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## Film Defects

Obvious defects can result from incomplete coverage during application of a coating, resulting in thin spots or holes, often called *skips* or *holidays*. Many other types of defects and imperfections can develop in a film during or after application. In this chapter we deal with the most important defects and to the extent possible, discuss the causes of the defects and approaches for eliminating or minimizing their occurrence. Unfortunately, the nomenclature for many defects is not uniform. Reference [1] provides definitions for coating terms, including those for film defects.

### 24.1. SURFACE TENSION

Many defects are related to *surface tension* phenomena. Surface tension occurs because the forces at an interface of a liquid differ from those within the liquid, due to the unsymmetrical force distributions on the surface molecules. The surface molecules possess higher free energy, equivalent to the energy per unit area required to remove the surface layer of molecules. The dimensions of surface tension are force exerted in the surface perpendicular to a line; SI units are newtons per meter or millinewtons per meter ( $\text{mN m}^{-1}$ ). [Older units, still commonly used, are dynes per centimeter ( $1 \text{ mN m}^{-1} = 1 \text{ dyne cm}^{-1}$ ).] Similar surface orientation effects are present in solids, which have surface free energies expressed in units of free energy per unit area, millijoules per square meter ( $\text{mJ m}^{-2}$ ) that are numerically and dimensionally equal to  $\text{mN m}^{-1}$ . Frequently, people speak of the surface tension of the solids; although not formally correct, errors do not result, because the values are identical. Reference [2] is an excellent discussion of surface and interfacial properties, including data on many polymers.

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# **CONCISE**

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# **ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING**

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**CAM.** See PROCESSING, COMPUTER CONTROL.

**CAOUTCHOUC.** See RUBBER, NATURAL.

**CAPROLACTAM POLYMERS.** See POLYAMIDES.

**CARBAMATES, POLYMERIC.** See POLYURETHANES.

**CARBANIONIC POLYMERIZATION.** See ANIONIC POLYMERIZATION.

**CARBOCATIONIC POLYMERIZATION.** See CATIONIC POLYMERIZATION.

**CARBODIIMIDES, POLY-.** See ISOCYANATE-DERIVED POLYMERS.

**CARBOHYDRATES.** See POLYSACCHARIDES.

## CARBON

Carbon is a nonmetallic element occurring in the native state and is also obtained industrially in varying states of order and purity. Unlike the other two forms of elemental carbon, diamond and graphite, carbon black is not found in the native state; it has been synthetically produced for several millennia. Carbon black is the generic name for the family of materials consisting essentially of elemental carbon in the form of spherical colloidal particles and coalesced particle aggregates of colloidal size obtained by the thermal decomposition of hydrocarbons. Carbon black is the only form of carbon that is used extensively in polymers.

### CARBON BLACK

#### Properties

**Morphology and Microstructure.** With the exception of coarse thermal carbon, carbon blacks rarely exist as individual spheroidal particles. Instead, particles exist in aggregates forming a coherent unit. The carbon black is also referred to as a domain or nodule, consisting of imperfect graphitic layer planes.

**Surface Area.** Surface area is inversely related to particle size for smooth-surface carbon blacks and affects the performance of carbon-black-filled polymers. Surface area is generally determined by nitrogen adsorption using the standard test method.

**Surface Activity and Chemistry.** The surface activity of carbon black is a function of the degree of heterogeneity of the surface and the nature and number of the functional groups on the edges of the graphitic layer planes. The carbon content ranges from ca 80 to +99 wt% depending on the manufacturing process and the aftertreatment.

The interaction between carbon black and polymers is a physical or chemical in nature, and probably involves several mechanisms that are frequently involved. The microstructure of carbon black is an important factor in the interaction with most elastomers.

#### Manufacture

Carbon black has been produced by five processes: furnace, impingement, acetylene, thermal, and furnace. The furnace process is the dominant worldwide process.

#### Economic Aspects

Worldwide carbon-black capacity was estimated at 1.02 million t in 1983; approximately 98% was made by the furnace process. The U.S. furnace-carbon capacity represents about 10% of the world capacity.

#### Applications

In 1982, approximately  $1.02 \times 10^6$  t of carbon black was consumed in the United States, 63% of which was used in products for transportation (mainly tires and truck tires) and 30% in industrial rubber products (belting, hoses, and other products) and 7% in inks, coatings, plastics, and other products. About 93% of carbon-black products are used in elastomers, mainly to improve strength and durability. Carbon black is the principal pigment in ink, and excels in preventing damage to polymers from uv radiation.

