Adhesion: Part 2

by Clive H. Hare,
Coating System Design

Last month, we reviewed the chemical aspects of adhesion. This month, we will consider the physical aspects of this phenomenon. The column begins with an introduction to mechanical adhesion; describes the roles of substrate contamination and surface preparation; discusses adhesion over contaminated surfaces and ways to enhance adhesion; and gives examples of adhesion failure.

Table 1
System Design Requirements for Maximized Adhesion

Substrate	Coating
High Cohesive Strength	Low Surface Energy
High Surface Energy	Polar Groups
Increased Surface Area	Reactive Groups Carboxylic Acids Hydroxyls
Pure Surface No Contamination	Low Resin Solution Viscosity Low Solids Low Molecular Weight Resins Polymerizing after Application
Presence of Active Sites Unbound Metal Oxides, Hydroxyls, Etc. Polar Groups	Slow Evaporating Solvent Systems
Porosity	Slower Conversion (Cure, Polymerization) Rate (Compared to Rate of Solvent Loss)
Solubility or Partial Solubility in Coating Solvent	Low Internal Strain Reduced Shrinkage on Polymerization
	Good Flexibility
	High Tensile Strength and/or Large Work to Break Values
	Low Permeability Use of Barrier Pigments/Chlorinated Binder Uniform High Cross-link Density Elimination of Hydrophilic Components
	Coupling Agents Silanes, etc.

Mechanical Adhesion and Penetration

For many years, it was thought that the increase in adhesion achieved by scarification techniques (abrasive blasting and sanding, for example) was derived from mechanical entanglements of the coating film within the pores and fissures of the scarified surface. Current thinking proposes that such techniques merely remove saturating impurities from potentially reactive sites on the substrate and simultaneously increase the real surface area with respect to the apparent (planar) area. Expansion of the surface area increases the number of potentially reactive sites on the substrate for either primary or secondary bonding. An increased number of reaction sites, rather than purely mechanical effects, is the principal reason for improved adhesion.

Mechanical adhesion is, however, entirely possible on porous surfaces such as wood, paper, leather, and concrete, where penetration by, and absorption of, the coating into the substrate play a significant role in adhesion. Similar submicroscopic effects are also possible on scarified metal surfaces; plastics; and other sanded, etched, or otherwise roughened substrates (including existing paint films). In achieving such adhesion, the coating must flow into the surface porosities and, for maximized effect, completely wet out the interior cavities, displacing occluded air. In some highly viscous or fast drying films, such air displacement from the substitute may produce bubbling of the recent film as the air becomes entrapped in the drying cavity. This type of defect is common over some zinc-rich primers and will be discussed in more detail in a later segment of this series.

Coatings that fill narrow-mouthed cavities can be dislodged only by producing lateral cohesive failure in the coating film or the substrate (Fig. 1). While extreme, this porosity is not unusual on naturally porous substrates such as wood, paper (including paper-surfaced drywall), and leather. It is also found on plaster, concrete, cinder block, and other porous masonry surfaces.

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It is more likely that the coating will only partially fill such cavities. When the coating polymerizes, subsequent shrinkage may cause voiding and cracks in the film or the substrate as the coating pulls away from the interior surface of the cavity. These cracks and weaknesses are generally the sites of initial disbondment, from which more widespread failure is propagated.[1] Incompletely filled cavities on coated metal substrates may also provide sites for water to begin to accumulate beneath the film. Water accumulation may lead to lateral adhesion loss, the accumulation of still more water, and eventual corrosion. Salt can also lodge easily in these cavities on corroded steel and cause difficulty in cleaning.[2]

The penetration of paint into cavities is a capillary phenomenon facilitated by the following:

- surface energetics (e.g., low surface tension binders and high surface energy substrates),
- an increasing size of the opening,
- low viscosity of the paint's continuous (resin solution) phase, and
- reduced rate at which solvent is lost and viscosity increases.

Wicks et al.[1] notes that the diameter of the pigment particles may be large relative to small surface irregularities, so that only the liquid phase of the paint may enter the substrate. A similar phenomenon is likely where the paint is applied over a porous surface, such as old, chalking films from which the original binder has been degraded by ultraviolet light and eroded by rain. The consequent partition of resin and pigment is shown in Fig. 2. The linseed oil binder wicks away from the bulk phase of the paint film and into the chalking surface of an existing film that has been primed.

The simplest way to reduce the solution viscosity of the resin is to reduce solids by adding solvent. Unfortunately, this approach is incompatible with trends in environmental regulations on solvent emissions. Also, for high molecular weight lacquers, penetration of even low solids solutions of such polymers into small porosities may be impeded by the size of the binder molecule. Therefore, resin solution viscosity is best reduced through resin design. In most systems, the viscosity of the resin solution phase is related to the molecular weight of the solid binder (the resin). Resins with low average molecular weight and minimal high molecular weight fractions at the time of application[3] will more readily penetrate and adhere to irregular surfaces. A study[3] notes the negative effect of increased molecular weight on wet adhesion. Microscopically, most surfaces are far from planar, especially after mechanical or chemical preparation. Therefore, it may be reasonable to discuss adhesion in terms of substrates as well as coatings (Table 1).

