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Industrial practice often requires that plastic parts be affixed to other plastics or to nonplastic materials. Of the methods available to engineers who must make judgements relative to the most suitable assembly technique, adhesive bonding must be seriously considered.

Adhesive bonding of plastic substrates is already a common practice; even greater utilization can be expected with the increasing availability of improved adhesives. Currently. adhesives compete with welding. fusion, and mechanical fastening. However, adhesive bonding ofier special advantages. Not least among them is the opportunity of weight savings compared with metal fasteners. It is of special appeal in the automotive industry, where vehicle lightweighting is crucial. alls. Of the methods available to engine

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1 17.1 ADVANTAGES

The use of adhesives may indeed be the only sensible route in some instances. The reasons are as follows:

- 1. The ability to attach materials that are impractical to bond in other ways. It is obvious that screws or bolts are not suitable for paper, glass or other brittle materials, thin films, fibers, and foams. Moreover, the shape of the substrate may render mechanical fastening diflicult or impossible.
- 2. The ability to join dissimilar materials. Significant differences in thermal coefficient of expansion may disqualify mechanical fastening. Thermal fusion is also disqualified for unlike polymers. Adhesive bonding of dissimilar materials often yields composites with enhanced properties by utilizing the best features or physical properties of each. component.

3. Uniform distribution of stress. In a simple bonded overlap, any load applied to the joint is distributed evenly over the entire bonded area as if the material were continnous. In terms of stress vectors in both tensile stress (away from the bond) and shear stress (across the bond}, all of the adhesive contributes to opposing the stress. In contrast the holes required for rivets, nails, screws or bolts are stress ooncentrators or focal points that contribute to failure. Adhesive bonded assemblies generally can resist shock, vibrational and fatigue failure better than mechanically attached assemblies. This often means that adhesive-bonded members can be thinner in cross-section and lighter in weight.

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- 4. Reduction in joint weight. This feature is partially related to the better performance possible with lighter weight parts because of the elimination of stress concentration points. Reduction in weight is possible because adhesives are generally of low specific gravity, and applied preferentially in thin layers. In many joints the forces of adhesion exceed the cohesive strength of the adherends.
- 5. Environmental protection. Although usually more important in metal-to-metal joining, the continuous contact between surfaces made by adhesives seals out corrosive or harmful agents. Both gases and liquids can be excluded by the adhesive.
- 6. Resistance to vibration. Elastomeric adhesives resist the fatigue and subsequent failure that is brought on by repeated deformations. In general the more flexible the adhesive, the greater the resistance to strain occurring in the adherends.
- 7. Smoother surfaces. Adhesive bonding, like thermal bonding, eliminates such imperfections as rivet-point dimpling, surface spots or projecting portions of devices that are common with mechanical fastening. This reduces finishing costs and makes possible more esthetic and more functional product design.

117.2 BASIC REQUISITES

All adhesives must be liquids, or at least capable of some degree of flow. A primary requirement for good adhesion is that the adhesive and adherend surfaces must be in close contact, since the attractive forces that promote adhesion vary as the inverse sixth power of the intermolecular distances. To get substrates close enough to effect a good bond, their surface roughnesses must be made to correspond. In essence, the adhesive must be a fluid because the solid adherend is never smooth in a microscopic sense. For solid polymers, this means that the adhesive must be melted or dissolved in a suitable solvent before application.

The adhesive must also be sufficiently mobile to quickly penetrate holes and depressions in the solid surface. If voids are left when the adhesive solidifies, the joint will be weak.

Finally, the adhesive must solidify to provide sufficient strength to resist unbonding stresses. (Pressure-sensitive adhesives, of course, do not solidify; their function is best described in terms of their viscoelastic properties). Solidification occurs either through evaporation of a solvent or through chemical reaction (polymerization), frequently called curing. Drying or curing converts the fluid material to a solid, which can be either rigid or elastomeric.

Wetting of the solid surface requires the selection of an adhesive that is suitable in terms of the surface energy or surface tension of the adherend. Any adhesive supplier can furnish this information. However, it is often necessary to alter the surface of the adherend to make it receptive to adhesives.

117.3 TYPES

There are five basic physical types of adhesives: curable liquids, solvent cements, hot melts, aqueous, and pressure-sensitive. The curable liquids undergo a chemical reaction or polymerization to attain a nonfluid condition. Often these consist of two parts, each of which is stable by itself but when mixed together undergo a chemical reaction. Solvent cements are simply dilute solutions of fully reacted adhesives that solidify by loss of solvent. Hot melts are 100% solids that become liquids on heating above their melting or softening points; they are applied hot and solidify on cooling.

Aqueous adhesives dissolved or dispersed in water may either simply dry to the proper physical form or undergo a reaction when the water is removed. Solvent-activated adhesives are deposited at the bond line in solid form and rewet with solvent just before making the

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assembly. As with all solvent-borne adhesives, better joints are formed with porous substrates that permit a faster evaporation of solvent.

Pressure-sensitive adhesives do not change form or harden but behave as high-viscosity fluids which, because of an increase modulus as the shear or deformation rate is increased, can be easily removed from the substrate. Pressure-sensitives are frequently used as temporary anchorage for components that must be repositioned.

