

Theory of Adhesion and its Practical Implications

A Critical Review

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Abstract

The quality and durability of a coating is directly related to the nature of adhesion. Chemists tend to associate adhesion with the energy liberated when two surfaces meet to form an intimate contact termed as an interface. In other words, adhesion may be defined as the energy required to dismantle the interface between two materials. Physicists and Engineers usually describe adhesion in terms of forces, with the force of adhesion being the maximum force exerted when two adhered materials are separated. There are many theories regarding the mechanism of adhesion such as adsorption (van der Waals forces), electrostatic, diffusion (entanglement of polymers with a substrate), chemical bonding, mechanical interlocking etc. all of which may play a significant role in interfacial bonding. The energy required to separate the adhesive (coating) and the substrate is a function of the adhesion level i.e. interactions at the interface, but it also depends on the mechanical and viscoelastic properties of the coating materials. It is definite that all the mechanisms mentioned could affect bond strength and adhesion. Because of the complexity of adhesion phenomena, there are many models for it. None of them, on its own, can fully explain adhesion. However, each model describes a part of the complex processes involved in adhesion.

For optimum adhesion it is therefore absolutely essential to ensure good wetting by the coating material applied, thus creating ideal conditions for causing the film forming agent molecules to approach the substrate. In general, for good substrate wetting the surface tension of the coating material (σ_p) should be lower than the surface tension of the substrate (σ_s), or they should at least be equal. The real reason for insufficient substrate wetting is the too high surface tension of the liquid coating, however, other factors will also influence how strongly this defect shows up. It can only be performed indirectly by measuring the contact angle of droplets of liquid which have been applied to the solid surface being examined. A measurement of contact angle has been discussed briefly. The range of chemicals used as adhesion promoters includes silanes, silicones, titanium compounds, zirconates, amides, imines, phosphates, and specially modified polymers. Furthermore, there are binders, plasticizers, and additives (e.g., wetting agents) which though intended for other purposes, have the secondary effect of providing good adhesive strength. In terms of adhesive strength, it is in many cases the overall formulation of a paint or other coating material which is decisive.

The mode of action of silanes has been briefly reviewed as these are the future commercially viable coupling agents (adhesion promoters) for external coating of pipelines. These coupling agents like epoxy and amino silanes are often applied as very thin layers on substrates such as steel/aluminium before an adhesive is applied. In many cases, only TOFSIMS is able to characterize the very thin layer of the coupling agent on the substrate.

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Introduction

A comprehension of the basic principles that describe and predict liquid flow and interfacial interactions is important for the effective formulation and the efficient application of coatings and related materials. The theoretical tools for managing the technology of coatings are rheology, the science of flow and deformation, considered with surface chemistry, and the science of wetting and dewetting phenomena. Viewing such rheology properties as viscosity in terms of their time dependency adds the necessary dimension for practical application of theory to practice. Such important coating attributes as leveling are affected by both viscosity and surface tension. Knowing the interrelationships allows the coating specialist to make adjustments and take corrective action with confidence.

Polymeric coatings are the result of an arranged entanglement between two different materials an organic or an inorganic substrate and a polymeric resin – which form adhesive bonds with each other. The quality and durability of a coating is directly related to the nature of adhesion. Chemists tend to associate adhesion with the energy liberated when two surfaces meet to form an intimate contact termed as an interface. In other words, adhesion may be defined as the energy required to dismantle the interface between two materials. Physicists and Engineers usually describe adhesion in terms of forces, with the force of adhesion being the maximum force exerted when two adhered materials are separated. There are many theories regarding the mechanism of adhesion such as adsorption (van der Waals forces), electrostatic, diffusion (entanglement of polymers with a substrate), chemical bonding, mechanical interlocking etc. all of which may play a significant role in interfacial bonding. The energy required to separate the adhesive (coating) and the substrate is a function of the adhesion level i.e. interactions at the interface, but it also depends on the mechanical and viscoelastic properties of the coating materials.

When a polymeric coating is applied on a substrate, a chemical reaction takes place between the two surfaces i.e. substrate as well as the coating. It is often desirable to modify the substrate to ensure the reactivity at the interface by removing contamination (fat etc.) and / or introducing functional groups. This simplified view of the interfacial or interphase bonding neglects physical forces between two materials, which are influenced by surface roughness. For a comprehensive characterisation of coatings, surface analysis of the substrate (chemical as well as topographic) and thermal analysis of cured polymeric coating materials are of great importance (Dr. Amir Hussain, Comtech GmbH, Munich Germany, Seminar paper on “Corrosion Protection by Organic Coatings in Gas and Oil Industry” presented at SSGC Karachi on 25th January, 2007).

If a coating even only partially becomes delaminated from its substrate, it no longer fulfils its purpose. Firm attachment of the coating to the substrate that also remains intact under the effect of moisture, light, salts, gases and cathodic protection under the influences encountered in practice, is a necessary requirement for long-lasting protection. On metal substrates good attachment suppresses the formation of corrosive products even if the coating is physically damaged.

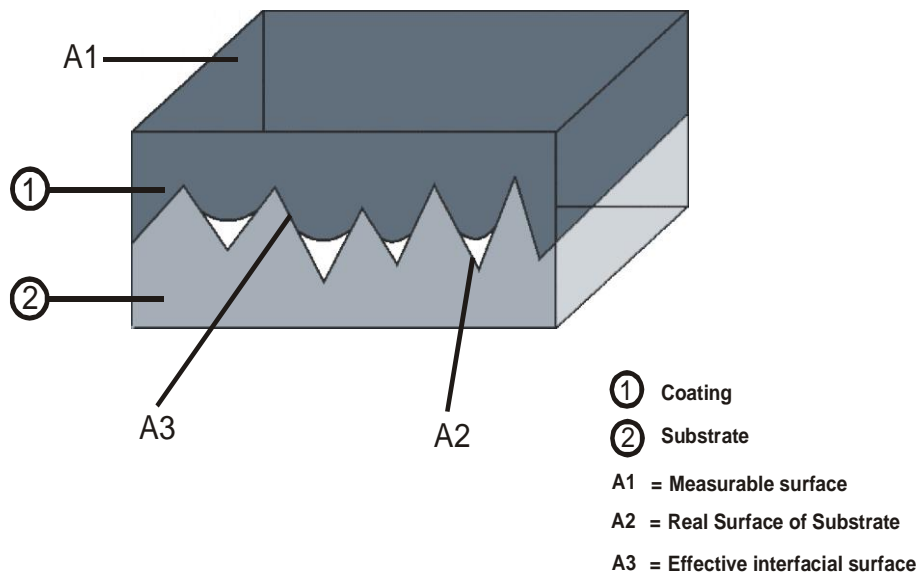


Figure 1: Scheme of surface effects determining the measurement of adhesion.
Source: BASF Hand Book on Basic of Coating Technology 2003

Definition of Adhesive Strength

The concepts of adhesion and adhesive strength are nowadays part of the accepted vocabulary of anyone concerned in whatever way with producing bonding. These bonds can be between materials that are the same or different, and can be produced by, for example, adhesive bonding, brushing, coating, or filling.

Whenever the terms adhesion and adhesive strength are used, a certain bonding strength is associated with it. For coatings, the adhesive strength is defined by DIN 55945. This defines the adhesiveness in terms of the resistance of the coating against mechanical separation from the substrate.

The adhesive strength of a coating on exposure to water and moisture is termed its wet adhesion. One of the ways in which the adhesion can be improved is by the use of adhesion promoters (coupling agents). This is a general term for all those substances that improve the adhesive strength of the materials that are to be joined.

Optimum Adhesion

The adhesion of a coating is not solely determined by the coating. Similarly, the special characteristics of the coated object also have to be taken into account. To create optimum adhesion, the coating process has to be preceded by cleaning processes or layer-forming pretreatments. Good levels of adhesion are therefore not solely due to the coating but result from appropriate selection and adaptation of coating materials and the substrate.

For the adhesion of coatings, in addition to the term adhesion, terms such as adhesive strength, adhesive ability and bond strength are also used. If one defines all the terms as synonyms for the area-related force which has to be applied to delaminate the coating one encounters problems because the reference parameter, area, has to be defined more precisely. The measurable surface

area of coating A1, the surface area of the partially highly textured substrate with all its A2 irregularities or only the effective common boundary surface area A3 are the reference parameters that can be considered (figure-1). The two latter parameters may be identical if the wetting of the substrate is good, but they are always very different from the macroscopically measurable area A1.