Table 1. Properties of Carbon Blacks

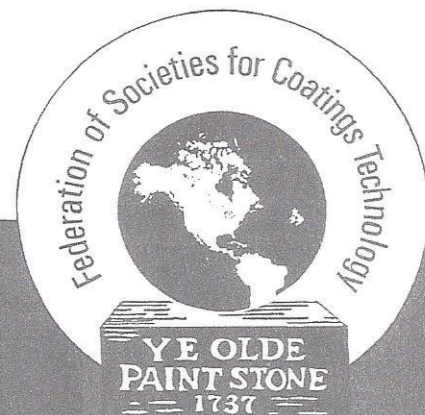
| Process grade         | 1983 U.S. production, 10 <sup>3</sup> t | Particle diameter <i>d</i> , nm | Porosity, % of total surface |
|-----------------------|---|---------------------------------|------------------------------|
| furnace               |   |                                 |                              |
| rubber                | 954                                     | 17-110                          | <12                          |
| ink                   | 38                                      | 18-70                           | <8                           |
| paint                 | 6.8                                     | 10-70                           | <45                          |
| plastics              |   |                                 |                              |
| color                 | 29                                      | 18-70                           | <36                          |
| conductive            | 6.8                                     | 15-30                           | >35 <95                      |
| lampblack replacement | 1.4                                     | 69-90                           | 0                            |
| other                 | 13                                      | 15-70                           | <75                          |
| thermal               | 18                                      | 150-500                         | 0                            |
| lampblack             | 1.6                                     | 100-130                         | 0                            |
| acetylene             | 6.8                                     | 35-50                           | 0                            |



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# Adhesion Aspects of Polymeric Coatings

by  
Jamil A. Baghdachi



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# Adhesion Aspects of Polymeric Coatings

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liquid state, mobility of the coating phase is also of great help. Wetting, therefore, may be viewed as intimate contact between a coating and a substrate. Schematic representation of complete and incomplete wetting is shown in Figure 12. In addition to initial wetting, in order for adhesion to remain between substrate and the coating it is important that intimate wetting and bonds remain intact after the coating has solidified.

Coatings solidify as a result of:

- (a) cooling to below the melting temperature (glass transition temperature,  $T_g$ ), or
- (b) a chemical crosslinking reaction, or
- (c) evaporation of solvents and diluents.

An example of a type (a) coating is the thermoplastic powder coating or the melt extrusion lamination of polymers to metals and to other polymers. Type (b) coatings include one- and two-part crosslinkable epoxy, polyurethane, or melamine cured acrylic systems. Printing inks and lacquer paints are examples of type (c) coatings where the pigment binders may also have some crosslinking ability on drying. The wetting of substrates by coatings is, therefore, central to bond formation and, hence, to adhesion.

1. WETTABILITY AND SURFACE ENERGETICS: Wetting is a necessary criteria for adhesion. Mechanisms of adhesion previously discussed are only operational if, and only if, effective wetting is present between the coating and the substrates. The wetting of a surface can be described in thermodynamic terms. The surface tension of the coating in its liquid state and the surface energetics of both the substrate and the solid coating are important parameters which can influence the strength of the interfacial bond and adhesion development.

The molecules or atoms at the surface of a homogeneous solid or liquid are in a different environment from those in the interior. In the interior, each molecule is surrounded by similar ones, and the average distance between them is governed by the trade-off between attractive forces pulling the molecules together and strong repulsive forces that prevent different molecules from occupying the same space. Molecules at the surface, however, are no longer attracted equally in all directions. They interact somewhat with the substance, normally air, lying above the surface, while they are attracted inwards by the molecules lying below the surface. The attraction of the underlying molecules tends to pull them inwards, minimizing the number of molecules at the surface, and hence, the surface area. This attraction gives rise to the *surface tension* of liquids and accounts for a liquid droplet behaving as though it were covered by an elastic skin. In addition, the surface molecules are generally at a greater intermolecular spacing than in the bulk and are therefore in a state of higher energy. Work must be supplied to move molecules from the interior to the surface. The increase in the Helmholtz free energy accompanying a unit increase in the surface area of a liquid is, by definition, the surface tension.

2. INTERFACIAL THERMODYNAMICS: The degree to which a liquid coating wets a solid surface is measured by the contact angle ( $\theta$ ) as illustrated in Figure 13. When  $\theta = 0$ , the liquid spreads freely over the surface and is said to completely wet it. Complete wetting occurs when the molecular attraction between the liquid and solid molecules is greater than that between similar liquid molecules.<sup>21</sup> The surface tensions are related to the contact angle by an expression from equilibrium consideration.<sup>22</sup>

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

Table 2—Surface Tensions of Typical Solvents Used in Coatings

| Solvent                      | Surface Tension dynes/cm |
|------------------------------|--------------------------|
| Water .....                  | 72.7                     |
| Ethylene glycol .....        | 48.4                     |
| Propylene glycol .....       | 36.0                     |
| o-Xylene .....               | 30.0                     |
| Toluene .....                | 28.4                     |
| n-Butyl acetate .....        | 25.2                     |
| n-Butanol .....              | 24.6                     |
| Mineral spirits .....        | 24.0                     |
| Methyl isobutyl ketone ..... | 23.6                     |
| Methanol .....               | 23.6                     |
| VM&P naphtha .....           | 22.0                     |
| n-Octane .....               | 21.8                     |
| Lactol spirits .....         | 19.9                     |
| n-Hexane .....               | 18.4                     |