Another way of looking at adhesives is in terms of their chemical composition. Table 117.1 lists in a simplistic sense the more common physical and chemical types (the actual chemistry of each is more complex and beyond the scope of this chapter). In addition to unlisted additional compositions that fall in each category, there are many mixtures or blends of two or more chemical types, called hybrids. Table 117.2 lists common adhesives and their typical properties.

117.4 LIMITATIONS

A key disadvantage of adhesive bonding is the need for fixtures or clamps in many such operations. Another is the slowness, relative to mechanical fastening or fusion welding, of adhesive bonding. Other disadvantages include the following:

Limited Shelf Life. Adhesives that depend on a curing reaction and are mixed beforehand, have a relatively short pot or storage mix. Some other adhesives must be carefully stored

Chemical

urethanes Polyamides, EVA,

phenolics Double-faced tapes

Methacrylates

Methyl, ethyl esters PVA, PVC, rubber, EVA,

acrylic, chloroprene

Acrylic, chloroprene,

Epoxy, PU, silicone,

polyamides Acrylic, cyanoacrylate,

epoxy, PU

Polyurethane, polyamide, EVA, polyester

nitrile, nitrocellulose phenolic, PU rubber,

Rubber

vinyl

polyesters, urethanes PVA, epoxies, silicones,

aminoplastics, rubbers,

TABLE 117.1. Adhesives Classified by Type Examples Types Physical Epoxies, urethanes, Curable liquids (one or two-component) acrylics, silicones Acrylics, elastomers, Solvent cements (includes water) vinyls, cellulosics,

Hot melts $(100\%$ solids) Aqueous (includes dispersions)

Pressure sensitive

Anaerobic Contact Cyanoacrylate Emulsions

Hot melt

Solvent-based (Cements)

High temperature use

Room temperature cure

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TABLE 1470 Common Adhanbon

in order to avoid premature reaction. Additionally, two-part adhesives have a working life that depends on their rate of reaction; the faster the cure, the shorter the pot life. For this reason it may be desirable to use dispensing machines that blend the two components immediately prior to application. In general, if rapid cure under ambient conditions is required, care must be taken not to pre-mix large quantities of the two components.

Need for Surface Preparation. Surface contamination of plastics can prevent the necessary intimate contact between adhesive and adherend. For example, low molecular weight substances can bloom to the surface, as can certain additives, creating a "film" that defeats the purpose of the adhesive.

Solvent Retention. Where solvents are used, or where a product of the curing reaction is volatile, there is always the danger that failure to dry the adhesive adequately can cause bubbles or voids. These imperfections can seriously weaken the glue line, since they function as stress concentrators that prevent intimate and complete contact of the two surfaces.

Temperature Limitations. At elevated temperatures, polymeric adhesives become unstable and will degrade. Some adhesives also become brittle and ineffective at low temperatures. Thus, temperature considerations are important in adhesive selection, and could in fact affect the decision as to whether adhesive bonding is suitable for a particular application.

Material Limitations. A primary disadvantage of adhesive bonding (excepting pressuresensitives) or welding is the inability to disassemble the parts for repair or inspection.

117.5 SELECTION FACTORS

Determination of the relative merits of a particular adhesive, involves a number of factors: need for a primer, amount of surface preparation, cure time, fixture time, need for heating, adhesive viscosity, cost, and properties of the cured adhesive.

Some of these considerations relate to the cost of the operation. Elimination of surface preparation and the need for a primer can be important factors in selecting an adhesive. If cure time or consequent fixture time is excessive, the resulting time delays may mitigate against an otherwise useful adhesive. If heating is necessary (either to effect complete cure or to reduce the time for reaction or solvent evaporation) an additional cost is involved. However, most adhesive operations require realtively low capital costs.

117.6 SURFACE PREPARATION 1645

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Other selection factors relate to the nature of properties of an adhesive. Viscosity must be suitable—either low enough to ensure good wetting of the adherend or high enough to prevent run-off on vertical surfaces. Further, the modulus of the cured or dried adhesive is a factor in terms of the flexibility or resistance to deformation required for the bond line. In turn, these considerations depend on the nature of the plastic and the anticipated uselife stresses or extent of strains.

A most critical factor in selection, of course, is adhesion to the plastic. Not all adhesives will function satisfactorily with all plastic surfaces; even within classes of adhesives or plastics, individual members differ in behavior.

Consideration of environmental resistance depends on the desired use life for the bonded assembly. For instance, water resistance obviously is required if the assembly is intended for outdoor exposure. Phenolics, epoxies, and acrylics are examples of adhesives that weather well. Similarly, the part may have to be exposed to oils or solvents and an adhesive should be chosen with that in mind. Also, certain rubber-based adhesives are contraindicated if long use life is contemplated, since polymers with unsaturated backbones undergo an oxidative degradation with time, which is accelerated by heat or light.

117.6 SURFACE PREPARATION

Improved adhesion can be obtained when the surface of a plastic part is prepared correctly. The adhesive must wet, spread and penetrate the rough surface of the adherend.

Cleanliness is a basic requirement in order for the adhesion to make intimate contact with the substrates to be bonded. Surface preparation entails both obtaining a clean surface and, if necessary, altering the surface tension of the substrates to correspond to the surface tension of the adhesive.