Chemical Bonds

The chemical bond is undoubtedly the most effective. It occurs when the coating and the substrate surface react together to form a true chemical bond. Under such conditions, adhesion of the coating is usually excellent. One of the more common chemical bonds is that of the inorganic zinc coating to steel. In this case, there is an oxygen bond from the silicate matrix of the inorganic coating to an iron atom in the metal surface. Figure 2 sketches this reaction as a primary chemical bond.

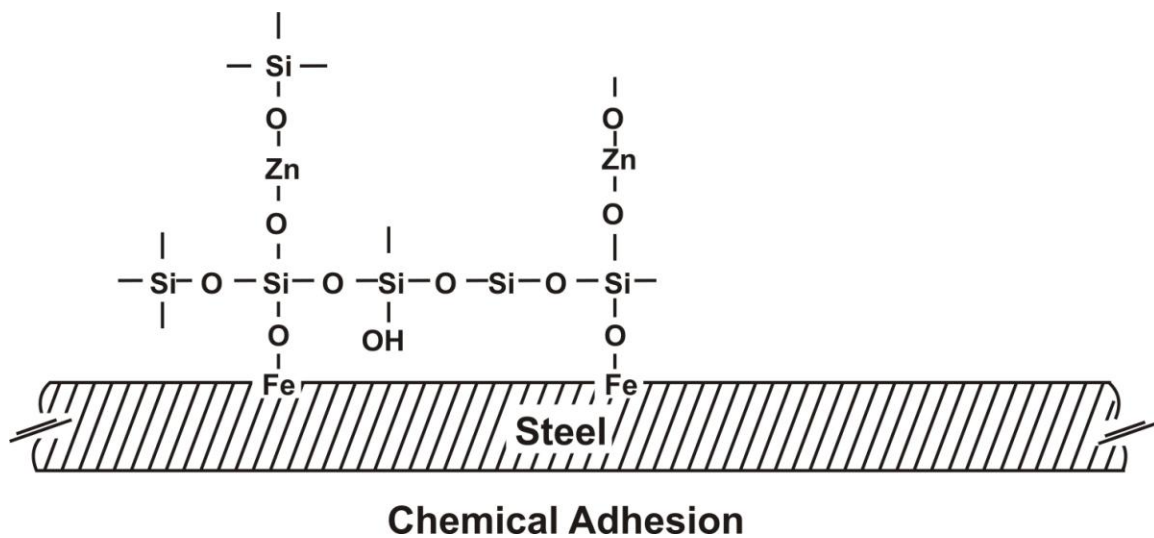


Figure2: Sketch showing chemical adhesion. In-organic zinc silicate coating chemically bonded to iron substrate

This chemical bond is also called a “primary valence bond” and it is possible that the epoxy molecules in an epoxy coating may be bonded to the metal surface through metal hydroxide groups by condensation reaction. Such a possible reaction is shown in Figure 3. Unfortunately, chemical adhesion is not the common type of bond usually found with coatings. Adhesion of most coatings is by polar or secondary valence bonding (Figure 4). This type of bond is much more common than the chemical reactions described.

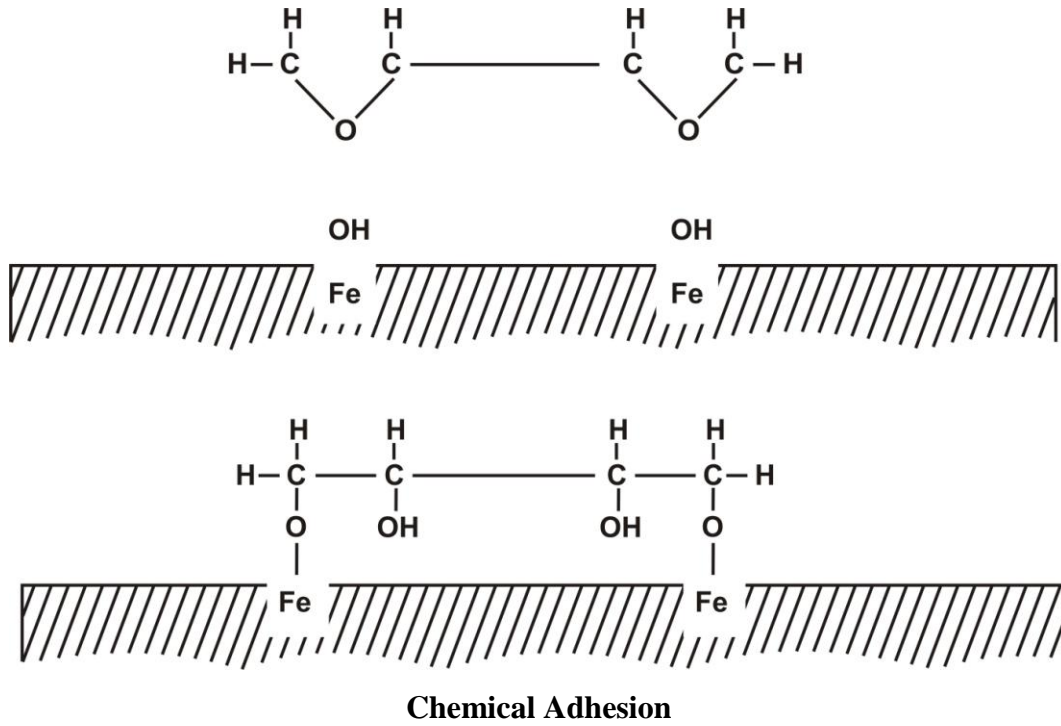


Figure 3: Sketch showing chemical adhesion. Possible reaction of an epoxy coating to steel substrate.

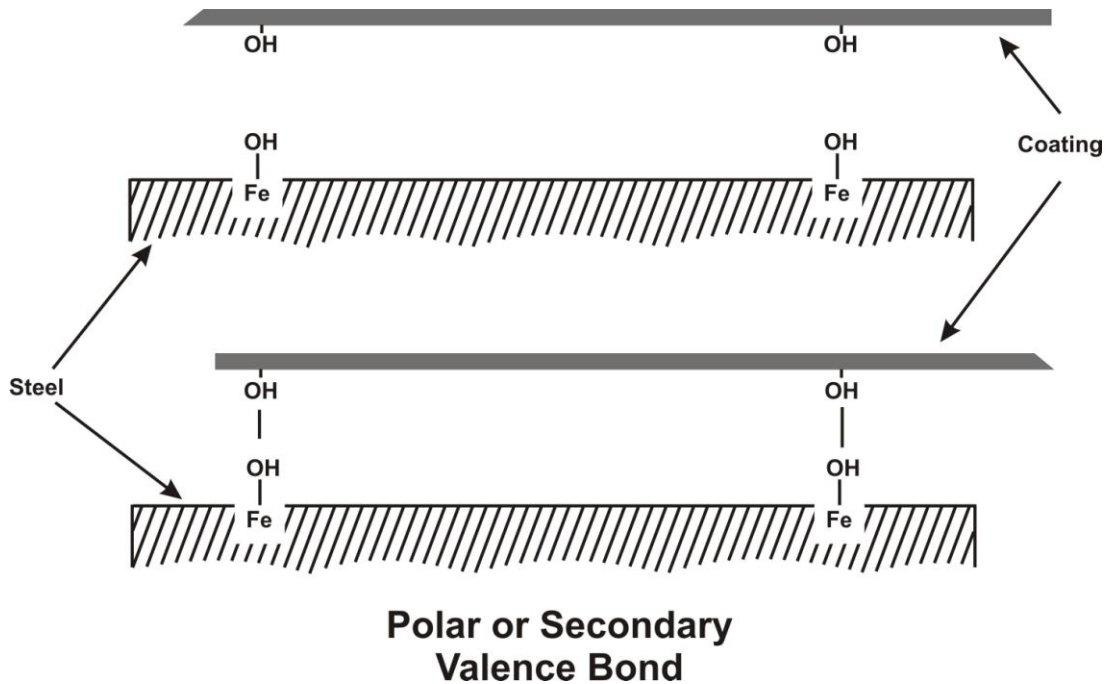


Figure 4: Sketch showing polar or secondary valence bond

Adhesion Mechanisms

For scientific examination of adhesion mechanisms it is useful to consider only the real common area, taking surface texture into account. To characterize the performance properties, however, an indicator calculated in this way is of little interest. Here the macroscopically measurable substrate surface or coated surface represents the more pragmatic reference parameter (Figure-5).

