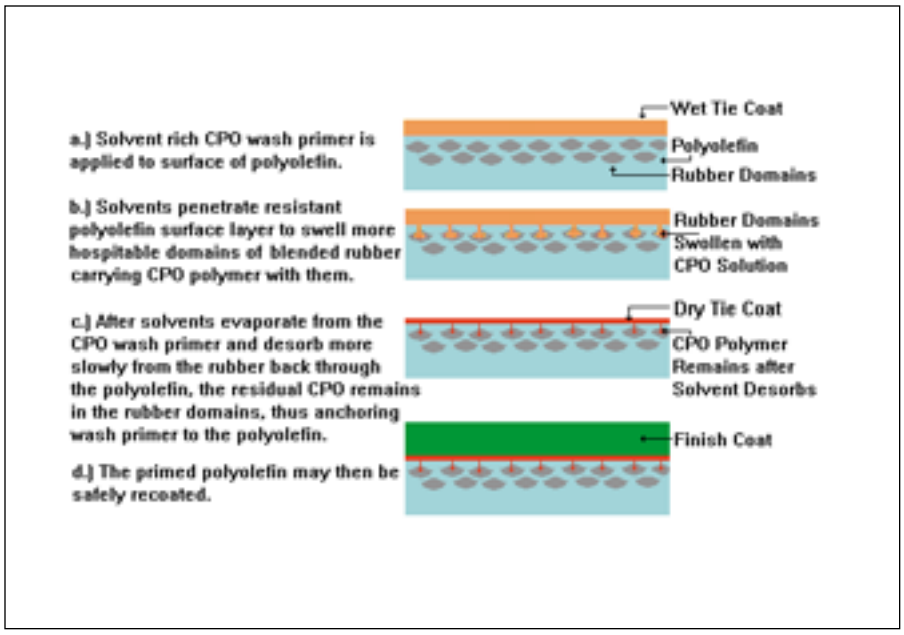


Fig. 2 - Adhesion to polyolefins with solvent-borne CPO (chlorinated polyolefin) tie coats.

Secondary Valency Bonding

Most coating binders attain adhesion by secondary valency associations, such as hydrogen bonds and Van der Waals forces. The bonding energies of this type of bonding are considerably reduced compared to primary valency or chemical bonds. (See the October 1995 *JPCL*, pp. 177-187.) With most coating binders applied and dried at room temperatures, there is far more opportunity for this type of chemical bonding, sometimes referred to as specific adhesion, than there is for primary valency adhesion on most substrates.

Polarity in substrates and paint binders is the key to secondary valency attraction. Binders rich in ether, ester, and amide linkages as well as other more reactive species (such as hydroxyls, carboxylic acid groups, and amines) adhere better than less polar systems such as poly-

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styrene and vinyl toluene copolymerized with butadiene. The preponderance of such groups in alkyds, epoxies, and polyurethane coatings has much to do with the excellent adhesion of these films.

Unfortunately, the very groups that improve adhesion, such as hydroxyls, favor the uptake of water, which can adversely affect coating system performance. This dichotomy and the appropriate formulation response will be discussed in a later column.

Most substrates are rich in polar groups, which interact with the paint film binder to attain good bonding. The surfaces of all metals, except the noble metals, are chemically different from their bulk phase and are naturally covered by reaction products of the metal and its environment. Where these products are tightly adherent, such as the oxide on aluminum, they will generally contribute to good adhesion. Where the oxide surface is less adherent (e.g., on iron) as noted above, it must be removed before coating. The thin, impermeable oxide layer that immediately reforms on the newly bared iron surface is, however, when newly formed, adherent and suitable as a substrate for good adhesion.

Glass and siliceous substrates are well endowed with silanol (-SiOH) groups. Wood, paper, and other cellulosics are rich in hydroxyls. As noted above, one key to obtaining adhesion on polyethylene plastics is the oxidation of its surface to introduce polar groups. These may serve as hydrogen bond donors and acceptors for polar groups on coatings.

The next article will continue the discussion of adhesion, focusing on non-ideal surfaces and techniques for upgrading adhesion.

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