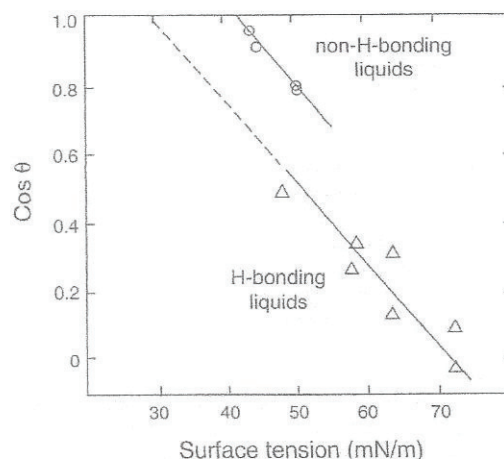


Figure 16—Comparison of Zisman plots of H-bonding and non-H-bonding liquids on polystyrene. (Data taken from reference 25)

Table 3—Surface Tensions of Typical Polymers and Additives Used in Coatings

| Polymer                                | Surface Tension dynes/cm |
|--|--------------------------|
| Melamine resin .....                   | 57.6                     |
| Polyvinyl butyral .....                | 53.6                     |
| Benzoguanamine resin .....             | 52                       |
| Poly(hexamethylene adipamide) .....    | 46.5                     |
| Epon 828® .....                        | 46                       |
| Urca resin .....                       | 45                       |
| Polyester melamine film .....          | 44.9                     |
| Polyethylene oxide diol Mw 6,000 ..... | 42.9                     |
| Polystyrene .....                      | 42.6                     |
| Polyvinyl chloride .....               | 41.9                     |
| Polymethyl methacrylate .....          | 41                       |
| 65% Soya FA alkyd .....                | 38                       |
| Polyvinyl acetate .....                | 36.5                     |
| Polybutyl methacrylate .....           | 34.6                     |
| Poly(n-butyl acrylate) Mn 32,000 ..... | 33.7                     |
| Modaflow® .....                        | 32                       |
| Polytetrafluoroethylene Mw 1,088 ..... | 21.5                     |
| Polydimethyl siloxane Mn 1,200 .....   | 19.8                     |
| Polydimethyl siloxane Mn 162 .....     | 15.7                     |

Raghdadi



## Coating Plastics - Some Important Concepts from a Formulators Perspective

Lawrence C. Van Iseghem, President  
Van Technologies, Inc.

### Introduction

In the automobile industry, the trend is to produce less expensive, lighter, and stronger components that appeal to the aesthetic tastes of the consumer. Appliance manufacturers produce units that have non-metallic casings and components that provide superior durability and function relative to their older counterparts. Composite materials are currently used to manufacture furniture including the use of laminate sheeting that provides the beauty and feel of real wood. Cassettes and enclosures are manufactured for the safe storage of static sensitive electronic components. Eyeglass lenses are produced and sold to wearers that are lighter, safer upon impact, and highly resistant to scratching. From automobiles, to appliances, to furniture, to electronics, to eyeglasses, and beyond, plastics represent materials that increasingly impact many facets of everyday life.

Often, plastic materials will require coatings or markings to enhance their function or appeal. Designers and manufacturers of technical coatings routinely experience unique challenges when dealing with plastics due to their chemical and physical nature.

This discussion will present concepts pertaining to the coating of plastics including the nature of plastic surfaces, wetting and adhesion, and adhesion promotion. With increased awareness of these topics, the formulator of coatings for plastic materials will be better able to design coatings having superior properties.

### The Nature of Plastics as Coating Substrates

Although, the term, "plastic" denotes materials that can be deformed, shaped, or molded, it is more common today to apply the term to synthetic high polymers that are thermally deformable. It is also quite common to see references to various thermosetting polymers and synthetic composites within the context of plastic materials. Plastics, therefore, encompasses a diverse family of polymeric materials.

For successful coating design, the coatings formulator must consider the physical and chemical characteristics of the polymer substrate or plastic surface to be coated. Surface tension, modulus, coefficient of thermal expansion, response to coating drying and cure, as well as the chemical structure and conformation of the polymer are just a few factors that influence the type of coating required for a particular application. The following will discuss these factors and offer some insight into their management.

#### A. Surface Tension:

Surface tension will directly influence a coating's ability to wet out, to penetrate, and to adhere to the porous structure of a surface. Although plastics may be present in a porous structure (as used in filtration media), details discussed below will be limited to the phenomenon of wetting and adhesion and the role that surface tension plays.