Roughening of the plastic surface provides an increased area for bonding and strengthens the joint against shear forces. Accordingly, instructions for surface preparation usually entail both cleaning and abrading the surface. The extent of surface preparation required for a particular bond depends on the physical requirements for the assembled part; more extensive preparation is indicated in instances where extreme in-use stress will be placed on the joint. Thus surface preparation may consist of one or more of the following: solvent cleaning; abrading and solvent cleaning; chemical treatment (to alter surface energetics).

Solvent Cleaning. For many operations, particularly where the joint will not be subjected to severe in-use stresses, cleaning the surface may require only a wipe with a suitable solvent or detergent solution. Different solvents are recommended for wiping various plastic surfaces. The choice of solvent is dictated by the solubility properties of the plastic. For example, most common solvents other than alcohols severely attack polystyrene, whereas, nylons are resistant to the same solvents. As a generalization, crystalline polymers are less likely to be attacked by common solvents.

Often, parts are solvent cleaned by more elaborate procedures, such as vapor degreasing, ultrasonic vapor degreasing, or immersion in a series of cleaning agents, which tend to give cleaner surfaces than wiping with cloth or paper. Commonly used solvents are halogenated to minimize flammability concerns. They include methylene chloride, perchloroethylene and similar materials Table 117.3.

Abrading and Solvent Cleaning. In the simplest case, plastic components can be wiped with a solvent, abraded with emery cloth and then wiped again to ensure removal of all debris. The plastic surface is not changed chemically but is altered physically; because some of the plastic may be removed the roughened surface now offers the possibility of mechanical interlocking Table 117.3.

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TABLE 117.3. Plastic Surface Cleaning®

Plastic	Method
Acrylics	Wipe with methanol
Aminoplasts	Scrub (detergent), scour, rinse
Cellulosics	Wipe with alcohol, scour
Epoxy	Degrease (acetone, MEK)
Fluorocarbon	Sodium (solubilized), acetone wash
Nylon	Phenol (12% aqueous); 1:1 resorci- nol-ethanol
Polyamide	Solvent-clean (acetone, MEK), scrub
Polyolefin	Oxidize (chromate or radiation)
Polystyrene	Wipe with alcohol
Polyurethane	Wipe with acetone or MEK
Rubbers (NBR, SBR, NBR, Neo- prene)	Scrape, scrub with toluene (immerse in acid)
Reinforced plastics	Wipe with MEK

"Most surfaces (except those chemically altered) are preferably abraded or roughened.

Chemical Treatment. Where optimum adhesion is required, chemical treatment of surfaces may be required. For low energy plastics, such as polyolefins and fluorocarbons, the chemical nature of the plastic surface must almost always be altered in order to give a more polar (higher-energy) surface.

Chemical alterations can be drastic in the case of the low energy plastics. For instance, chromic oxidation involves using a liquid used to remove organic contaminants from glassware. It is hazardous to use, and proper safeguards must be exercised. Similarly the defluorinating solution (utilizing a form of sodium) is dangerous and requires expertise in disposal.

To avoid the problem of hazardous chemicals, sheets of fluorocarbons can be purchased already chemically modified.

An alternative approach to activating plastic surfaces that does not require the use of hazardous fluids is radiation treatment. Such treatment renders polyolefins more amenable to adhesive bonding. Other techniques for enhancing adhesion of plastics include flaming and plasma treatments. Detailed instructions on surface preparation for plastics are available in the literature.

117.7 SOLVENT CEMENTING

A variation of adhesive bonding, solvent cementing is particularly useful for noncrystalline thermoplastics. Crystalline polymers generally do not dissolve in ordinary solvents at room temperature.

Solvent cementing depends on active solvents to soften and swell the plastic surfaces; after assembly and evaporation of the solvent, a monolithic clear joint is obtained. Individual solvents are seldom used; a combination of solvents is a more common way to attain the properties desired. Solvents frequently contain some dissolved polymer (of the same type as that to be bonded), to aid in gap filling and to speed up drying. With cements thickened with dissolved polymer, it may be necessary to mask the area around the joint to facilitate removal of excess cement squeezed from the bond line by clamping pressure.

Masking has general application in solvent cementing when the parts to be assembled are soaked in the solvent as a preliminary to adhesion. Cellophane tape rather than masking a sa mga pagkatang pangangang ng pangalang ng pangangang ng pangangang ng panganggang ng panganggang ng pangan

paper, is preferred. Parts can also be masked using commercially available masking compounds based on animal glues or gelatins. The masking compounds are applied hot and carefully stripped away for application of the solvent cement.

Another method used in joining is capillary action. Fine wires are used as shims. and the adhesive applied from a dropper or needle. After capillary action has adequately spread the cement, the wires are removed.

Table 117.4 gives some examples of bonding with solvents or solvent cements. The plastics listed are not necessarily always bonded this way, however. For example, ABS can be readily paper, is preferred. Parts can also be m
pounds based on animal glues or gelati
carefully stripped away for application c
Another method used in joining is c
the adhesive applied from a dropper or r
the cement, the wires joined using epoxy or acrylic adhesives. This avoids the long drying times associated with solvents. Care must be taken in choosing solvents for polystyrene; caution must be exercised to avoid solvent crazing.