Paint films that slowly build molecular weight after application are inherently more suited to good adhesion than high molecular weight lacquers. For this reason, linseed oil-based red lead primers of low molecular weight adhere well to rusty steel. The surface energetics and the slow rate at which viscosity increases (through both solvent evaporation and polymerization) also play a considerable part. The longer the paint can stay against the cavity in a wet, low viscosity state, the more penetration will occur. Thus, high boiling solvents provide better adhesion than fast evaporating solvents.

It has also been suggested[1] that some of the improvement in adhesion in baked systems results from the initial reduction in viscosity produced by the rise in film temperature before cure begins. Similar phenomena (along with glass transition [T_g] and free volume effects discussed in the December 1995 and

Fundamental Techniques for Cleaning Substrates

Solubilization
Soluble inorganics (e.g. Salts) dissolved in water. Soluble organics (e.g. Oils) dissolved in solvent.

Emulsification
Lifts and emulsifies insoluble organic and inorganic soils in detergent solutions.

Saponification
Chemically hydrolizes and renders water soluble non-soluble esters and salts.

Chelation and Sequestration
Removes calcium and magnesium from hard water, iron, and other metal oxides from metal surface by chelating mechanisms.

Deflocculation
Wets, lifts, and disperses contaminating dirts, surrounding particles with surfactant barrier which suspends dirt residues as a dispersion and prevents resettlement and recontamination.

General Precautions
Materials applied by dipping, spraying, wiping, or brushing (spreading techniques less efficient in removing residues).
Efficiency increases with temperature and pressure (e.g., as in steam cleaning).
Rinsing (in clean water or pure solvent) is an important necessary final step.

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January 1996 issues) are involved in the increased adhesion of post-baked thermoplastic coatings.

However, the shrinkage that occurs on curing is counterproductive to adhesion.[4] Giving superior adhesion, epoxies shrink far less than do true condensation systems, such as amino-cured baking coatings, and free radical-induced systems, such as unsaturated polyesters.

Substrate Contamination

Many conditions may compromise the nature and uniformity of a surface. Substrates may be contaminated with oils, greases, waxes, dirt, laitance, loose powders, rust, scales, and surface chalk (pigmentary residues from the weathering-induced degradation of old paint films). In 1 study of salt contamination on 78 bridges in Germany, Gross[5] detected 20 types of residual salts, mainly sulfates. Similar deposits are likely to occur on most exterior surfaces, particularly in areas prone to acid rain. In coastal areas, chloride salts are also on most paintable exterior surfaces. Road dirt, a combination of dirt, oils, and these salts, is found on the road-facing surfaces of many bridge structures, while paintable surfaces in other industries may be plagued by other residues common to mining and manufacturing processes. Loose residues from a carelessly prepared surface can include unremoved blast debris (and debris from sanding) and chlorides from muriatic acid etching procedures. These residues are as damaging to subsequent adhesion as the deterioration of the original surface that required the surface preparation. Chalk residues typical of old paint films may be particularly difficult to recoat with some coatings (e.g., latex paints) and may be quite difficult to remove by washing alone.

All of these conditions may be considered as more or less poorly bound films of little cohesive strength. Problems in coating such surfaces are similar to those experienced in dealing with the painting of old whitewash, calcimine, and similar loosely bound paints called distempers. Failure to remove these films will lead to adhesion problems. Subsequent delamination is actually a cohesive failure within the continuum of the loose film. The adhesion of the new coating to the surface layers of the loose film is good. As a consequence of such cohesive break-up, substantial debris will be left on the backside of the delaminating coating film and on the re-exposed substrate itself. The driving force of the delamination may be the shrinkage stresses incurred in the system as the new film dries and polymerizes. Another cause is the hygrothermal stresses produced as the system is put in service, expanding and contracting under the influence of environmental moisture and temperature.

Less often, delamination may result from cohesive insufficiencies in the substrate, more so in relatively weak wood and cementitious surfaces than in metal.

Surface Preparation

The purpose of surface preparation is to remove all anomalous substances and conditions and render the surface a better approximation to the theoretically "pure" substrate. The efficacy of surface preparation depends on the type of contamination and the surface preparation method. Various cleaning techniques may be used, but none is truly universal. (See box on page 80.) Optimized surfaces will depend on the cleaning methodology. Simply washing the surface with water, for example, will have a nominal ef-

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fect on removing low energy organic contaminants such as oil films and grease deposits. Solvent washing and solvent vapor degreasing, which may more effectively remove oils and greases, will have little effect on inorganic salts. These contaminants may be more easily removed with water. The efficacy of cleaning in both cases depends on the solubility of the contaminant in the cleaning media. Fortunately, solubilization of the contaminant is not the only process for cleaning the surface. Emulsification of the contaminant is an alternative. Detergent washing, for example, may effectively emulsify non-soluble contamination while dissolving water-soluble matter.