It is generally seen that the lower the surface tension, the more problematic it is to coat the surface uniformly with good adhesion. Within the family of plastic materials, there is a considerable range of surface tension that the formulator must consider when examining various types of polymers (Table 1.). It is also noteworthy that the surface tension of a given polymer or plastic material will vary upon changes in molecular weight and temperature. Fortunately, once the molecular weight ( $M_w$ ) of a polymer reaches approximately 2000 - 3000, the surface tension will reach within 1 dyne/cm of the surface tension at infinite molecular weight. As temperature fluctuates between 10<sup>o</sup> C and 50<sup>o</sup> C (normal process temperatures), the surface tension is fairly constant but is seen to decrease at significantly elevated temperatures. It is not uncommon to see a reduction in surface tension of 20% to 30% at 150<sup>o</sup> C for particular plastic material. Therefore, for practical considerations, the formulator need not be overly concerned with polymer molecular weight, but should consider any elevated process temperatures that may impact surface tension factors especially when applying thermoset coatings<sup>1</sup>. Table 1. illustrates the surface tensions of various polymers.

## TABLE 1. Surface Tension of Various Polymeric Materials<sup>1</sup>



| Polymer                            | Surface Tension (dyne/cm)@ 20° C |
|------------------------------------|----------------------------------|
| Cellophane                         | 45                               |
| Cellulose                          | 36 - 42                          |
| Cellulose acetate                  | 46                               |
| Cellulose acetate butyrate         | 34                               |
| Epoxy Resins                       | 45 - 52                          |
| Ethylcellulose                     | 32                               |
| nitrocellulose                     | 38                               |
| Nylon 12                           | 36                               |
| Nylon 6                            | 38                               |
| Nylon 6,6                          | 47                               |
| Phenoxy Resins                     | ~ 43                             |
| Poly(2-ethylhexylacrylate)         | 30                               |
| Poly(acrylamide)                   | 52                               |
| Poly(acrylonitrile)                | 50                               |
| Poly(butadiene)                    | 43 - 49                          |
| Poly(butadiene-acrylonitrile)      | 51 - 53                          |
| Poly(chloroprene)                  | 44                               |
| Poly(ethylacrylate)                | 37                               |
| Poly(ethylene)                     | 33 - 37                          |
| Poly(ethylene-acrylic acid)        | 41 - 60                          |
| Poly(ethylene-propylene)           | 30 - 34                          |
| Poly(ethylene-propylene-hexadiene) | 35                               |
| Poly(ethylene-vinyl acetate)       | 30 - 36                          |
| Poly(ethyleneterephthalic acid)    | 45                               |
| Poly(ethylmethacrylate)            | 36                               |
| Poly(hydroxyethylmethacrylate)     | 37                               |
| Poly(isoprene)                     | 31 - 34                          |
| Poly(methacrylonitrile)            | 39                               |
| Poly(methylmethacrylate)           | 41                               |
| Poly(oxyethylene)                  | 43                               |
| Poly(propylene)                    | 29 - 30                          |
| Poly(styrene)                      | 39 - 41                          |
| Poly(styrene-acrylonitrile)        | 37 - 43                          |
| Poly(tetrafluoroethylene)          | 24                               |
| Poly(vinyl acetate)                | 37                               |
| Poly(vinyl alcohol)                | 37                               |
| Poly(vinyl butyral)                | 38                               |
| Poly(vinyl butyrate)               | 31                               |
| Poly(vinyl chloride)               | 42                               |
| Poly(vinylidene chloride)          | 45                               |
| Poly(vinylidene fluoride)          | 33                               |
| Polycarbonate of bisphenol A       | 43 - 45                          |
| Polyimides                         | 38 - 41                          |
| Polyimines                         | 22 - 26                          |
| Polysiloxanes                      | 19 - 26                          |
| Polysulfone                        | 47                               |
| Polyurethanes                      | 36 - 39                          |
| Starch                             | 39                               |