Solvent cementing is the method of choice for many plastics. Acrylics, for example, are readily bonded with such chlorinated solvents such as methylene chloride, ehtylene chloride 1,1,2—trichlorocthane, or chloroform. If a more viscous cement is desired, a solution of acrylic chips (from 2 to 8% by weight) in the chlorinated solvent can be used. Cellulosics » also are good candidates for solvent bonding. A typical cement for cellulose acetate is a 10% solution of the polymer in a mixture of acetone and methyl cellosolve. For acetate butyrate, a cement based on equal parts of acetone and ethyl acetate is useful.

Poly(vinyl chloride) is frequently bonded using solvents like acetone or methyl ethyl ketone. Sometimes more powerful solvents like cyclohexanone or tetrahydrofuran have to be used. Here the cements not only contain polymer (PVC) but plasticizer as well. It is important to remember that solvent cementing is generally employed only when the

parts to be joined are of the same plastic. Finding a mutually satisfactory solvent mixture for two different plastics is often difficult.

117.8 PREFERRED ADHESIVES

Choosing an adhesive for a particular plastic is not so easy as one might suppose. The adhesive providing the strongest bond to a given plastic may not necessarily be the best for a particular job. Primary consideration must be given to the form of the plastic, to its modulus, and to the conditions to which the bonded assembly will be subjected in actual use.

TABLE 117.4. Solvents for Cementing

"Usually l to 7% of plastic is dissolved in solvent.

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 b MEK = methyl ethyl ketone, THF = tetrahydrofuran, MIBK = methyl isobutyl ketone.

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Flexible parts should be bonded with flexible adhesives. When bonding dissimilar materials, the adhesive must be resilient enough to allow for differences in coefficients of thermal expansion.

Choice is complicated by the fact that an unfilled plastic behaves difierently from the same material reinforced. It frequently happens that adhesives that give relatively low bond strengths with the unfilled plastic will give greatly improved performance with the same material filled with a polar inorganic substance, particularly after abrading. As earlier noted, organic polymers are low energy materials, in contrast to the higher-energy surface (like glass) to which most adhesive readily adhere.

Table 117.5 lists a number of plastics along with recommended adhesives. However, resin formulations often differ within the same family, and this can afiect the performance of the adhesive. For example, structural acrylics are often formulated with different monomers and a particular grade may be more (or less) receptive to one adhesive than to another. However, adhesives can be formulated to vary considerably in polarity and in terms of the Flexibility of the cured adhesive. Where flexibility is crucial, rubber-based adhesives may be
flexibility of the cured adhesive. Where flexibility is crucial, rubber-based adhesives may be
all TABLE 117.5. Recommended Adh

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preferred over others that have higher adhesion values. Cyanoacrylates, for instance, cure so quickly that jig or fixture time may be avoided, but they are usually quite inflexible.

Plastics and adhesives designed for very high temperature use are not covered in this discussion because there are some special problems with these systems. Manufacturers, particularly those in the aerospace industry, may wish to consult government sources for recommendations.

A comment is in order about a relative newcomer, acrylic structural adhesives. Their great advantage is hardening to handling strength in seconds without heat. This capability translates into markedly reduced process costs and greatly increased process speeds. Structural acrylics are much tougher and higher in impact resistance than cycanoacrylates, and are more resistant to environmental factors.

Offshoots of this adhesive category are UV-curable and visible light-curable types. Otherwise similar to chemically curing grades, they solidify in less than 10 seconds. Their utility for certain applications utilizing transparent plastics is promising.

117.9 JOINT DESIGN

There are a variety of ways to effect adhesive joining of plastic components (lap, scarf, strap, etc). Whichever is used, it is always best to design joints to minimize peel stresses. It is important that the joint be designed so that the adhesive is subjected to compressive and shear forces in use.

The effect of joint design can be summarized:

Other generalizations about adhesive bonding:

1. Width of the bonding area increases yoint strength linearly; increasing the length of the bonded area, although beneficial, does not make as great a contribution to strength. 2. Thickness of the bond line should be controlled to about 4 to 6 mils $(0.1-0.15 \text{ mm})$ of adhesive. A greater gap in the distance between adherends has a deleterious effect on peel and cleavage strength of the bond.

3. Stiff adherends (high-modulus plastic substrates) are less sensitive to joint geometry than flexible adherends.

117.10 APPLYING THE ADHESIVE

Techniques for applying liquid adhesives depend on the sophistication of the job as well as on production-volume needs. Thus, applicator equipment ranges all the way from conveyorized and automated dispensing systems to eyedroppers or brushes. Typical single type applications are /

· Spray gun (air or airless)

· Brush

Metal Surface Characteristics **Affecting Organic Coatings**

by Bruno M. Perfetti

FEDERATION **SERIES ON** COATINGS TECHNOLOGY

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Figure 2-Schematic representation of the typical constituents and contaminants on metal surfaces

the treatments and finishes applied to their surfaces. Although, ideally, the two concerns would or should be complementary, in reality they are often in opposition to one another and the preferred choices and requirements for optimizing the performance of the treatments and coatings in a particular application must be subordinated to the intended function and performance of the metal's end use. The choices one may make in selecting a preparative treatment or practice for a given application are often dictated or limited by circumstances entirely unrelated to the achievement of optimal preparative results. When and where such situations prevail, a well-founded understanding of the technology of surface preparation will be invaluable in effecting a sensible compromise for satisfying the conflicting demands of the problem.