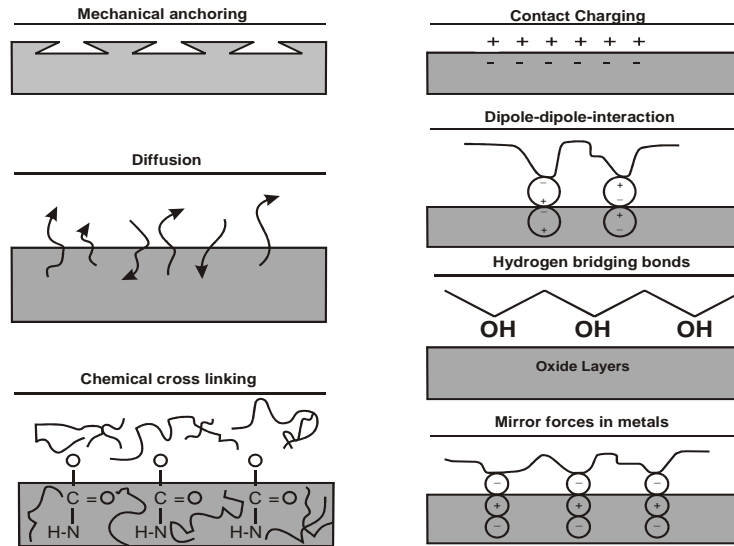
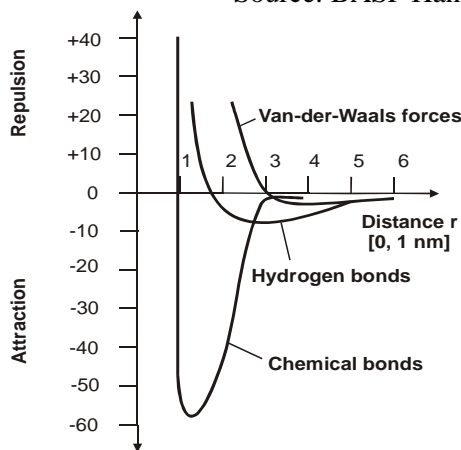


Figure 5: Physical and chemical causes for the adhesion of coatings to the substrate
 Source: BASF Hand Book on Basic of Coating Technology 2003



Type of van-der-Waals forces	Average energy	Range
Orientation forces Dipole-dipole (Keesom forces)	24 kJ / mol	$E = \frac{2 \mu^4}{3k T r^6}$
Induction forces Dipole-induced dipole (Debye forces)	15-20 kJ / mol	$E = \frac{2 \alpha \cdot \mu^2}{r^6}$
Dispersion forces (London forces)	5-10 kJ / mol	$E = \frac{3 h \nu_0 \cdot \alpha}{4 r^6}$
Hydrogen bridging bonds	40-50 kJ / mol	$E = e^{-kr}$

Figure 6: Curves and numbers of the potential energies of van-des-Waals forces as well as hydrogen bonds as causes for adhesion

Source: BASF Hand Book on Basic of Coating Technology 2003

If one endeavours to establish the causes of interactions, one encounters numerous theories in the literature, some of which are very different [Prof. Dr. Artur Goldschmidt/Dr. Hans-Joachim Streitberger, auditors, BASF Handbook on Basics of Coating Technology]. The explanations range from mechanical attachment of the coating on the cavities and fissures in the substrate (press-stud theory or mechanical anchoring) and attachments of film forming agent molecules by diffusion or contact charges and the creation of mirror forces through to interactions of polar functional groups, hydrogen bridging bonds or chemical links between the coating and the substrate. (Figure-5)

Main Causes of Adhesion

It is definite that all the mechanisms mentioned can affect bond strength and adhesion. It is also undisputed that the individual mechanisms of adhesion only make significant contributions if the prerequisites have been met. Mechanical attachment to rough metals and wood are without doubt beneficial for bond strength. Links by means of penetration when coating plastics, primers and fillers are evident as well. When coating glass and polished metals it would be wrong to chiefly hold the press stud and diffusion theories responsible for the bond. The interactions summarized by the term van-der-Waals forces have to be classified differently. Regardless of the type and morphological features of the substrate these are generally the main causes of adhesion Figure 6 shows curves and numbers of the potential energies of van-der-Waals forces as well as hydrogen bonds as causes for adhesion. Van-der-Waals forces are orientation forces (dipole-dipole) induction forces (depole/induced dipoles) and dispersion forces. Assuming a suitable chemical structure and an appropriate substrate there are also effective hydrogen bridging bonds [Prof. Dr. Artur Goldschmidt/Dr. Hans-Joachim Streitberger, auditors, BASF Handbook on Basics of Coating Technology].

Models for Interpreting Adhesion Phenomena

Because of the complexity of adhesion phenomena, there are many models for it. None of them, on its own, can fully explain adhesion. However, each model describes a part of the complex processes involved in adhesion. [Bischof, C., Possart, W., *Adhasion – Theoretische und experimentelle Grundlagen*, Akademie Verlag Berlin, 1983]

The core concept of mechanical adhesion is that the liquid coating material hardens within the hollows or pores of the surface of the substrate, where it is mechanically anchored as with dowels or press-studs. The established view nowadays is that this effect, although certainly present to a greater or lesser extent, is only of limited importance. This is being increasingly replaced by the opinion that the greater adhesion observable when the “roughness” of a substrate surface is increased can be attributed to the increase in the effective surface area. [Bischof, C., Possart, W., *Adhasion – Theoretische und experimentelle Grundlagen*, Akademie Verlag Berlin, 1983]

Adhesion is almost always due to physically and chemically induced intermolecular interactions in the interface or interface layer. The physical interactions include the formation of: [Gahde, J., *Frabe und Lack*, 1995, Vol. 101, p.689]

- Permanent dipoles (bond energy $< 20 \text{ kJ mol}^{-1}$)
- Induced dipoles (bond energy $< 2 \text{ kJ mol}^{-1}$)
- London dispersion forces (bond energy $< 40 \text{ kJ mol}^{-1}$)

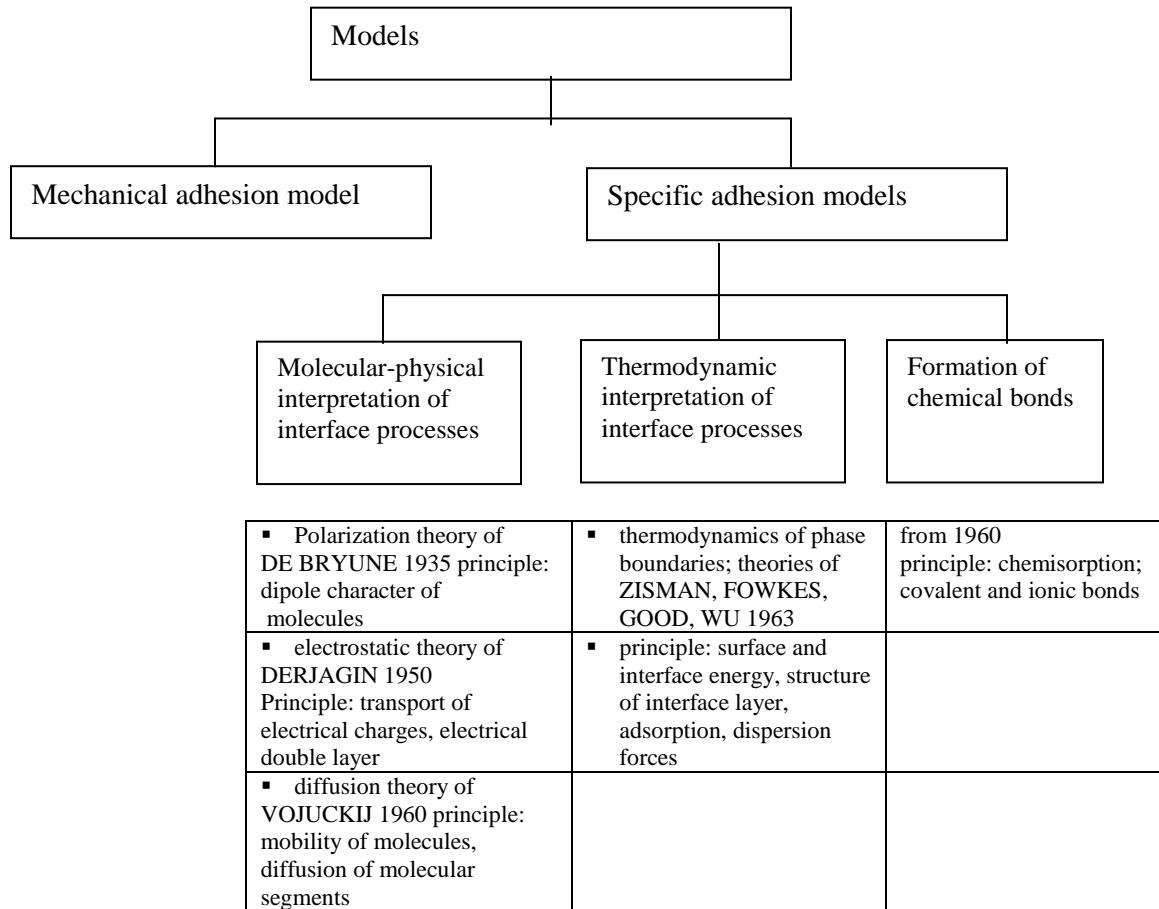


Figure 7: Models for interpreting adhesion phenomena

The bond energies for hydrogen bonds, which are also of importance, are less than 50 kJ mol^{-1} .