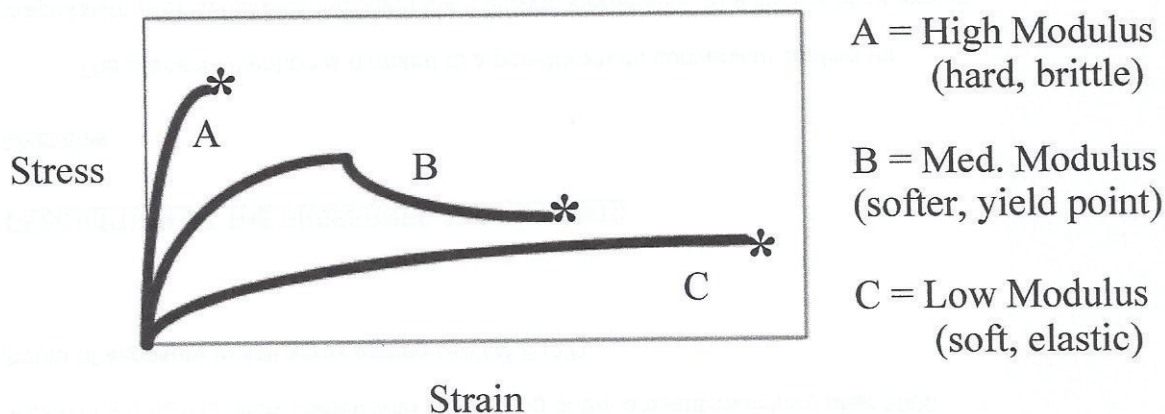


It is possible to enhance a coatings performance through chemical modification of the plastic surface. Chemical modification will alter the surface tension of the plastic material, and is generally done by positioning polar groups on the surface such as pendant hydroxyl, chloro, amino, and carboxyl groups. Notice in Table 1. the influence that polar functionality has on surface tension. Compare, for example, the relatively high surface tension of epoxy resins with that of poly(propylene). These two materials will exhibit different properties with the same coating fluid.

#### B. Modulus:

The modulus characterizes the stiffness or resistance to deformation of a material. It is common to examine modulus through the relationship between the stress imposed on a material and the resulting strain exhibited by the material. A material of low modulus exhibits deformation with minimum force applied, whereas a material of high modulus exhibits significant resistance and is typically hard and brittle. A material having an elastic modulus will show relative ease in elongation with recovery, provided the elongation has not been taken to the break point. Figure 1. illustrates various types of materials and their stress/strain behavior. Plastic materials are seen to respond, typically, according to scheme "B" but higher and lower modulus plastics do occur.

**Figure 1.**



In the design of quality coatings, the stress/strain behavior of the coating composition when dry and/or cured should be consistent with that of the substrate material. Even though this is true under ideal circumstances, it is often the case that: a.) high modulus coatings are applied to lower modulus substrates, b.) low modulus coatings are applied to higher modulus substrates.

#### 1. High modulus coatings on lower modulus substrates:

For decorative coatings and other application, it is generally not advised to apply a coating when the modulus of the cured coating is substantially higher than that of the substrate as failure may occur in the form of cracking and/or loss of adhesion. This statement must be qualified, however, since the formulator must consider the range of stress imposed on the coated product or article during its specified life cycle. To illustrate this point, take for example the relationship of a very high modulus hardcoat composition used for polycarbonate and other plastic molded articles. Although the modulus of the hardcoat composition is significantly higher than that of the substrate, during the normal use of the coated article the stress imposed may never be enough to result in failure. Therefore, the formulator must balance the modulus of the dry and/or cured coating with that of the substrate and the expected stress that will be imposed on them during use.

#### 2. Low modulus coatings on high modulus substrates:

Many applications occur where a coating composition that exhibits softness and flexibility is applied to a



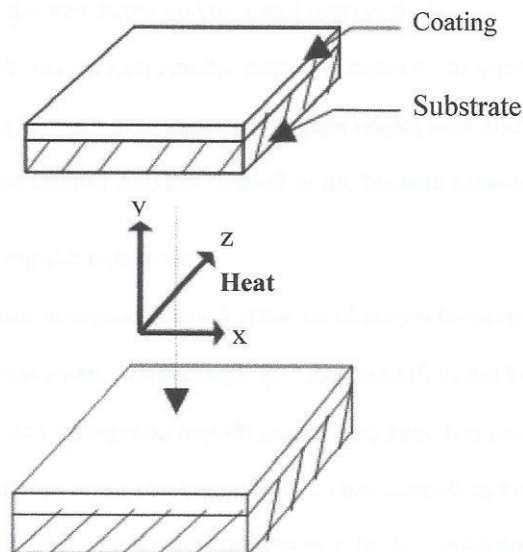
surface that is hard and brittle. Recent developments in “soft feel” urethane coatings illustrate this point quite well. The bulk mass of the substrate plastic material will support the dimensional stability of the coating and permit adequate performance in use. Under certain circumstances, low modulus coatings on a high modulus substrate may provide impact resistance. A good example of this behavior is seen with glass chemical storage containers that have a chemically resistant vinyl protective coating.

### C. Coefficient of Thermal Expansion:

Plastics exhibit various coefficients of thermal expansion and it is important to consider the temperature range that the coated product or article will be exposed to during its life cycle. A disparity in the coefficient of thermal expansion between the coating and the substrate can result in poor interfacial stability as temperature fluctuates. It is, therefore, common to cycle coated articles through extremes of temperature. Failure, when it occurs, will usually take the form of checking, crazing, cracking, and loss of adhesion. Other non-fatal flaws can also occur, such as curl and wrinkling. Most often, problems are witnessed when a coating of high modulus and low coefficient of expansion is applied to a plastic of moderate to low modulus and a relatively high coefficient of expansion.