Metal products comprise one of the largest classes of materials which are coated and painted and their usage spans virtually the entire spectrum of consumer goods and markets. Appliances, automobiles, containers, buildings, housing, machinery, ships, trucks, transmission pipe, tanks, fixtures, furniture, and an almost endless list of other items require the application of coatings at some time in their service lives. Each of these applications has unique functional and quality prerequisites and service requirements. Carbon and specially-alloyed steels, coated steels and aluminum, in a variety of grades, are the predominant metals being used in these applications, and each class of metal has its own characteristic response to preparative treatments and coatings. It is interesting that these characteristic responses often do not reflect the properties and compositions of the bulk of the solids concerned but rather are determined by the unique attributes of their surfaces. In turn, the surface attributes of metals are strongly determined by both their chemical composition and metallurgical structure and by the history of their prior processing. The surface compositions of the various metals consist primarily of a mixture of the oxides, hydrates, and salts of the metallic elements which make up the metal compositions and usually very little of the free metal itself (note Figure 2). This multi-derivatized surface is what must be accommodated by the preparative treatment employed to properly dispose the surfaces to receive the coatings to be subsequently applied. In addition to the naturally derived constituents to be expected on the metal surfaces, as noted, there may also be present contaminants which accumulate on the surfaces of the metals as the result of the prior processing, handling, and various incidental or ambient exposures. These latter constituents on steel might include such species as surface carbon, oils, and rolling and forming lubricants, metal fines, non-metallic surface inclusions, rolled-in scales, large surface carbides, dirt and grit, corrosion products, extraneous soils and the by-products of bacterial action, mildews, and other fungal deposits. Zinc surfaces will primarily carry oils, lubricants, corrosion products, metal fines and dusts, dirt and grit, and extraneous soils, but not the other contaminants noted for steel. Aluminum surfaces are very much like those of zinc but they tend to develop very heavy deposits of aluminum oxide. Although the aluminum oxide is not actually a classical contaminant itself, it may inhibit the removal of any true contaminant species otherwise present.

There are no universal means that will remove all the possible contaminants on a metal surface short of actual dissolution or removal of a layer of the surface itself. Alkaline cleaning media normally will be effective against residual oils and lubricants, most soils, dirt and grit, relatively loose metal fines, and bacterial and fungal by-products because these materials are generally sensitive to the dissolution, saponification, emulsifying action, and detergency functions by which alkaline media operate. Except for saponification action, acidic cleaning media are also effective against the soils noted and operate by the three remaining processes noted for the alkaline cleaners. Where organic solvents can be tolcrated, solvent cleaning is an excellent means of removing heavy deposits of oils, grease, and other organic materials suitably soluble in various hydrocarbon, ester, ketone, and chlorinated solvents. Vapor degreasing is a common means for solvent cleaning smaller parts easily accommodated in the enclosures required by this practice.

Surface carbon (see Figure 3) generated during the annealing of steel is not readily removed except by electrolytic action or acidic dissolution (pickling) of the metallic surfaces. Surface inclusions and rolled-in scale on steel respond to pickling and surface grinding provided they are only superficial and not deeply embedded. Surface car-

Figure 3-Surface carbon wiped from a steel surface after it was cleaned by a hot alkaline power washing

impair the performance of the pretreatment and the coating applied over it.

F. Priority of Mechanical Performance Over **Surface Requirements**

It must be acknowledged that the first priority in the manufacture of a metal substrate is the development of its intended mechanical properties. Metals are used principally because they offer strength, rigidity, and barrier qualities in a particular application (Figure 13). It is only after these mechanical requirements are satisfied that other considerations, such as the surface variables affecting coating, can be addressed. As a rule, the characteristic surfaces which result from the required metallurgical processing of the metal are those that must be handled, whatever their condition, in the preparative processes employed for organic coating. Rarely is a particular metal substrate chosen for an application because it will have the easiest or best surface for subsequent coating. Consequently, compromises are frequently necessary in the selection of a preparative process or in the cost of preparation to accommodate the mechanical property priorities of the substrates being cleaned and treated. An example can be cited to illustrate this point.

A steel structure, such as a bridge, may be constructed with a high strength-low alloy steel to reduce its weight. yet maintain its structural integrity. The subsequent painting of the alloy steel will be somewhat more costly, since the rate of cleaning the surfaces of the alloy steel by abrasive blasting will be slower, because the surfaces tend to be slightly more resistant to oxide removal than those of carbon steel. The higher cost of preparation and painting

Figure 13-A press drawn quarter panel of an automobile body (The panel illustrates the stringent mechanical requirements which must be satisfied by metal sheet ahead of any finishing d emands)

is accepted to gain the advantage of the mechanical strength and ridgidity of the alloved steel structural members.

The foregoing discussions and illustrations are instructive because they clearly point up the necessity of anticipating the numerous chemical, physical, and operating interactions that can impact on the preparative efforts required to enhance the receptivity of metal surfaces for organic coatings. By recognizing the critical elements that contribute to the selection process, one can make the rational and technically sound compromises needed to choose the best preparative methods for a variety of intended purposes.