Heat and mechanical energy will improve the efficiency of the cleaning operation when applied with water, solvent, or detergent solutions. High temperature detergent cleaning techniques, such as steam cleaning, are very effective. Hot cleaning solutions are more effective than cold ones because of the increased kinetic energy of the molecules (contaminant and cleaning agent) at high temperature. Mechanical force helps remove contamination even more effectively. Wiping, rubbing, scrubbing, sanding, and water and abrasive blasting represent increasing levels of force that can be used to remove surface contaminants. Techniques that provide sufficient energy to remove the contamination and scarify the surface may be particularly useful because they will simultaneously clean the surface and increase the true surface area of the substrate compared to its apparent planar area. High energy mechanical cleaning methods such as abrasive blasting may not, however, be suitable for weak substrates such as plaster and wood.

Mechanical force alone may not entirely remove organic solubles. For example, heavy grease deposits will normally have to be removed from surfaces with solvent washes before abrasive blasting. Nor will dry blasting completely remove inorganic salts that have formed salt nests on old, corroded steel surfaces. Wet blasting with abrasive and water may be required to more effectively remove inorganic salts (chlorides and sulfates) from old, rusting steel surfaces, especially where the surface is porous. Salt-contaminated high alloy steels below bridge decks have in some cases displayed porosity after several years in service.[2]

Chemical cleaning techniques[6,7], such as acid etching and alkaline deoxidation, accomplish the same thing as blasting for metal, although alkaline cleaning gives no profile. Abrasive blasting and acid pickling will also chemically remove tightly bonded oxides and other scales that cannot be removed by other techniques. These techniques strip away oxide films that chemically saturate metal surfaces and free up reactive groups on the surface for subsequent reaction with potentially complementary groups on the paint binder. If we remove heavy oxide deposits, we leave nascent steel surfaces with thin, adherent metal oxide and hydroxide films. These will then react with the coating. Chemical cleaning, including the acid etching of concrete surfaces, must be followed by an adequate rinsing step to remove loose salts and other residues left after cleaning.

Adhesion to Contaminated Surfaces

In practice, optimum surface preparation may not always be feasible. Cost, access difficulties, environmental concerns, and substrate sensitivity may force coating application over imperfectly prepared surfaces. Whether inadvertent or deliberate, application of paint over surface contaminants often produces catastrophic peeling failures. However, risk management, environmental con-

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a. Porous substrates such as wood and even metal may contain narrow-necked cavities.

b. High wetting, low viscosity paints may be able to penetrate these cavities, displacing air and filling them. This provides excellent anchorage for the film. Subsequent adhesive failure must necessarily, therefore, involve additional cohesive failure of the film across the neck of the cavity.

c. Complete air displacement is rarely possible, however, and some reopening of cavities may occur as films shrink on polymerization. Solvent diffusion from these areas may also be very slow. On metal, cavities may also contain corrosion product and soluble salts, which are not easily accessible for removal by surface cleaning.

d. In service, unfilled, reopened, or contaminated cavities will form sites at which penetrants (such as water) passing through the film may accumulate. This may be particularly problematic on metal in water service or condensing environments, where osmotic and electroendosmotic gradients may lead first to blistering and then to underfilm (intra-cavity) corrosion. Where the cavities contain depassivating chlorides and sulfates, these highly aggressive electrolytes may lead to high corrosion rates.

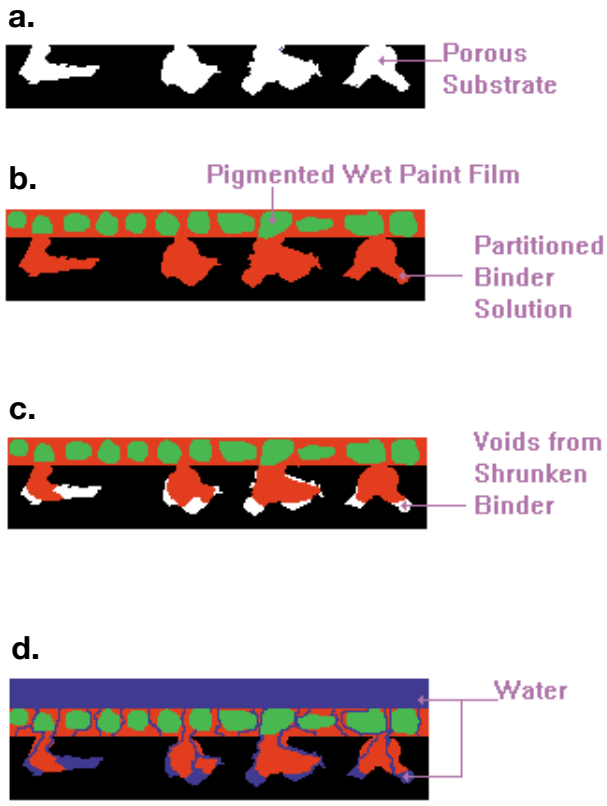


Figure 1 - Mechanical Adhesion and Potential Trouble
Figures courtesy of the author.

cerns, and the cost of hazardous waste disposal encourage attempts to apply new coating systems over marginally prepared surfaces.

Just as the effectiveness of any method of surface preparation depends on the type of contamination and the nature of the method, the success of limited preparation is largely governed by the specific nature of the surface to be coated and the coating itself. Unless the coating can assimilate the contamination (a rare circumstance), the success of the system must depend on the ability of the coating to displace or penetrate the contamination and reach sound surface beneath. Assimilation is possible, for example, where a waterborne paint is applied over a damp surface or where a brush is used to work a long oil alkyd into a dusty surface.