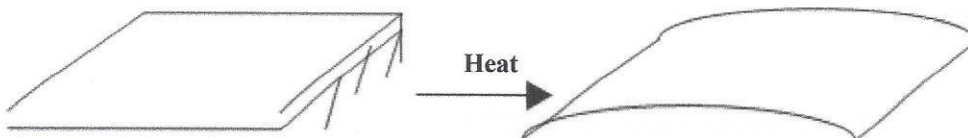
The formulator should recognize that expansion in volume is a three dimensional phenomenon. An applied coating at equilibrium is fixed in two dimensions by the surface area of the substrate. The third dimension is determined by the application thickness (Figure 2). As the temperature changes to induce expansion, the coating and substrate will respond accordingly. Flexible substrates and coatings usually respond to stresses by exhibiting curl (Figure 2a. and 2b.). In the case of more rigid substrates and hard, non-flexible coatings, differing coefficients of expansion will cause significant internal stress to be localized at the interface of the two layers. This may result in failure of the coating as shown in Figure 3.

**Figure 2.**



The expansion due to applied heat under ideal circumstances will occur in three dimensions, but with thin film flexible substrates, a mismatch in the coefficient of thermal expansion will result in interfacial stress causing curl.

**a.) Case 1.** The coating has a higher coefficient of thermal expansion vs. the substrate:





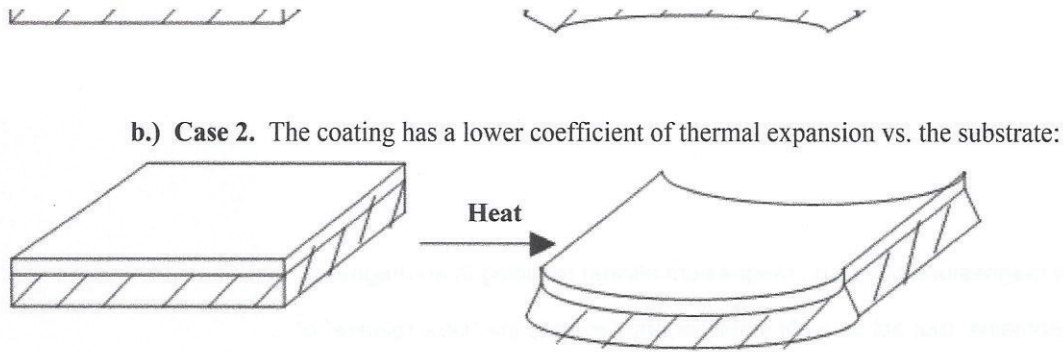
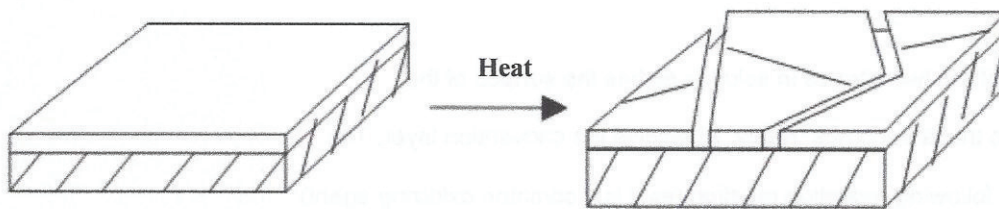


Figure 3.



Coatings of relatively higher modulus may respond to interfacial stress to the extent that any substrate thermal expansion will cause cracking, crazing, and loss of adhesion. Such failure may not occur until the system has been repeatedly cycled through extremes of temperature.

#### D. Response to Coating Drying and Cure:

The action of the drying and cure of a coating composition on the surface of a plastic is also very important for the formulator to consider. In many aspects, the elements presented in the previous section (Coefficient of Thermal Expansion) will apply to the concepts of drying and cure. This is due to the fact that shrinkage is the primary phenomenon to control. Coatings that are less than 100% non-volatile will experience shrinkage. Again, since this is a volume relationship, three dimensional forces will be active. Not only does the thickness change from wet thickness to dry, but stress will be imposed on the coating interface due to shrinkage forces in the plane of applied coating. This usually results in curl as shown in figure 2b. In dealing with this situation, higher solid coatings are preferred, soft flexible coatings work reasonably, and at times the plastic can be back coated.

Curl can also occur due to the cure of a coating composition, especially if by a condensation type reaction. Addition reactions show better resistance to curl. Back coating on the opposite side of the plastic may be necessary or the plastic may need to be thicker or supported to maintain flatness.

#### E. Chemical Structure and Conformation:

##### 1. Structure:

As indicated above, the chemical structure of a polymer will influence the ability of a coating to wet out and adhere to the polymer surface uniformly. The adage that, "Like - Likes - Like" applies, however, many instances require coatings of dissimilar chemistry to be applied to a plastic surface. Knowledge of the plastic in both its structure as well as conformation will guide the formulator to successfully develop coatings.