II. SOME THEORETICAL AND TECHNOLOGICAL **CONSIDERATIONS OF METAL SURFACES**

A reasonably good understanding of the scientific principles concerned with metallic elements and their associated compounds is necessary to properly appreciate both the similarities and the differences these materials exhibit when they are prepared for coating. Regarding the technology of metallic substrates, two very important concerns are the characteristic attributes of metals which have an effect on their surfaces and the constitutional features of metallic surfaces which may be altered by the preparative processes preceding coating. Other aspects of metal surfaces which must be considered are the effects of the mechanical and thermal treatments they have undergone and the effects of the surface geometry and texture on their response to coating. Finally, a consideration of the effects of surface energy and wetting phenomena and those of passivation and corrosion resistance properties are needed to complete the theoretical perspectives attending the chemical performance of the metals in cleaning and treatment operations.

A. Characteristics of Metals Affecting Surfaces

The metals of interest to the current discussion are those which are solids having well defined bounding surfaces. These metal solids will tend to resist deformation

but will also display some elasticity when they are stressed. The surfaces of the solids will ordinarily be polar and possess an inherent high surface energy." Because the metals and solid surfaces of practical interest here are well removed from the high temperatures at which they soften and melt or the very low temperatures where they might fracture and shatter, the impact of the effects of extremes of temperature on their performance is of little concern for the present purposes. Of greater interest are the nature of and disposition of the surface elements, the surface energetics and their consequences, and the effects of prior history of the solid on its chemical responses, because these are the major factors which affect preparative practices and processes.

The elements which reside on a metal substrate may be present in substantially different concentrations and chemical states than those found in the sub-surface or interior composition of the metal.) An alloy or a metal with only traces of internal elemental impurities may diffuse one or more of these constituents to the surface of the metal when the metal is processed, such as by heat treatment or hot-rolling, and thus enrich the surface in that element or those elements. Alternately, an element of the bulk composition may migrate to the surface because of a diffusion gradient induced by oxidation of the element at the sur-

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CORROSION ENGINEERING

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two alloys are quite similar in chemical composition. Both alloys exhibition in the state in good resistance to stress corrosion.

See Fig. 3-71 for the effect of ferrite on resistance to stress corrosion by CF-3. CF—8._ and CF»8M. compared to types 304 and 316. s: :

The Materials Technology Institute published in 1981 two manuais titled Performance and Reliability of Corrosion Resistant Castings. Manual — '7702 No. 5 covers Phase 1, "Causes of Unsatisfactory Performance", and No. 6 covers Phase 2. "Casting Discontinuities."

Table 5-4 lists mec}iani'cal properties of several stainless steels in each cf . . the four groups. Note the wide range of properties available from these $7:2$: $\frac{1}{2}$ materials. The high-strength materials exhibit good strength-weight ratios for aircraft and missile applications. High hardness is desirable for wear **the set of the set of the** and some applications where resistance to erosion is required (c.g., trir: :_ . for high-pressure steam valves). \blacksquare is the state of the state

The 200 and 300 series stainless steels all exhibit roughly the same mechanical properties in the annealed condition. The major exception \mathbb{T}^{\perp} involves cast alloys with duplex microstructures. Note the higher yield $\frac{1}{2}$ strength (and accordingly higher design strength) for CF-8 containing 15° ferrite as compared with type 304. The austenitic steels retain good ductility. \Box and impact resistance at very low temperatures and are used for handling .'.f : liquid oxygen and nitrogen. FCC metals and alloys (austenitic stainless. :-~ .3 copper, and aluminum) all possess good properties at cryogenic temperatures. They only method available for hardening the austenitic stainless steels is cold-working. This usually decreases corrosion resistance only slightly, but in certain critical environments a galvanic cell could form between cold-worked and annealed material. Type 301 is utilized mostly in the cold-worked condition for such applications as train and truck bodies. The austenitic steels can be cold-rolled to strengths in the neighborhood of \mathbb{R}^2 is \mathbb{R}^2 300,000 lb/in.² in wire form. Types 301 and 302 are not used for severe corrosion applications. The former because of its lower Cr and Ni. and the latter because of higher carbon.

High-temperature properties are discussed in Chap. 11.

5-9 Aluminum and Its Alloys

Aluminum is a reactive metal, but it develops an aluminum oxide coating or film that protects it from corrosion in many environments. This film is quite stable in neutral and many acid solutions but is attacked by alkalies. This oxide film forms in many environments, but it can be artificially produced by passage of electric current. This process is called anodizing. The high-copper alloys are utilized mainly for structural purposes. The copper-free or lowcopper alloys are used in the process industries or where better corrosion. resistance is required.

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5-30 Magnesium and Its Alloys

Magnesium is one of the lightest commercial metals, specific gravity 1.74. It is utilized in trucks. automobile engines. ladders. portable saws. luggage. aircraft. and missiles because of its light weight and also good strength when alloyed. However, it is one of the least corrosion resistant and is accordingly used as sacrificial anodes for cathodic protection (Chap. 3) and dry-cell batteries. It is generally anodic to most other metals and alloys and must be insulated from them.

Magnesium exhibits good resistance to ordinary inland atmospheres due to the formation of a protective oxide film. This protection tends to break down (pits) in air contaminated with salt. and protective measures are required. These include coatings and "chrome" pickling. which also provides a good base for the coating. Corrosion resistance generally decreases with impurities and alloying. Alloys are quite susceptible to stress corrosion and effect on corrosion. The metal is susceptible to erosion corrosion. Magnesium is much more resistant than aluminum to alkalies. It is attacked by most acids except chromic and hydrofluoric. The corrosion product in HF acts as a protective film.