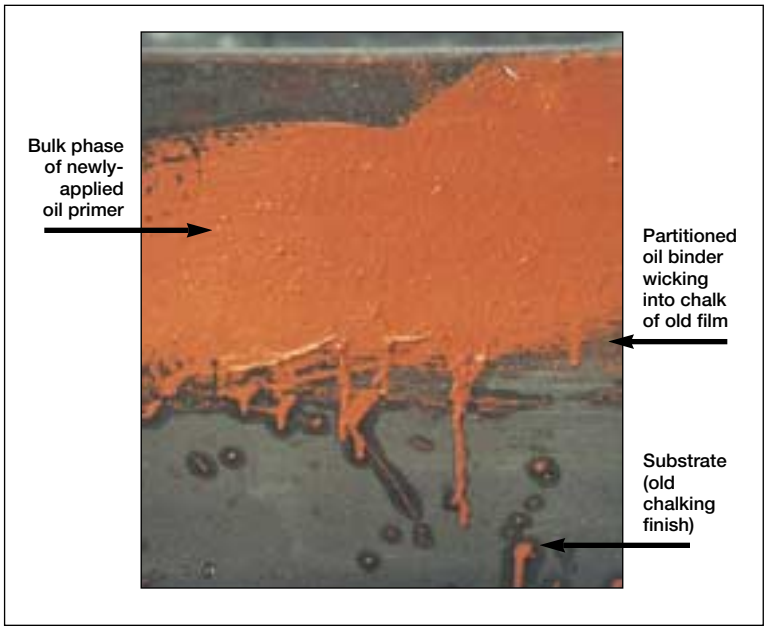


Fig. 2 - The lateral portion of an oil binder wicks away from the bulk phase of a red lead/linseed oil primer into a layer of surface chalk on an old paint film.
Photo reproduced from The Painting of Steel Bridges and Other Structures *by Clive H. Hare with permission from Van Nostrand Reinhold*

Displacement occurs when a high wetting resin system (e.g., epoxy) is applied to wet steel (in extreme cases, below water). The resin or resin and solvent mix associates with the substrate more strongly than does water, and thus displaces the water.

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The displacement of water allows the coating to adhere in the presence of the external aqueous bulk phase. Polyamide- and amidoamine-cured epoxies are particularly effective in this regard because of the hydrophobicity of the curing agent. Displacement cannot occur when the surface tension of the coating is higher than that of the contaminated surface. Therefore, water-borne paints ciss, crawl, and bead up over oily surfaces, while a low energy oil paint may wet and achieve satisfactory adhesion over the same surfaces.

An example of penetration is when a red lead linseed oil paint is applied to a rusty steel surface and soaks into and through the rust. However, it would be virtually impossible for a high molecular weight vinyl lacquer to adhere to a dusty surface. The molecular weight of the coating is too high to allow good penetration of the resin solution into the dust, and the solvent system generally evaporates too quickly. Similarly, latex paints have much less success in penetrating old, chalking films than alkyds, particularly those with high oil content.

On surfaces contaminated with loose particles, chalk, rust, and dirt, the effects of penetration are the same as those noted in the discussion of mechanical adhesion. The same may also apply to porous, poorly bound substrates, such as old calcimine films and certain plasters. The relative surface energetics of the paint and substrate are critical. The low surface tension of oil paints is responsible for the excellent service record of these coatings over contaminated surfaces. Oil paints, however, also have a low continuous phase viscosity and a highly protracted rate of conversion. Both properties allow the wet coating to soak into and through the interstices of the contamination, eventually reaching and wetting out sound substrate and also wetting and binding much of the contamination. As the surface tension of the binder increases, wetting becomes increasingly less likely. The ability of the coating to enter and penetrate the interstices of the contamination is reduced as the viscosity of the continuous phase of the paint increases. Reduced penetration is common where drying times are short or molecular weight and, therefore, viscosity increase rapidly during cure.

Latex paints have particular difficulty penetrating contamination and wetting the substrate. Although latex paints have poorer wetting characteristics than solvent-borne systems, it might appear that the low viscosity of the high molecular weight *dis-*

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persions would facilitate penetration compared to high molecular weight *solutions*. In fact, the individual latex particles may be larger than the interstices of many porous films (the chalking surfaces of existing paint films, for example). This size difference prevents the latex from entering the interstices and pores of the chalking layer, although the water may do so. Therefore, coalescence of the latex particles occurs over, instead of within, the contaminating layer, resulting in a dry film that rides on top of the chalk. The film is then vulnerable to adhesive difficulties. An apparent adhesive failure in this film may be a cohesive failure within the chalk layer.

Attempts have been made to use latexes of very fine particle size (<0.1μ).[8] Presumably, fine particle size latexes are more likely to fit into the existing porosities of the porous chalk than resins of larger particle size. Carboxylated latexes are now used as grinding vehicles in surfactant-depleted pigment dispersion phases. They are used as latex emulsions for chalk binding and adhesion over marginal surfaces because of the improved wetting and binding properties of these vehicles.