Polar functionality, when present in a polymer structure will promote ease in coating application. For example, it is typical for the formulator to find that epoxy resin products show better coating application properties versus polyolefin products, given the same coating formulation. The presence of polar functionality is especially beneficial when working with waterborne coatings. Not only does water tend to wet out more readily due to surface tension forces, but polar groups will promote adhesion through



potential hydrogen bonding of suitable functionality of the coating polymer composition.

The converse situation is also important to recognize, where polar functionality present in the chemistry of the coating composition will influence the performance of the final coated product. The higher the polar functionality of the plastic surface or substrate and/or the coating composition, the greater the probability of good interfacial stability.

The formulator needs to recognize that chemical reactions occur between polymeric materials just as they do with low molecular weight, monomeric materials. The difference, however, often is in the slower rate of reaction due to steric hindrance that is evident with high polymers. The reactions most commonly utilized at a coating/substrate interface are condensation reactions. For these chemical reactions to occur, the reactant functionality must be oriented appropriately. Any catalyst used to speed the rate of reaction must be present at the reaction site. With low molecular weight materials, this is typically not a problem. With high molecular weight materials, the coating/substrate interface is, at best, a liquid/semi-solid system. Molecular mobility is limited in the substrate, thus limiting the potential for reaction. Further complicating the situation is the viscosity of the coating composition and the potential for viscosity increase as volatiles are evaporated during drying. The coating composition, therefore, may be or become restricted in molecular mobility preventing the reaction from proceeding at the desired rate.

To enhance molecular mobility, a few things may be done. First, solvent selection for the coating composition is vital. A blend of solvents of varying evaporation rate, in the coating composition, usually promotes coating uniformity and can provide ample molecular mobility at the latter stages of drying. Secondly, the solvent that has the lowest rate of evaporation will be the last solvent out of the coating composition during drying. Ideally, this solvent should be selected from those that are good solvents for the resins of the coating composition, and for the polymer constituting that of the plastic surface. Solubility parameters of solvents should always be referenced for proper formulation. Careful attention should be given to the units in which the parameter values are expressed in, as the various tables available for solubility parameter reference do not all use the same unit of measure.

## 2. Polymer conformation of the plastic surface:

The formulator needs to keep in mind that although chemical functionality may be present, it may not be readily available to provide the anticipated benefit that the formulator desires. Polymer conformation may be such that the available functionality is "hidden" simply by the way the polymer is situated in space. Furthermore, interpolymer chain interactions may occur, including hydrogen bonding, and may effectively prevent the expression of chemical functionality. In these instances, the formulator should consider the use of selective solvents or co-solvents in the coating formulation to "open-up" the plastic surface and promote final coating properties. Also, the effect of drying and cure temperature may be examined to induce improved coating performance. For plastics of high modulus, it is recommended to bring the drying temperature above the glass transition temperature ( $T_g$ ) of the plastic. This will promote both molecular mobility and increase the potential for coating polymer interpenetration with that of the plastic surface. It is possible that the application of heat may only need to be localized at the plastic surface via IR radiant energy, and may be applied to the surface just prior to coating application to be effective.

The formulator of coatings for plastic applications inevitably will encounter materials having varying degrees of crystallization. In general, the higher the degree of crystallization, the harder, less flexible, more brittle, and more solvent resistant the polymer or plastic will be. Also, with higher degrees of crystallization, more difficulties may be experienced in coating design. Polymers are commonly classified according to their degree of crystallization and are termed amorphous when having a low degree, semi-crystalline for a moderate degree, and crystalline for a high degree of crystallization. Polymer chain to chain packing influences the tendency for a polymer to crystallize where linear structure promotes tight chain to chain packing and higher degrees of crystallization. Any polymer chain branching and the presence of bulky substituents will decrease the likelihood of crystallization. When working with plastic coatings, knowledge of polymer structure will guide the formulator in the usage of the appropriate solvent balance and the temperatures required to effectively and efficiently process a



given coating composition.

### Wetting and Adhesion

Regardless of the coating and the surface it is applied to, the coating must adequately wet out, and usually adhere well to that surface. The formulator will find challenges in determining the correct balance of coating ingredients to achieve the desired wetting and coating uniformity. There are three (3) principle wetting phenomenon that apply to coatings. These are spreading, adhesional, and penetrational or immersional wetting. Spreading and adhesional wetting will directly impact the application of a coating to a particular surface. Penetrational or immersional wetting will impact the application of a coating to a porous surface structure or the dispersion of particulate matter (including the possibility of a plastic or polymer media, pigment, or filler) into a coating composition. The discussion that follows will address only spreading and adhesional wetting<sup>2</sup>.

One key concept that the formulator needs to keep in mind is that in the action of wetting, one fluid displaces another from a surface. In the action of coating a substrate, usually the displaced fluid is air. We find that surface tension guides the action of wetting, both that of the substrate (plastic) and of the coating fluid.