If bond energies are considered, then chemical bonds between the coating and the substrate must result in high adhesive strengths. A distinction is made [Gahde, J., *Frabe und Lack*, 1995, Vol. 101, p.689] between:

- covalent bonds (bond energy $60\text{-}700 \text{ kJ mol}^{-1}$), and
- ionic bonds (bond energy $600\text{-}1000 \text{ kJ mol}^{-1}$)

In addition to the formation of specific bonds at the phase boundary, an important part is also played by the wetting of a surface. W.A. Zisman therefore arrives at the general finding that a substance can only be adsorbed by a surface when the surface energy is less than (or at most equal to) the critical surface energy of the solid. [Bischof, C., Possart, W., *Adhasion – Theoretische und experimentelle Grundlagen*, Akademie Verlag Berlin, 1983]

Wetting

The wetting of a surface by a liquid is expressed by the equilibrium contact angle. The prerequisite for wetting is a contact or wetting angle of less than 90° .

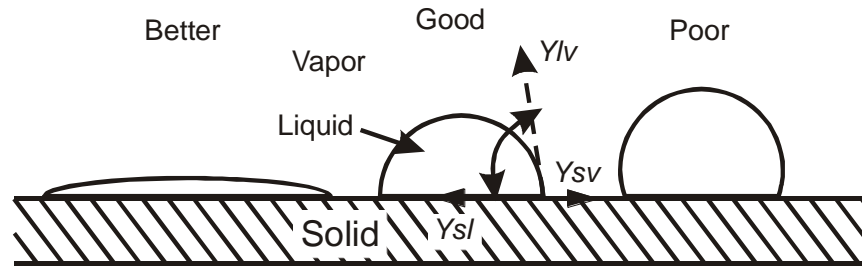


Figure 8: Schematic illustration of good and poor wetting

Surface tension is an important factor that determines the ability of a coating to wet and adhere to a substrate. The ability of a paint/coating to wet a substrate has been shown to be improved by using solvents with lower surface tensions. Wetting may be quantitatively defined by reference to a liquid drop resting in equilibrium on a solid surface (Figure 8). The smaller the contact angle, the better the wetting. When θ is greater than zero, the liquid wets the solid completely over the surface at a rate depending on a liquid viscosity and the solid surface roughness. The equilibrium contact angle for a liquid drop sitting on ideally smooth, homogeneous, flat, and nondeformable surface is related to various interfacial tensions by Young's equation:

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl}$$

Where γ_{lv} is the surface tension of the liquid in equilibrium with its own saturated vapor, γ_{sv} is the surface tension of the solid in equilibrium with the saturated vapor of the liquid, and γ_{sl} is the interfacial tension between the solid and liquid. When θ is zero and assuming γ_{sv} to be approximately equal to γ_s (which is usually a reasonable approximation), then from above Equation, it can be concluded that for spontaneous wetting to occur, the surface tension of the liquid must be greater than the surface tension of the solid. It is also possible for liquid to spread and wet a solid surface when θ is greater than zero, but this requires the application of a force to the liquid.

With fractions of nanometers the ranges of van-der-Waals forces and the hydrogen bridging bonds are extremely short. For optimum adhesion it is therefore absolutely essential to ensure good wetting by the coating material applied, thus creating ideal conditions for causing the film forming agent molecules to approach the substrate. A liquid placed on a flat, horizontal solid surface either will wet and flow out, or it will dewet to form a semispherical drop. An in-between state may also occur in which the liquid neither recedes nor advances but remains stationary. The angle that the droplet or edge of the liquid makes with the solid plane is called the contact angle. The conditions for good wetting are always fulfilled whenever the surface tension of the substrate is higher than that of the still liquid coating material. Such a requirement can easily be fulfilled when coating metals on account of the high surface tension. With various unpolar plastics such as polyethylene or polypropylene with values less than 30 mN/m it is not possible to achieve good adhesive coatings on account of the inferior wettability without polarizing surface treatments.

The surface tension values of the involved materials, (in most cases) the liquid coating and the solid substrate, are most important for substrate wetting. In general, for good substrate wetting the surface tension of the coating material (σ_p) should be lower than the surface tension of the substrate (σ_s), or they should at least be equal.

$$\sigma_p \leq \sigma_s$$

If the surface tension of the coating material is higher than of the substrate, poor wetting may occur (Figure 8). The real reason for insufficient substrate wetting is the too high surface tension of the liquid coating, however, other factors will also influence how strongly this defect shows up. Film thickness is, for example, quite important: wetting problems are easily seen in thin coating layers; a high film buildup may cover the defects. The viscosity/rheology of the coating plays, in a similar way, an important role: low-viscous systems with more Newtonian flow behaviour will show substrate wetting problems at once, whereas highly viscous systems will not show the defects at all.

The situation is further complicated by the fact that the polarity of the substrate and possible surface structures (porosity, roughness) will also influence the final appearance. Furthermore, specifically with “natural” surfaces such as wood, the surface tension will not be the same across the whole surface but will vary. Additional surface tension irregularities can be due to contamination of the surface, which will then cause wetting problems in the form of craters in some areas. Finally, there is also a time aspect. Immediately after application, the liquid paint film may have a surface tension that is lower than the surface tension of the substrate, and therefore substrate wetting is perfect. But this situation can change until the film formation process is finished, and dewetting effects may occur. The surface tension of the substrate is constant, but the surface tension of the liquid phase changes due to solvent evaporation and crosslinking reactions. If, in this process, the surface tension of the liquid exceeds that of the substrate, dewetting can occur, if the film viscosity is still low enough. Rheology, the science of flow and deformation, is critical to the understanding of coating use, application, and quality control. Viscosity, the resistance to flow, is the most important rheological characteristic of liquids and therefore of coatings and inks. Even more significant is the way in which viscosity changes during coating and printing. Newtonian fluids, like solvents, have an absolute viscosity that is unaltered by application of mechanical shear. However, virtually all coatings show a significant change in viscosity as different forces are applied. Other important forces are gravity, surface tension, and shear associated with the method of applying the material.

Viscosity Effect

Fulfillment of all the physical boundary surface requirements is not sufficient to achieve the best possible bond. In addition, viscosity has to be sufficiently low in order to give the functional groups capable of bonding an opportunity for orientation towards the substrate. Furthermore, the rise in surface tension due to evaporation of the solvents, which normally have lower surface tensions, has to be set so that the wetting behaviour is not negatively influenced by film formation. If it should happen that at still relatively low viscosity the surface tension of the coating exceeds that of the substrate, coating defects in the form of wetting disturbances can be expected because of the dewetting. Surface chemistry is the science that deals with the interface of two materials. The interface may exist between any forms of matter, including a gas phase. For

the purpose of understanding the interfacial interaction of decorative liquid materials, we need only analyze the liquid-solid interaction. Although there is a surface interaction between a liquid coating and the air surrounding it, the effect is small and may be ignored. Every liquid has a specific surface tension value.

Surface Tension

Liquids with high surface tension, such as water (73 dynes/cm), demonstrate a high intramolecular attraction and a strong tendency to bead up (form spheres). Liquids with low values have a weak tendency toward sphere formation that is easily overcome by countering forces. It is therefore useful to adjust the values of surface tension in coating in such a way that in the cured film there are similar, or rather the same, surface tensions in relation to the substrate. Material adjustments which meet these requirements can only be formulated if surface tensions of solids are known and can be measured. Table 1 gives the surface tension of selected substrates.