High wetting coalescents such as n-methyl-2-pyrrolidone can also improve the penetration of chalking films and the adhesion by solvation of the more substantial underlayers of the old film. In this respect, hydrophilic coalescents such as the aliphatic glycol ethers may be more efficient than water-immiscible coalescents (e.g., the aromatic glycol ethers and trimethylpentanediol monoisobutyrate). Water-immiscible coalescents associate more strongly with the non-continuous (resinous) phase of the new latex being applied and are not present in the penetrating water.[9,10] Paradoxically, hydrophilic solvents are less efficient as coalescents than less miscible materials that partition into the latex because they tend to remain in the water phase.

None of these techniques for enhancing adhesion to chalk is as effective as the traditional approach of modifying the latex binder with up to 20 percent by weight of low molecular weight (very long oil) alkyds, epoxy esters, vegetable oils, or polyesters. The modifiers are emulsified by the surfactant system of the latex paint to form a barely compatible whole. On application, these slow drying, high wetting modifiers partition themselves from the bulk latex binder and penetrate the loose chalking layer. They may partially solvate the substrate and markedly improve the adhesive strength of the latex paint to the contamination. The modifiers may also increase the cohesive strength of the loose chalking contamination.

Alkyd modification compromises the long-term exterior durability, mildew resistance, color retention, and drying time of latex paints. However, the benefits of oil and alkyd modification usually outweigh these disadvantages.

Latex de-adhesion over porous, chalking, and otherwise contaminated films is also affected by the T_g and mechanical properties of the final latex film. Latex systems with high T_g are similar to other strong films of high modulus that do not readily dissipate strain from either internal or external stress, unless they cohesively or adhesively break. Therefore, they tend to transfer the stress into other parts of the composite and induce cohesive failure in the loose substrate layer. More flexible films of reduced T_g and modulus deform more readily with stress and produce less strain within the weak chalk layer.

The strength and nature of the recoat system will also markedly affect

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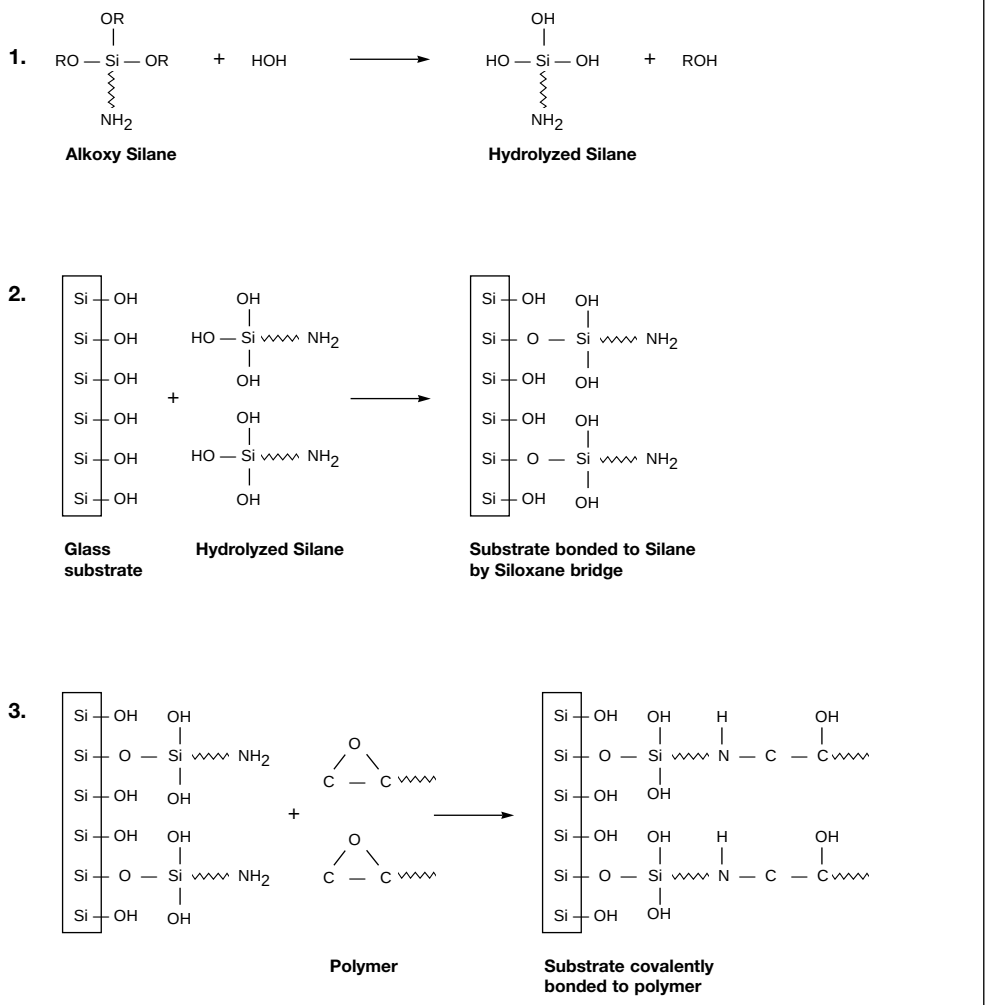


Fig. 3 - Adhesion Promotion with Silanes. 1) Alkoxy silane is hydrolyzed by water to form silanol groups; 2) Silanol groups on hydrolyzed silane react with silanol groups on the substrate to form siloxane bridges, which anchor the silane backbone to the substrate; 3) Organo-reactive groups (e.g., amines) on the opposite end of silane react with complementary organo-functional groups (e.g., epoxy) on the polymer. The polymer is thus covalently bonded to the substrate.

the success or failure of any coating applied over marginally prepared substrates. This factor becomes increasingly significant as the interfacial adhesion between substrate and recoat is further compromised. Finally, the adhesion is also influenced by the nature of the contamination and the surface beneath it.