#### A. Spreading Wetting:

The spreading of a liquid over a solid is defined by Equation 1.

$$S_{L/S} = \gamma_{SA} - (\gamma_{LA} + \gamma_{SL}) \quad \text{Eq. 1}$$

Where,  $\gamma_{SA}$  denotes the surface tension of the substrate under air,  $\gamma_{LA}$  denotes the surface tension of the liquid coating under air, and  $\gamma_{SL}$  denotes the interfacial tension or free energy of the substrate/liquid coating interface.

When  $S_{L/S}$  is:

- a. positive, coating fluid spreading is spontaneous,
- b. zero, coating fluid spreading is spontaneous,
- c. negative, coating fluid spreading is not complete.

The surface tension of the plastic is given by the nature of the polymer used to construct it. Table 1. lists several types of plastics and their respective surface tensions. When evaluating coating compositions, it will be quite evident whether the coating fluid has a comparable surface tension. If the coating does not flow out well, pinholes or fisheyes occur, or if thick edges or picture framing occurs, the coating surface tension is probably too high relative to that of the plastic surface. Of the terms in Equation 1, the formulator has control of only the surface tension of the coating fluid. Interfacial tension is not typically determined accurately with ease but is assumed to be made minimal when the surface tension of the substrate and the coating fluid are the same or near the same. Therefore, for best coating uniformity the formulator should keep  $\gamma_{LA}$  and  $\gamma_{SL}$  as low as possible relative to  $\gamma_{SA}$ .

Another method of determining spreading wetting is through contact angle measurement. The contact angle is simply the angle tangent to the edge of a droplet of fluid in contact with a surface as shown in figure 4. Equation 2 describes spreading wetting in terms of the contact angle that the fluid makes with the substrate.

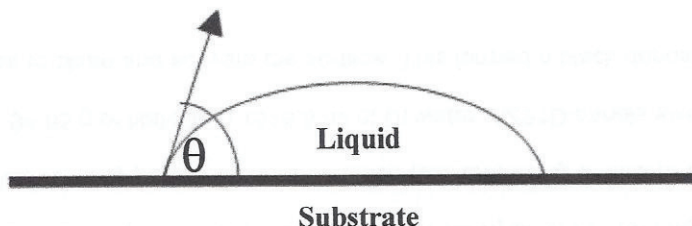
$$S_{L/S} = \gamma_{LA} (\cos \theta - 1) \quad \text{Eq. 2}$$

The contact angle must be zero for spontaneous spreading wetting, unless the surface is rough. Equations exist which account for substrate roughness or rugosity, and we find that spontaneous spreading can occur, provided that the contact angle is less than 90° .



Contact angle measurements are very useful in situations where (as is usually the case)  $\gamma_{SA} < \gamma_{LA}$ , and when  $\gamma_{SA} > \gamma_{LA}$ , the contact angle will always be zero.

**Figure 4.**



The contact angle that a liquid makes with the surface it is sitting on provides a means of determining surface tension relationships. A contact angle of zero implies spontaneous spreading wetting, although spontaneous spreading wetting can occur provided that the contact angle is less than  $90^\circ$ .

The formulator needs to keep in mind the following guidelines for good spreading wetting:

1. Adjust the fluid surface tension to match that of the substrate.
2. Check the contact angle and maintain it below  $90^\circ$ .
3. When using surfactants to adjust fluid surface tension, select surfactants to perform to the highest potential at the lowest concentration.

#### B. Adhesional Wetting:

In spreading wetting, the area wetted by the fluid increases over time, whereas, adhesional wetting brings two surfaces together in intimate contact. Adhesional wetting is defined by Equation 3.

$$W_A = \gamma_{SA} + \gamma_{LA} - \gamma_{SL} \quad \text{Eq. 3}$$

This equation is key to the understanding of why plastics are difficult to adhere to relative to other types of coating substrates. Equation 3 tells the formulator that coating adhesion is best when the surface tension of the substrate and the coating fluid are both as high as possible. Plastics, according to our discussion above, have generally low surface tension and, therefore, contradict the requirements for tight adhesion, as stated in Equation

3. Therefore, the conditions for best adhesion of a coating to a substrate are to keep the interfacial tension ( $\gamma_{SL}$ ) as low as possible, and both  $\gamma_{SA}$  and  $\gamma_{LA}$  as high as possible.

At times, however, it is desirable to design a coating that will release from the substrate (protective purposes, free cast films, etc.). Since substances do not adhere well to surfaces of low energy, equation 3 directs the formulator to minimize the surface tension of the substrate and maximize the surface tension of the coating composition (there will likely be an increase in the interfacial tension under these circumstances). This will provide a good release coating condition.

#### Adhesion Promotion

Adhesion promotion is a topic of great interest to the plastic coating industry. This discussion will provide an overview of some of the methods used to enhance adhesion to plastics, thus providing the formulator with some insights to integrate with other coating design factors. The following lists the more common approaches to the topic of adhesion.

1. Solvent and co-solvent composition of the coating fluid