Table 1: Surface tensions of selected substrates

<i>Substrate</i>	σ [mN/m]
Stainless steel	1000
Phosphated steel	34
Mercury	480
Glass	74
Polypropylene	30-35
Polyamide	40-43
PVC	36
Polystyrene	32
Polycarbonate	37
Polyester	40-45

Influencing the Surface Tension of Coatings

The surface tension of the liquid coating is primarily defined by the selection of the resins and the solvents; the pigments have no influence. In practice, however, selection of these raw materials is normally not based on their surface tension but on other properties. Resins are selected e.g., their crosslinking mechanism, the required chemical resistance, and the mechanical properties of the dry film. For the solvents it is important that they can easily dissolve the resins in questions; other important properties are evaporation behaviour, flash point, and – more and more important these days – their ecological performance.

Therefore, it is very convenient to control the surface tension of the liquid paint in dependently from other raw materials by suitable additives. It was shown above the improvement of substrate wetting requires a reduction of the surface tension of the coating. Additives which can do exactly this are polysiloxanes and fluoro surfactants. Polysiloxanes modified in many ways (“silicone additives”) have found broader usage than the fluoro compounds. Silicone additives are very versatile products and they are used in coatings for more reasons than just surface tension reduction.

In some cases it is necessary to increase the surface tension of the coating instead of reducing it; this cannot be achieved with additives. In such a situation it is necessary to identify those components in the formulation, which are responsible for the low surface tension and then try to replace them with other materials with higher surface tension.

Measurement of Surface Tension

Surface tension is defined as the excess force per unit length at the surface (N/m); it is reckoned as positive if it acts in such a direction as to contract the surface. The tendency of a system to decrease its surface area is the result of the excess surface energy, because the surface atoms are subjected to different environment as compared to those in the bulk. Surface tension of liquids and polymer melts can be measured by methods such as capillary tube, Du Nouy ring, Wilhelmy plate, and pendent drop. We should focus our discussion on practical methods for coating purposes.

Whilst for determining the surface tension of liquids there are numerous methods available, direct measurement of the surface tension of solids is not possible. It can only be performed indirectly by measuring the contact angle of droplets of liquid which have been applied to the solid surface being examined. Measuring the contact angle is a simple technique for determining the relative difference between the two surface tension. A high contact angle signifies a large departure, while a small angle suggests that the two values are close, but not equal. If the surface tension of the liquid σ_L , is higher than that of the substrate σ_S a different contact angle is created in relation to it.

One can estimate liquid surface tension by applying drops of the liquid onto smooth surfaces of known values until a wetting just occurs, signifying that the two surface tensions are equal. Conversely, the surface energy of a solid may be estimated by applying drops of standard surface tension liquids until wetting is achieved. A surface tension kit can be made up from simple mixtures for testing surfaces. Table 2 given below provides formulas.

Table 2: Surface Tension Test Kit

Surface Tension	Castor Oil	Toluene	Heptane	FC48/FC77
15dynes/cm				0/100
17				100/100
19				100/0
22			100	
22.4	12.0	49.2	38.8	
24.5	55.2	25.0	19.8	
27	74.2	14.4	11.4	
30	0	100.0	0	
32.5	88.0	4.5	3.5	
35	100.0			
63	(100 glycerol)			
72.8	(100 water)			

Mixtures are in weight percent.

Source: Various sources and tests by K.B. Gilleo (Coatings Technology Handbook Editor, Arthur A. Tracton, Taylor & Francis Group, London 2006)

Low energy surfaces are difficult to wet and can give poor results for coating, painting, and printing. The standard surface tension kit may be used to estimate the surface energy of a plastic to be decorated. If the particular plastic shows a much lower than that reported (in Table 3) as under contamination is suspected. Mold release agents, unless specially made compatible for decorating materials, can greatly lower surface energy of a plastic part, making it uncoatable.

Table 3: Surface Tension of Polymers

Polymer	Surface Tension (dynes/cm)
Polyperfluoropropylene	16
Polytetrafluoroethylene (Teflon)	18.5
Polydimethylsiloxane	24
Polyethylene	31
Polystyrene	34
Polymethylmethacrylate (acrylic)	39
Polyvinyl chloride (PVC)	40
Polyethylene terephthalate (polyester)	43
Polyhexamethylene adipate (nylon)	46

Source: Bikales, N.M., Adhesion and Bonding, Wiley-Interscience, New York, 1971.

Because of the importance of the surface tension for paint application in general and specifically for substrate wetting, convenient methods to measure the surface tension of liquids and of solid surfaces should be available. [Osterhold, M., *Farbe+Lack* 99 (1993), no. 6, pp. 505–511]

The static surface tension of liquids can easily be determined with the ring detachment method of Nouy. For higher-speed application processes (printing, roller coating) the dynamic surface tension needs to be measured, for example, with the *bubble method*. [Mysels, K.J., *Langmuir J.* 2 (1966), p. 428]. For both methods and other similar methods, suitable instruments are commercially available.

The determination of the (critical) surface tension of solid surfaces is possible with the contact-angle method. It is quite time-consuming, but automatic instruments are available nowadays, which have made this method routine. [Osterhold, M., Armbruster, K., Breucker, M., *Farbe+Lack* 96 (1990), no. 7, p.503]. A procedure is derived from the contact-angle method, which allows a qualitative estimation of the surface tension of the substrate by the application of different test liquids. [Norm DIN 53 364]. For systematic and scientific investigations it is absolutely necessary to measure the exact surface tension, but for many practical purposes, however, a quick application test is often faster and – due to the fairly complex interrelations – often gives more reliable results.

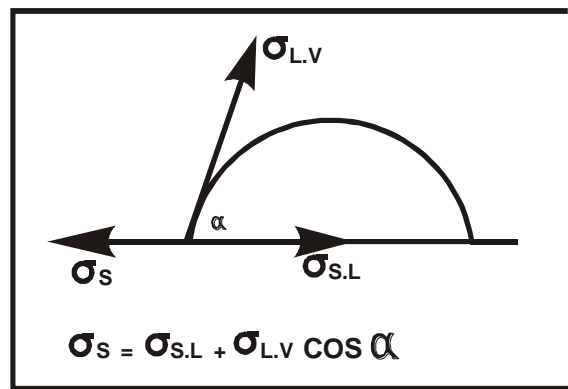


Figure 9: Definition of the contact angle according to DIN EN 828

If the contact angle α approaches 0, the boundary surface tension $\sigma_{s,l} = 0$ and hence $\sigma_{L,v} = \sigma_s$. Since small contact angles α cannot be determined with sufficient accuracy, one uses the Zisman method whereby several liquids a, b and c with different but also higher surface tensions than the substrate are measured with regard to the resultant contact angle and each calculated cosine is plotted in relation to the surface tension of the liquids. Then the curve has to be extrapolated to the values $\cos \alpha = 1$. To perform the measurement optical benches are available which allow precise recording of the wetting angles.

From experience in dealing with the determined critical surface tensions σ_c it is known that in many cases deviations from the surface tension of the substrate can occur. However, conversion of the critical surface tension σ_c to the surface tension of the substrate σ_s becomes possible by means of adjustment using Good's interaction parameter Φ .

$$\sigma_c = \Phi^2 \sigma_s$$

The interaction parameter says something about the spatial fulfillment of the interacting groups and hence about the quantity of the maximum number of bonding sites. Its calculation is difficult for interactions of polymers. It is therefore usually determined by experiment. The Good factor assumes the value 1 if all the polar groups of coating material and substrate can interact. However, it can also drop to values of around 0.3.