Enhancing Adhesion with Coupling Agents

The most effective techniques for promoting adhesion are enhancing the substrate condition, removing contamination, and, particularly, increasing the real surface area per apparent area of surface. Whether these results are achieved by mechanical (sanding or abrasive blasting) or chemical techniques (acid pickling or alkali deoxidation) is less important than the results.

On the other side of the interface, the selection and design of the resin, coating, and coating system can significantly affect adhesion. Unfortunately, the selection of coatings involves many other aesthetic and engineering considerations in addition to adhesion, such as drying speed, hardness, chemical resistance, gloss, and color. These properties are not always compatible with optimum adhesion.

There is, of course, no universal potion that will transform a coating that does not adhere into one that does. In some cases, acids, usually phosphoric acid, have been used towards this end on suitable substrates (e.g., steel), but results vary from system to system.

Over the past several decades, however, formulators have successfully designed additives to upgrade adhesion to certain substrates. An example is the effect of silane modification on the adhesion of coatings to glass and siliceous surfaces.

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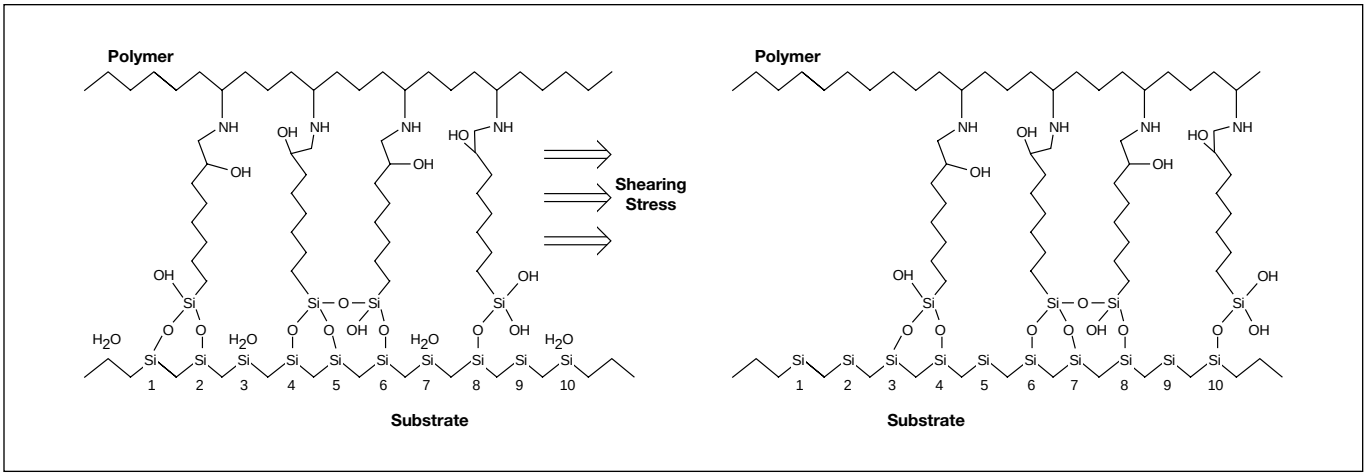


Fig. 4 - Stress Attenuation Through Silane Slippage - In the presence of interfacial moisture, a reversible silanol reaction allows the siloxane linkages of the interface to break and rapidly reform. Under shear stress, this allows the siloxane bridges to slip from silicon atom to silicon atom along the substrate surface. The bonded coating can thus move along the substrate, dissipating strain without catastrophic disruption in adhesion.

In some respects, silanes are similar to surfactants in structure. All are characterized by the presence of trialkoxysilyl groups on one end of a hydrocarbon chain, the other end of which is terminated by an organo-reactive group such as an epoxy, an amine, a vinyl group, or a mercapto functionality. Typical materials are shown in Table 2. After hydrolysis with surface water, at least one of the resultant silanol groups on the silane triols reacts with silanol groups on the substrate to form a siloxane bridge. The organo-reactive group on the other end of the silane is available to react with the binder to give a chemically bonded bridge across the interface between binder and substrate (Fig. 3). For example, an amino-terminated silane may react with an epoxy, and a vinyl silane with an unsaturated polyester. Because the silane has trifunctionality, remaining silanol groups on adjacent silane molecules may intercondense to give a thin, polysiloxane film along the immediate surface of the glass.[11]

Unlike most examples of molecularly engineered adhesive improvement that require modification of the paint binders, silane modification can be used by the paint formulator to improve adhesion. Silanes improve the adhesion of coatings through their use as pretreatments, in resin modification before the incorporation of pigments, or in modification of the primer during paint manufacture. Pretreatments are 1 to 2 percent solutions of silanes in water and suitable solvents that are applied to the surface before priming. The silane may also treat the pigment before its incorporation into the paint. While this technique would seem more likely to improve the cohesive strength of the coating film, it apparently also upgrades wet adhesion. Improved wet adhesion may be related to the closer association of the pigment and binder.