Magnesium and its alloys are available in a variety of wrought forms and die castings. Tensile strengths in the approximate range 15,000 to 50,000 lb/in.² are obtainable.

5-ll Lead and Its Alloys

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Lead is one of our oldest metals. It was used for water piping during the time of the Roman Empire. and some of it is still in operation. Lead ornaments and coins were utilized several thousand years ago $\sqrt{\text{Lead}}$ forms protective films consisting of corrosion products such as sulfates, oxides, and phosphates. Most of the lead produced goes into corrosion applications : a large portion involves sulfuric acid. [See isocorrosion chart in Chap. 7.) Lead and its alloys are used as piping. sheet linings. solders {Pb—Sn). type metals. storage batteries. radiation shields. cable sheath. terneplate (steel coated with Pb-Sn alloy}. bearings. roofing. and ammunition. Lead is soft. easily formed. and has a low melting point. Lead-lined steel is often made by "burning on" the lead. It is subject to erosion corrosion because of its

When corrosion resistance is required for process equipment, chemical lead containing about 0.06% copper is specified, particularly for sulfuric acid. This lead is resistant to sulfuric, chromic. hydrofluoric, and phosphoric acids: neutral solutions: seawater: and soils. It is rapidly attacked by acetic acid and generally not used in nitric. hydrochloric. and organic acids.

Chemical lead exhibits a tensile strength of about 2300 lb/in.² at room

GENERAL CHEMISTRY

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CHAPTER THIRTY-FOUR

CARBON

Less than 0.2 per cent of the earth's crust is carbon. Yet we can safely say that had carbon been omitted from the roster of elements we should not exist. All organic compounds are compounds of carbon.

1. Occurrence Carbon occurs as the pure element in nature in two allotropic forms, diamond and graphite. The Belgian Congo is the world's

richest source, although deposits in Brazil and South Africa are important. Owing to the large demands of the war for diamonds in grinding tools and for dies through which wire is drawn, the deposits in Arkansas are being developed. Deposits of graphite, a second allotropic form of carbon, occur in Ceylon, Russia, Germany, Mexico, Madagascar, and Canada. Although anthracite coal is 94 per cent carbon, its carbon atoms are combined with one another and with hydrogen atoms. Hence, strictly speaking, coal contains little free carbon.

Inorganic compounds of carbon

FIG. 34-1. Star of Africa diamond. (Courtesy of American Museum of Natural History, New York.)

include carbon dioxide in the atmosphere, and carbonates. Limestone, chalk, and marble are calcium carbonate. Magnesite, MgCO3, is abundant, and whole mountain ranges are composed of dolomite, MgCO₃.CaCO₃. We have mentioned that all organic substances are carbon compounds.

2. Properties. No one has to describe the beauty of a diamond, but its extreme hardness, which is really its most valuable property, may be everlooked. It is more than twice as hard as its nearest competitor. Hardness is the ability of a substance to resist penetration of its surface by anther substance. The relative hardness of two substances can be determined easily by rubbing an edge of one on the surface of the other, and

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allopatric almoner

Allopathie : Gk. allos, other --pathie, -pathy.] --affo-path'-

ie (âl'2-path'/k) adj , --affo-path'-cal-y adv.]

ie (âl'2-path'/k) adj , --affo-path'-cal-y adv,

widely differing geographic areas. [ALLO- + Gk. patra, fa-

PURIN(E) + -0L².

all-or-nome (b²/ar-nom²) *adj*. Characterized by either com-

plet response or total lack of response or effect, as in neu-

rological action above a threshold.

al-lo-ster^{rik}y *adj*. Of or relat

al-lot (a-lot') tr.v. -lot-ted, -lot-ting, -lots. 1. To distribute by as for the two particles. However, the original state is portion: allocate: allot three weeks to a project. [ME alotten \le OFr, alote: a., to (\lt Lat. ad-) + lot, portion, of Germanic orig.] —al-

: a_7 to (< Lat. ad) + lot , portion, of Germanic orig.) --al-
lot'ter n.
al-
different (a-lôt'mant) n. 1. The act of allotting. 2. Some-
al-lot-ment (a-lôt'mant) n. 1. The act of allotting. 2. Some-
hing that is allott

octave.1

octave.) or to whom something is allotted.
all out *adv*. With every possible effort.
all out *adv*. With every possible effort.
all-out (δ l'out') *adj*. Using all one's resources: *an all-out ef-*

all over adv. 1. Over the whole area or extent: embroidered

Jore and over any 1. Over the whole area or extent: *embroidered*
all over with roses. 2. Everywhere: *searched all over for the*
money. 3. In all respects: *She's her grandmother all over*
all-o-ver (o²l'o²y-r) *ad*

dare, to praise, and Med. Lat. allocate.] $-\text{al}-\text{al}-\text{val}$
low'a-ble adj. $-\text{al}-\text{val}-\text{val}$ and $-\text{val}$ and $-\text{$

tedly.

tedly.

al-loy (al'oi', 2-loi') *n*. 1. A homogeneous mixture or solid

al-loy (al'oi', 2-loi') *n*. 1. A homogeneous mixture or solid

solution, usually of two or more metals, the atoms of one

replacing or occupying int to hind.]