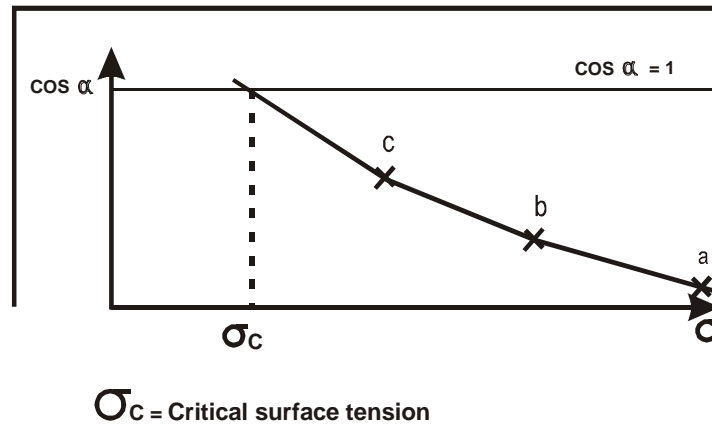


Figure 10: Zisman diagram to determine the critical surface tension

With regard to adhesion, experience teaches that even if the surface tensions of coating and substrate are optimally adapted the expected optimal values are not always found. Better conformities between experiment and theory are obtained if the surface tension does not enter the calculation as a total value of all the Van-der-Waals forces and hydrogen bridging bond forces. After splitting the surface tension into polar and dispersed components σ^d and σ^p

$$\sigma = \sigma^d + \sigma^p$$

Better forecasts can be made regarding the maximum adhesion possible if the polar components of substrate and coating assume the same value. The best adhesion possible is therefore achieved if.

$$\frac{\sigma_L^p}{\sigma_s^p} \longrightarrow 1$$

One must bear in mind that best possible adhesion of the system says nothing about the absolute level of the adhesive forces. These are performed owing to the polarity of the interacting surfaces and are merely optimized by adaptation of the surface tensions. The importance of the ratio between polar components of surface tensions in the substrate and the coating for adhesion has been verified using various plastics. Taking acrylic resins and alkyd resins as examples there are systematic interrelationships as shown in figure-11.

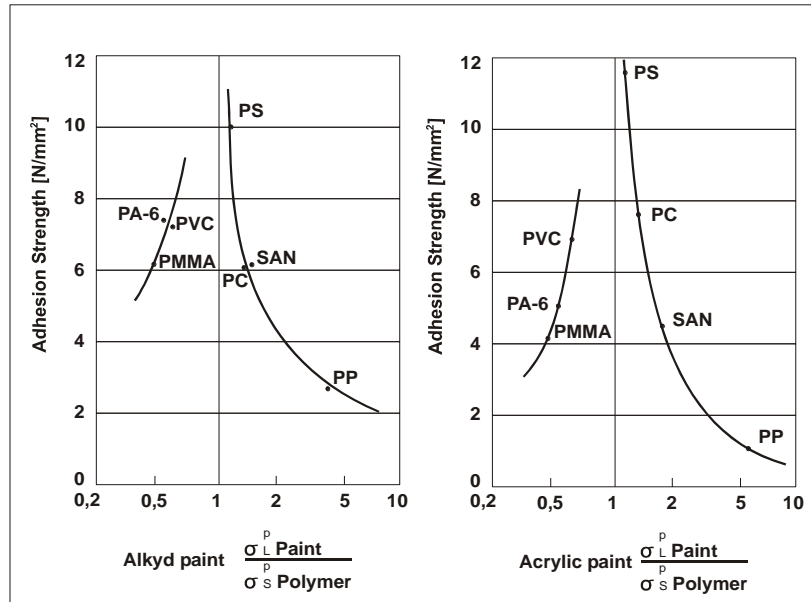


Figure 11: Adhesion in N/mm^2 as a function of the share of polar adhesion forces of alkyd and acrylic resins on different substrates

To determine the polar and dispersed components several teams have produced practicable approaches. According to Owens the boundary surface tension is represented as the geometric mean of the individual constituents. If $\Phi = 1$, it follows that:

$$\sigma_{SL} = \sigma_S + \sigma_L - 2 \cdot (\sigma_s^d \cdot \sigma_L^d)^{1/2} - 2 \cdot (\sigma_s^p \cdot \sigma_L^p)^{1/2}$$

After taking Young's equation into consideration and conducting wetting tests with liquids of known dispersed components σ_L^d for measuring contact angles, after further mathematical processing it becomes possible to calculate dispersed and polar components of the surface tension of the substrate σ_s^d and σ_s^p .

$$\frac{\sigma_L \cdot (1 + \cos \sigma)}{2 \cdot (\sigma_L^d)^{1/2}} = (\sigma_s^p)^{1/2} \left[\frac{\sigma_L - \sigma_L^d}{\sigma_L^d} \right]^{1/2} + (\sigma_s^d)^{1/2}$$

$$(Y = a \cdot x + b)$$

Adhesion Promoters

The market offers a large number of different chemical varieties of adhesion promoters. The range of chemicals available includes silanes, silicones, titanium compounds, zirconates, amides, imines, phosphates, and specially modified polymers. Furthermore, there are binders, plasticizers, and additives (e.g., wetting agents) which, though intended for other purposes, have the secondary effect of providing good adhesive strength. In terms of adhesive strength, it is in many

cases the overall formulation of a paint or other coating material which is decisive. For instance, it is known that viscosity-reducing additives such as solvents, for example, improve the adhesive strength by improved mechanical anchoring of the film. In this context, the partial dissolution and/or swelling of the substrate (plastic substrates, under-coat) may also contribute to an improvement in adhesion. [Kittel, H., *Lehrbuch der Lacke und Beschichtungen*, Bd, III, pp. 379 – 181]

It is generally assumed that the mode of action of adhesion promoters is based partly on the formation of chemical bonds with the substrate surface and the binder, and partly on an increase in the wet ability of the surface or on the formation of an interlayer between substrate and binder. [Nicholson, J., *Polym. Paint Colour J.*, Vol. 181, no. 2483, 1991, p. 264]

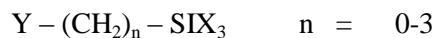
Silanes, titanates, and zirconates have similar activity, which is tied to the similarity of their substituents. They generally include three identical or different substituents in the form of alkoxy groups, and a linkage to the substrate is formed by way of these groups. The fourth substituent is an organic radical which has the capacity to interact with the binder.

Some adhesion promoters can be used as additives to the formulation in question, or can be employed in the form of a surface pretreatment. The advantage of the latter procedure is that the adhesion promoter is located directly in the boundary layer and so is best able to exert its effect. The additional working step, however, is a disadvantage.

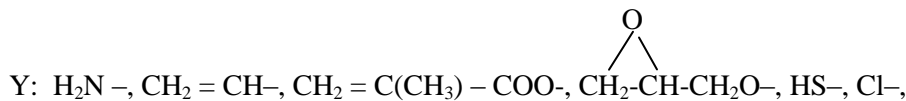
Organofunctional Silanes

Structure and Difference from Alkylsilanes

Organofunctional silanes have the general structure: [Huls AG Marl, „DYNASILAN – Anwendung von organofunktionellen Silanen“, No. 15.01.002/07.94, 1994]



With the organofunctional group

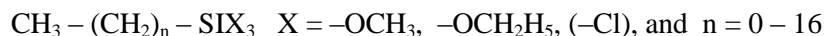


and the silicon functional group

X: usually $-OCH_3$, $-OC_2H_5$ (generally alkoxy groups, sometimes also $-OCOCH_3$, $-Cl$)

Difference from alkylsilanes:

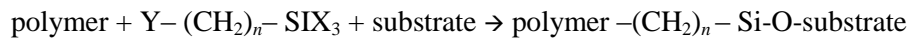
In addition to the functional organosilanes there are also so-called nonfunctional organo- or alkylsilanes. These are silanes of the general structure:



However, the alkyl group is unable to form a bond to the polymer, and so alkylsilanes are inactive as adhesion promoters. They are used merely to make inorganic materials water-repellent and organophilic.

Mode of Action

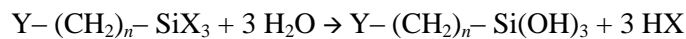
In very general terms, their mode of action is explained by the alkoxy group or silicon functional groups (X) interacting with the substrate, while the organofunctional group (Y) establishes the bond to the polymer: [Huls AG Marl, DYNASILAN – Anwendung von organofunktionellen Silanen⁷, No. 15.01.002/07.94, 1994]



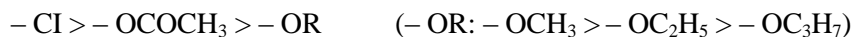
The mode of action of organofunctional silences consists of a number of possible substeps:

1. Reaction of the Silicon Functional Group

By reaction with the surface moisture of the inorganic substrate (glass, metal, fillers, pigments) or when an aqueous solution is prepared, the alkoxy groups hydrolyse to form reactive silanols:



The rate of Hydrolysis decreases according to the following series:



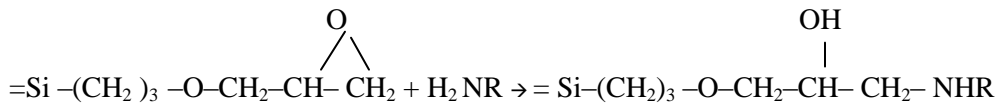
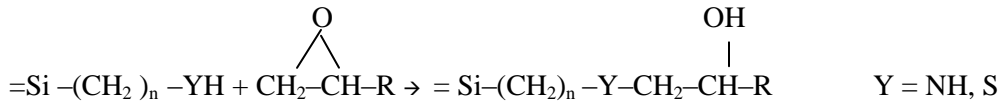
The process is accelerated by acid or base catalysis and by catalysis with certain organometallic compounds, such as tin compounds (dibutyltin dilaurate). Except for the aminosilanols, the resultant silanols are unstable. Condensation with OH groups of the inorganic surface produces a firm bond to the substrate.