In addition to modifying surface coatings on glass, this technique is claimed to upgrade adhesion to metal surfaces. While success here is less universal than on glass, there is much evidence to support these claims.[12,13,14]

Not all silanes bear reactive groups that complement groups on the polymer. However, there is evidence that these silane materials too may upgrade adhesion. In this case, physical entrapment of the pendant silane chains within the polymer may be responsible for the improved adhesion.[12]

The question of permanence of the -Si-O-Si- bonds at the siliceous substrate (and possibly -C-O-Si- bonds at the metal interface) is interesting. The bonds are susceptible to reversible hydrolysis. Here, the siloxane hydrolyzes back to silanol groups in the presence of any water that may reach the interface under wet conditions. Performance of coatings modified under wet conditions does not indicate that this reversal is complete enough to be problematic, however. Walker[12] has shown the the importance of using silane modification to improve wet adhesion, which has great significance for the controlling of corrosion. It has also been claimed that, in direct consequence of reversible hydrolysis, silane-bonded systems are stress attenuating. Under stress, the siloxane bonds at the substrate will cleave in the presence of water, allowing the system to slip across the substrate plane to form again at new (less constrained) sites on the substrate after the stress has been removed (Fig. 4).[11,15,16]

The value of similar materials as adhesion promoters has also been claimed. These substances include certain organo titanates[17], such as isopropyl tri (n-ethylamino-ethylamino) titanate, and zircoalum-

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Table 2
Typical Organo-Reactive Silane Adhesion Promoters

Formula	Functionality	Typically Used With
$CH_2 = CHSi(OC_2H_5)_3$	Vinyl	Unsaturated Polyesters
$CH_2 = CHSi(OC_2H_4OCH_3)_3$	Vinyl	Acrylics, Vinyls, Alkyds, and Vinyl Esters
$CH_2 = C(CH_3) - C(=O) - OC_3H_6Si(OCH_3)_3$	Methacryl	
$HSC_3H_6Si(OCH_3)_3$	Mercapto	Urethanes and Epoxies
$HSC_2H_4Si(OC_2H_5)_3$	Mercapto	
$H_2NC_3H_6Si(OC_2H_5)_3$	Amino	Epoxies, Alkyds, and Urethanes
$H_2NC_2H_4NHC_2H_6Si(OCH_3)_3$	Amino	
$CH_2\text{-}O\text{-}CHCH_2OC_3H_6Si(OCH_3)_3$	Epoxy	Amines, Amides Urethanes, and Formaldehyde Systems

inates.[18] These materials seem even more system-specific than the silanes, however, and inappropriate selection of the titanates can dramatically reduce adhesion.[17] Silanes and, to a lesser extent, the titanates and zircoaluminates have also been used to treat siliceous pigments, such as silica, wollastonite, and mica.[11,19] Here, the silane reacts with the pigment surface so that the pigment presents the organo functional tail of the silane to its environment. In effect, the pigment becomes covered with a mechanically bonded "hairy" layer (Fig. 5). When used to pigment judiciously selected binders, the organofunctional end of the silane will react with the binder, producing a chemically bonded internal matrix between pigment and resin (analogous to that between resin and substrate in adhesion promotion). The cohesion of the resulting paint film is augmented. In these applications, the pigment is effectively encased in the mono layer of organic treatment. Depending on the type of treatment used, the pigment may present reactive amine, epoxy, vinyl, and mercapto groups to the potential binder.

Improved pigmentary interfaces not only improve the physical properties of the coating, but may also reduce permeability of water and other penetrants through the interstices of the pigment and binder. A separate advantage of such treatment is that the treated pigments are much lower in oil absorption than their untreated counterparts, which translates into high critical pigment volume concentrations, lower viscosity, and applications in coatings with low volatile organic compounds. Commercial examples of pigments embodying this technology are used with and without inhibitive pigments in anti-corrosive primers.[19]

Adhesion, Cohesion, and Coating System Response to Stress

The adhesion of a coating film to a substrate is part of a complex system of forces. These forces must maintain a satisfactory equilibrium in the presence of an equally complex system of stresses that play upon (and

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strains that play within) the total applied composite. To attempt to accurately characterize or predict coating system performance by measuring the adhesion of the primer alone is as simplistic as attempts to characterize the mechanical behavior of the total applied composite paint system by studying the stress and strain response of the unsupported finish coat.