to bind.]
all-pur-pose (δ 'pūr'pas) *adj.* Useful in many ways.
all right *adv.* 1. Satisfactory: average. 2. Correct: *These fig-
ures are perfectly all right.* 3. Uninjured. 4. Very well: yes.
5. Without a doubt: *He'*

wou.
all-right (ôl'rīt') adj. Slang. 1. Dependable: honorable: an
all-right fellow. 2. Good: excellent: an all-right movie.
all-round (ôl'round') adj. Variant of all-around.
All Saints' Day n. November 1, a church festival all saints.

all-seed (δ 'sed') *n*. Any of several plants having many seeds, such as knotgrass.
All **Souls' Day** *n*. November 2, observed by the Romar.
Catholic Church as a day of prayer for souls in purgatory-
difference (δ ' a spice.

a spice.
all-star (6)'stär') *adj*. Made up wholly of star performers: *an* all-star cast. $-n$. Sports. A player chosen for an all-star

all-time (ôl'tīm') adj. Informal. Of all time: an all-time a:-

team.

1. Then (ol'tim') *adj.* Informal. Of all time: an all-time a:

tendance record.

11 total action of the verything considered: in all,

all-lude (a-lood') intr.v. -lud-ed, -lud-ing, -ludes. To make an

indirect ref

alluvium. alluvial fan n. A fan-shaped accumulation of alluvium de-

alluvial fan *n*. A fan-shaped accumulation of alluvium de-
posited at the mouth of a ravine.
al-luvi-on (a-loo've-an) *n*. 1, Alluvium, 2. The flow of wate-
against a shore or bank. 3. Inundation by water; flood
4. Law:

arian deposited by flowing water, as in a fiver bed, flock
plain, or delta. [Lat. < alluvius, alluvial < alluere, to was
against. —see ALLUVION.]

against. —see ALLUVION.]

al-ly $(q$ --liff all'₁ v-lies. —tr. 1. To unite connect in a formal relationship or bond, such as by treaty

2. To unite or connect in a personal relationship. such

2. To unite or connect in a associate. [ME allien < OFr. alier < Lat. alligare, to bind to see ALLOY.]

-see ALLOY.]

al-ly (al'2) *n*. The univalent organic radical CH₃:CHCH₂

[Lat. *allium*, garlic + -x1. (so called because it was firs

[Lat. *allium*, garlic)] -al-lyl¹ic (2-lil^{TR}k) *adj.*
 Al-magest (al'ma-jest

(composition), fem. of megistos, greatest, superl. of mega great.

al-ma ma-ter or Al-ma Ma-ter (âl'ma mä'tar, äl'ma)

reading them. of *megatios*, greatest, supert, or *mega-*
great.]
al-ma ma-ter or Al-ma Ma-ter (almo matter, all map) =
1. The school, college, or university that one has attended
2. The anthem or school song of an

à pat / å pay / år care / ä father / b bib / ch church / d deed / ě pet / ě be / f fife / g gag / h hat / hw which / í pit / í pie / ír pier j judge / k kick / l lid, needle / m mum / n no, sudden / ng thing / ð pot / ð toe / ð paw, for / oi noise / ou out / ðo took / đồ boo

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APPENDIX G-3

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 10 9 8 7 6 5 4 3 2 1

Figure 20.4. Representative phthalocyanine pigments.

The alpha form is redder, but not as stable; in some cases, when some grades of the alpha form are used, there can be serious problems of change of color and strength during storage of coatings or during baking. More stable alpha form pigments are available; these incorporate various additives that stabilize the crystal form and minimize problems with flocculation of dispersions. Some grades of phthalocyanine blue are slightly chlorinated; these have greener blue shades.

Phthalo greens are made by halogenating copper phthalocyanine to produce mixtures of isomers in which many of the 16 hydrogens of CPC have been replaced with chlorine or mixtures of chlorine and bromine. Phthalo greens with 13 to 15 chlorines but no bromine have blue-green shades. Partial replacement of chlorine with bromine shifts the color toward a yellow-green shade. The yellowest shades have a high ratio of bromine to chlorine, an example is PG 36, which has on average about 9 bromines and 3 chlorines.

20.2.4. Black Pigments

Almost all black pigments used in coatings are carbon blacks. They absorb UV radiation as well as light, and with most binders, black colors are the most stable on exterior exposure. Carbon blacks are made by a variety of processes of partial combustion and/or cracking of petroleum products or natural gas. Depending on the process, the particle size and therefore the degree of jetness (intensity of blackness) varies. High color channel blacks have the smallest particle sizes, with diameters of 5 to 15 nm, and have the highest jetness. They are used when intensely black, glossy coatings are desired. Furnace blacks have larger particle sizes, are lower in cost, and give less jet black coatings. Various grades are available, with average diameters of 50 to 200 nm. Lampblacks have a still larger particle size, on the order of $0.5 \mu m$, and have lower color strengths than other carbon blacks. They are primarily used in making gray coatings. They are preferable to high-color blacks for this purpose; if a small excess of high color black is added by mistake, it may be necessary to increase the batch size 50% or more to make up for the mistake. The shade of gray obtained changes much more slowly with the addition of lampblack, making color matching easier.

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