Also of great importance for a good bond in this context is the formation of hydrogen bonds. Different inorganic materials possess different surface activity with respect to silanes. Glass, quartz/stone and mica are regarded as good. Magnesium oxide, kaolin, talc, silicatic fillers, iron oxide, titanium dioxide, and inorganic pigments possess moderate activity, while carbon black, chalk, barium sulphate, and calcium sulphate (gypsum) are of poor activity. Metals with good affinity include iron, aluminium, zinc, and copper. Good bonding can also be established with mineral building materials such as natural stone, concrete, lime sandstone, bricks, and roof tiles. When using silanes as adhesion promoters it must be remembered that, depending on the silane concentration and the pH, water-insoluble polysiloxanes may be formed and that the resultant silanols and the coating binder may also react.

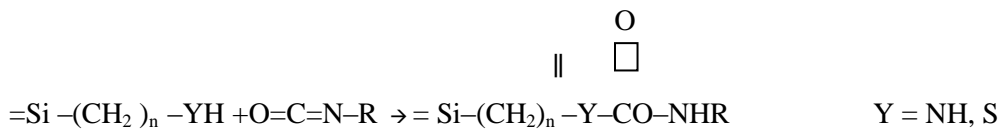
2. Reaction of the organofunctional group

The organofunctional radical, on the other hand, forms a connection with the organic polymer. Examples of the possibilities are:

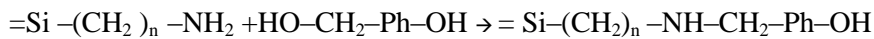
- free epoxides:



- for polyurethanes:



- for phenolic resins:



Lists silanes which may be suitable as adhesion promoters for the various types of binder. [Kittel, H., *Lehrbuch der Lacke und Beschichtungen*, Bd, III, pp. 379 – 181]

Table 4: Selection of silane adhesion promoters

Organofunctional group of the silane adhesion promoter	Recommended for the following polymers
Amino	Epoxy, phenol, melamine, furan, urea, PVC, urethane, polyvinylbutyral, polyimide, polychloroprene, nitrile rubber, etc.
Vinyl, methacryl	Unsaturated polyesters, EPDM, polyolefins, urethane, alkyd
Epoxy	Epoxy, phenol, epichlorohydrin, PVC, polyester, urethane, polysulphide
Mercapto	All elastomers, urethane, polysulphide, PVC
Urea	Phenol, urea or melamine resins, epoxy resins
Chloro	Epoxy resins, polyurethane, thermoplastics

Properties and Use

Organofunctional silanes are soluble in the usual organic solvents, are flammable, are sensitive to hydrolysis, and have favourable toxicological properties. They are highly effective adhesion promoters when the task at hand is to improve the adhesion of inorganic materials (glass, minerals, metal) to organic partners (thermosets, thermoplastics, elastomers). [Huls AG Marl, DYNASILAN – Anwendung von organofunktionellen Silanen', No. 15.01.002/07.94, 1994]

The use of organofunctional silanes as adhesion promoters was patented in the mid – 1940s for glass – fibre – reinforced plastics, its first major application. Vinylsilane – and methacrylsilane-treated glass fibers are state of the art for polyester laminates. The use of aminosilanes and epoxysilanes has become established for phenolic and epoxy resin laminates.

For use in coatings, varnishes, and paints their particular advantages are:


- the improvement in adhesion, especially after exposure to water, when coatings often separate automatically from the substrate
- the improvement in chemical resistance
- the hydrophobization
- the improved corrosion protection

The adhesion of coatings and sealants to organic substrates is, in some instances, improved by silanes, although there is no satisfactory explanation for such activity. In these applications the silane adhesion promoter is also selected according to the possible reaction of the organofunction group with the binder used.

The silane adhesion promoter can be employed either as an additive or in the form of a primer (silane content 1–2%) for pretreating the substrate. When introduced as an additive, larger quantities are required than for the primer form. The competitive effect of mineral components present in the mixture may have to be born in mind. Added silane is absorbed by inorganic compounds and is then no longer available to effect external adhesion. [Huls AG Dusseldorf, „Silicium ist unser Element ‘, no. 16.01.103/4.97/1500/P.AD., 1997]

The primer is produced by preparing a dilute silane solution (silane content 1–2%) and then applying it thinly. Suitable solvents are organic ones such as alcohols, ketones, or aromatics; small amounts of water may also be present. Aqueous solutions can also be employed; the silane is hydrolysed when water is present in concentrations of 0.2–2%, when acid has been added (usually acetic acid), and the pH is between 3 and 4. Depending on the type of silane, the result after 5 to 60 minutes is a clear, aqueous solution which, however, remains stable for a limited period only, owing to the formation of oligomeric siloxanes. For the amino-functional silanes, no acid needs to be added to prepare the aqueous solution. In comparison to the other types, moreover, their aqueous solutions are stable for a substantially longer period. Aqueous silane solutions developed their full activity about 30 minutes after preparation. Table. 5 shows examples of important organofunctional silanes. Figure 12 shows the mechanism of silane coupling agents on an inorganic surface.

Table 5: Examples of silane – based adhesion promoters

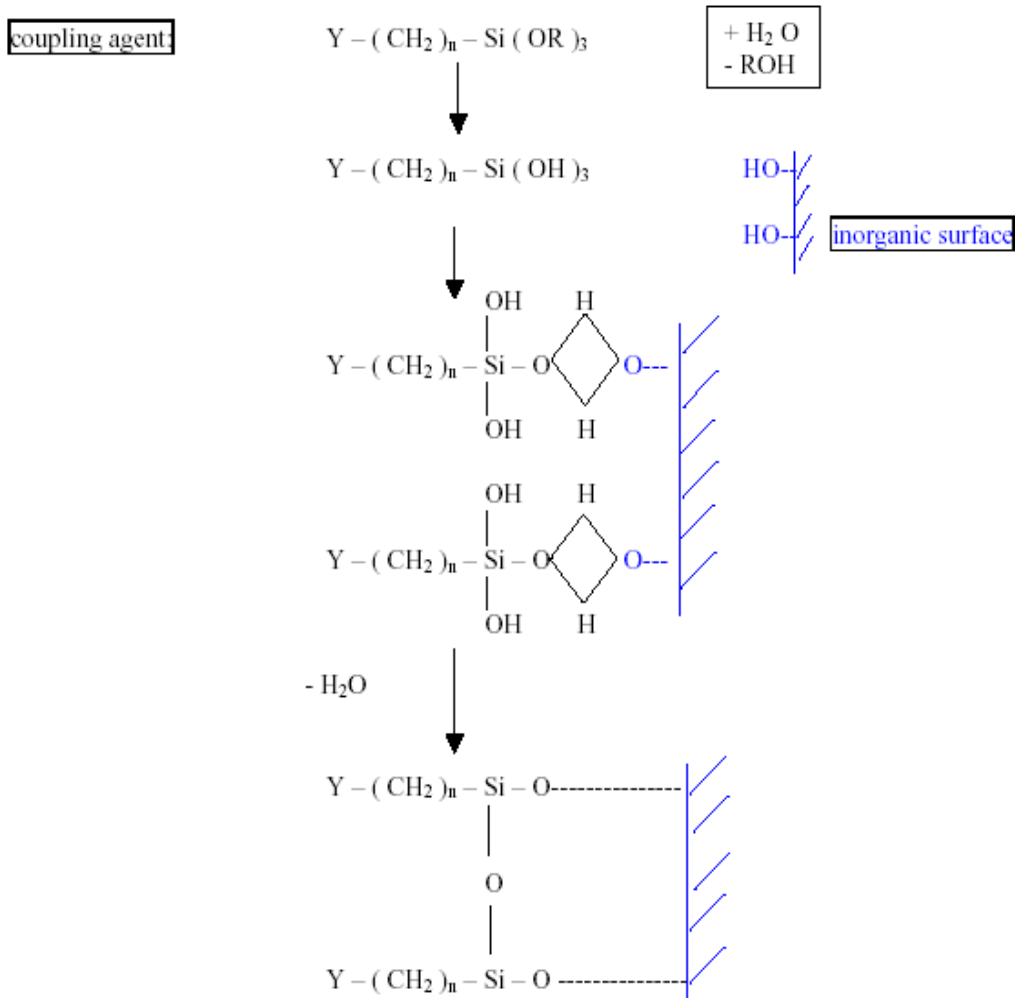
Name	Structure
(3-Aminopropyl) trimethoxysilane	$\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$
(3-Aminopropyl) triethoxysilane	$\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$
(3-Aminopropyl) diethoxymethylsilane	$\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{CH}_3)(\text{OC}_2\text{H}_5)_2$
(N-Aminoethyl-3-aminopropyl) trimethoxysilane	$\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$
(N-Aminoethyl-3-aminopropyl)dimethoxymethylsilane	$\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{CH}_3)(\text{OCH}_3)_2$
Triethoxy –(3-ureidopropyl)silane	$\text{H}_2\text{NCONH}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$
Triethoxy –(3-methacryloxypropyl)silane	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$
	