While our understanding of the interplay of forces within the multicomponent system remains incomplete, we can appreciate the effects of film strength and thickness of a multi-coat (or even a single-coat) paint system on paint film failure. It is no accident that wash primers and pre-treatments are applied and cured as ultra-thin film coatings. Ultra-thin films minimize the effects of high film cohesion on adhesion. As the film thickness increases from 1 to 5 to 50 mils (25 to 125 to 1,250 micrometers), the negative impact of high cohesive strength and increased internal stress on adhesion becomes more extreme. In our zeal for good corrosion protection, it has become popular to advocate thicker, rather than thinner, films. Unfortunately, the disadvantages of the thicker films, such as their negative effects on the adhesion and cohesion of the system, have been unrecognized, underplayed, or ignored.

The author advised a contractor many years ago that as long as his anchor pattern was deep enough, he need not worry about putting too much coal tar epoxy on the interior walls of a water cooling plant. Several weeks later, the same contractor returned with several paint chips to complain that a six-mil (150-micrometer) anchor pattern did not prevent the film from sheeting from the newly blasted steel shortly after it had been put into service. The paint chips were ⅞ in. (22 mm) thick.

In a separate instance, another contractor had been convinced to do a quick repaint job on the ceiling of an old mill. The job had hardly started when the newly applied film began to delaminate profusely from the ceiling, which bore heavy deposits of calcimine. Calcimine is one of a series of underbound paints used on ceilings in the early years of this century. The mill owner was outraged, not least with the author, who suggested in lieu of a complete removal of the existing calcimine, to abandon the alkyd flat being used in favor of the cheapest, most underbound paint that he could find. Happily, the author's recommendation prevailed, and the ceiling was satisfactorily recoated (aesthetically, if not from an engineering standpoint) without further peeling, at least until the next repainting.

The thick, strong, cohesively bonded epoxy film of high modulus, unlike the cheap ceiling paint, was unable to dissipate strains that had built up within the continuum on curing. Consequently, adhesive forces had to be of a very high order to avoid adhesive failure response. In the old, cohesively weak calcimine, the adhesive forces that held the film to the substrate were infinitely weaker than the epoxy. Film cohesion was also much weaker. The strain that developed within the coating as a result of solvent loss and curing could be effectively dissipated by cohesive microcracking along the pigmentary and vehicle interfaces. In short, the coating film cracked because it was too weak to peel. The cracks were too fine to be visible to the unaided eye.

Problems could still occur when the weak calcimine was subsequently recoated with strong alkyd finish in the first abortive repainting that produced the original failure. While the cohesion of the initial calcimine did not change, the cohesive strength of the total composite did because the coating applied as a recoat was much stronger. Alternatively, recoating with the weak finish did not substantially add to the cohesive strength of the upper strata of the system. Therefore, internal strain was minimized and dissipated in a microcracking of the new film. Cohesive failure in the lower strata was avoided. Eventually, as more and more coats come to be applied over the same weak underbound paint, the total system response to curing and service stresses will produce so much strain within the system that the cohesive and adhesive integrity of the early poor film (by far the weakest element of the entire system) will disintegrate. The weak paint, or part of it, along with every coat applied over it, will delaminate.

Conclusion

In the above examples, the majority of the total stresses producing adhesive (or cohesive) failure are derived

continued

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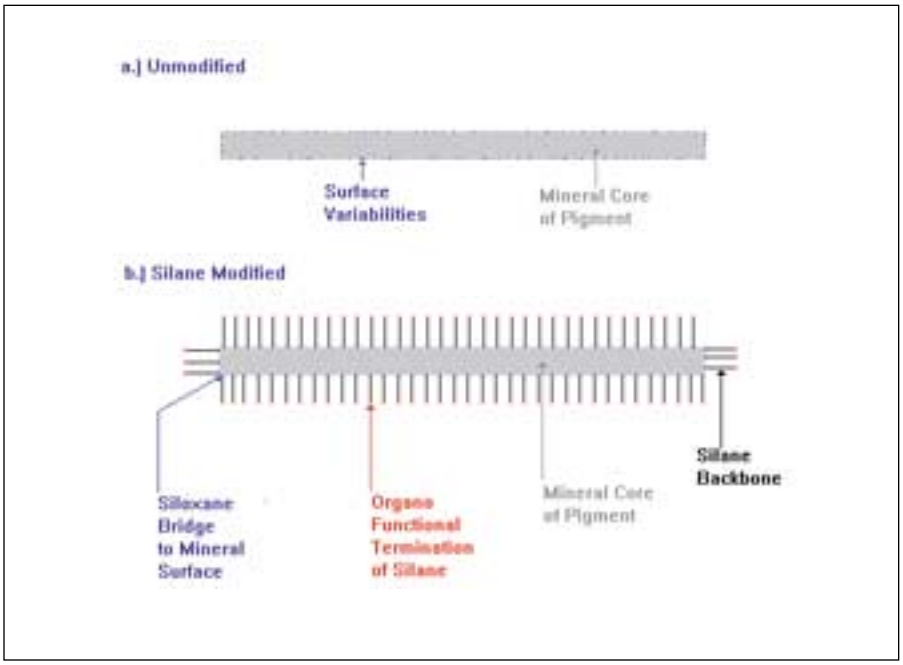


Fig 5 - Structure of Surface-Modified Pigment

from the application of new coatings over old ones, not from the service environment.

These types of stresses, called internal stresses, will be the subject of the next article in this series. **JPCL**

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