(3-Glycidyloxypropyl)trimethoxysilane	$\text{CH}_2-\text{CHCH}_2\text{O}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$
(3-Mercaptopropyl)trimethoxysilane	$\text{HS}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$
(3-Chloropropyl)trimethoxysilane	$\text{Cl}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$
Trimethoxyvinylsilane	$(\text{CH}_2)=\text{CHSi}(\text{OCH}_3)_3$

Examples of commercial products:

Dynasilan	(Degussa-Huls AG)
Prosil	(PCR Incorporated)
Silquest	(OSi Specialties)
Additive grades	(Dow Corning)
GF grades	(Wacker-Chemie)

Coatings Plus-CP as a Means of Corrosion Control

At the time of establishment of SSGC and SNGPL (early 1950,s) there were a few Governmental and International regulations to contend with nationally and internationally. In the United States of America today the Department of Transportation – Office of Pipeline Safety (DOT/OPS), Occupational Safety and Health Administration (OSHA), and the Department of Environmental Resources (DER) are among the many regulatory agencies influencing or controlling the pipeline industry. This is also applicable Internationally and Pakistan is no exception.



Y can be an amino-, epoxy-, etc. group that is chemically incorporated into the adhesive.

Figure 12: Silane Coupling Mechanism on an Inorganic Surface

These regulations, alongwith the development, introduction, and acceptance of new pipeline coatings, have made major changes and will continue to affect the selection and use of pipeline coatings in the future.

Economics, while still a factor, is being replaced by safety and environmental concerns to obtain the best available pipe-coating systems supplemented by CP system. The coatings by themselves may not be the one perfect answer to corrosion control, they are extremely effective when properly used. A properly selected and applied coating will provide all the protection necessary on most of the pipeline surface to which it is applied. On a typical well-coated pipeline this

should be better than 99% and, along with the CP (Cathodic Protection) should give total protection. Successful control of external corrosion of pipeline is nearly totally dependent on effective coating plus cathodic protection system properly designed, installed and monitored. NACE standard RPO169-96 Section 5: Coatings, is a useful guide to pipe coatings. The overall economics of the coating plus CP concept are adversely affected by poorly applied coating. Unfortunately perfect coatings do not exist presently.

CP is used to supplement the coating. When used with an unstable coating, a CP system that is fully adequate during the early life of a pipeline may no longer provide full protection as the coating deteriorates (as indicated by a reduction in the effective electrical resistance of the coating), which will require additional current. This means that continued expenditures will be necessary for additional CP installations. The overall economics of the coating-plus-CP concept are adversely affected by poor coating performance.

Water in the electrolyte (soil) chemically dissociates into hydrogen and hydroxyl ions. The hydrogen ions have a positive electrical charge and are attracted to exposed pipe surfaces, which have a negative electrical charge produced by the CP system. The hydrogen ions collect on the exposed surfaces of the pipe and form a protective barrier between the pipe and the surrounding electrolyte. Formation of this protective barrier is referred to as “cathodic polarization,” and the resulting barrier is referred to as the “polarization film.” In fact, the polarization film functions as a protective coating and prevents the occurrence of corrosion.

Disbondment of Coatings of a Gas/Oil Transmission Pipeline

The problem is of immense importance for the national gas/oil transmission pipeline industry as the failure of first line of defense i.e. coatings which is the cause of ultimate corrosion failures.

All Coatings Fail Eventually

All coating systems are liable to fail eventually. The important issue is the nature of the eventual failure itself. The time to failure is dependent on the coating system and the environment, this can be a major problem for the industry and their concerns, what happens after the disbondment of the coating. Recent articles in Material Performance (NACE) provide information regarding the performance difference B/W various coatings (1985 to 2002).

Cathodic Shielding

Cathodic shielding occurs when a coating system fails in such a way as to allow water to reach the steel pipe surface and prevents cathodic protection (CP) from reaching the failed area. It has been established, in case of coating systems that are backed with thermoplastics such as polyethylene (PE) and polypropylene (PP), have been known to create shielding of CP, when they fail.

Adhesion Failure

It is the adhesion that gives way in such coating failures leaving the coating intact as a pocket over the steel pipe. The gas/oil transmission companies have such a similar behaviour of failure (disbondment) for 3L/PE coatings and other coatings water ultimately will find a way to migrate to a disbondment areas through holidays existing in these coatings. (Figure 13)

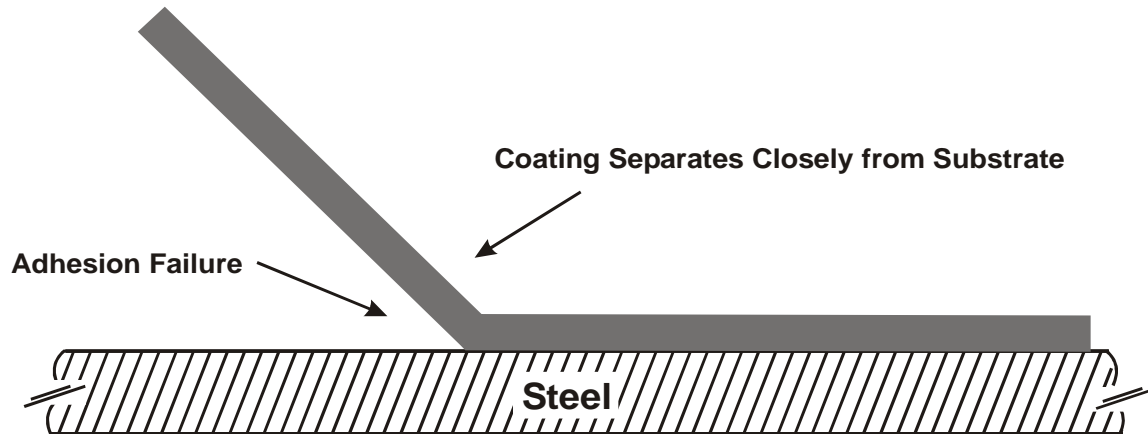


Figure: 13 Adhesion failure of a coating

Water Film Formation Causes CP Shielding

The fine water film B/W the disbonded coating and the steel pipe substrate has greater electrical resistance and the CP current has great difficulty in penetrating the failure pockets. It cannot reach these areas unless, there is a low resistance path (continuous electrolyte). The ultimate result is the failure of cathodic protection system as a whole.

CP Shielding Big Concern-Not Easy to Detect CP-S

A big concern regarding CP shielding is the inability to detect the problem using routine commercially available CP monitoring techniques. The CP potential measurements made by the gas transmission staff will not indicate this effect of CP shielding.

Corrosion Damage by CP Shielding

Thus CP shielding means that the pipe line is shielded from CP and from the ability to measure actual pipeline potential. The problem is not detectable until corrosion damage is discovered by the use of smart pigging and excavation examinations.

Adhered Coating CP-Shielding No Problem

All coatings shield CP when they are adhered to the steel pipe line and function properly. That is why the industry uses the coating and CP together.

Gas/Oil Companies in Trouble

The gas/oil transmission pipeline companies are facing the problem of disbondment of coatings which is liable to shield CP. The solution to the problem of adhesive failure of the coating is the

development of data base system in the country as an integrated efforts if coating supplier, user and the applicators.

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