SPECIAL FOCUS



The processes used to apply most liquid paints to plastics are not much different than those employed for painting metals, although powdercoating is still quite unusual on plastics. Additionally, certain specific painting methods widely used on metals, such as chemical deposition (autophoretic) and electro-deposition coating, are not possible with plastics. But all the other techniques such as brushing, dip coating, flow coating, curtain coating, including all the variations of spraying and rotary atomization, are used to coat both metals and plastics. With the advent of UV radiation curing and low temperature curing of select powdercoatings, powder application on certain somewhat heat-resistant plastics is now being performed, although this technology is still in its infancy.

The paintability of all the metals commonly utilized in manufacturing is rather similar. This is possible in part because values for the surface energies, electrical conductivities, heat conductivities, and heat resistances of metals are all quite close together. This is decidedly not true for plastics. In general, the values for these attributes of plastics are much lower than for metals, and also, the values among various plastics show extreme variation. Even within a given family of plastics, their paintabilities can be surprisingly dissimilar due to differences in molecular weights of the plastics and the incorporation of different additives in the manufacture of the various resins. The base plastic composition might consist of just a single resin or it could be a blend of two or more different resins. Formulated into a resin composition may be an assortment of fillers, extenders, and plasticizers. Additives are often added to resins to produce desirable physical and chemical properties; pigments are introduced to alter gloss or provide color. The chemical nature and amounts of these additives are likely to change the paintability of that particular formulation significantly. Even parts manufactured from the same resin formulation are not necessarily equal in paintability. The molding, extruding, or other forming process used to produce the part can play an important role in the paintability of the part as well, due to induced part stress resin and crosslinking.

The chemical nature of the resin largely determines the surface energy of the plastic. In general, a surface with a higher surface energy is more readily "wetted" by paint and hence is more "paintable", meaning that coating adhesion will be better. It has been noted that paint adhesion to metals is often superior to adhesion on plastics because metals typically have substantially higher surface energies than plastics. The low polarity of the molecules in plastics such as polyethylene and polypropylene is the cause of the low surface energy (and poor paintability) of these plastics. Increasing the surface energy, and hence paint adhesion, is one of the major purposes for pretreating plastics.

Cleaning Plastic Substrates

As with any other surface to be painted, plastics need to be reasonably free of any soils or foreign materials. Common soils found on plastic items to be coated include fingerprints, dust, lint, and mold release residues. Usually, detergent cleaning can satisfactorily remove salts and oils deposited on plastic by touching them with bare hands. Fingerprint soils can be totally avoided if workers handling the parts from the forming process to the paint application step wear lint-free gloves.

Most plastics are either insulators or ineffective electrical conductors. As a result, they have a tendency to build up static charges that attract and tenaciously hold particles of lint and dust. Wiping with a tack cloth may not remove all of these contaminants. An excellent method of removing statically attracted lint and dirt is to use a destaticizing air blowoff. The destaticizer should generate both positive and negative charges; most units use a weak radioactive emission source in the blow-off air source. Intake air is filtered and ion-laden air is blown across the part so that positive and negative ions neutralize all static charges. Destaticizing needs to be performed immediately before painting so that the parts are as clean as possible just going into the coating process. Delays between destaticizing and painting will allow charges to reform and as a consequence, parts will re-accumulate particulate on their surface.

By installing the plastic painting operations inside a "clean room", dirt such as dust and lint is more easily controlled. The air



supply should be filtered and kept at around 50% relative humidity. Only authorized persons wearing lint-free coveralls, hair nets, and shoe covers should be permitted in this room at any time.

Mold Releases and Plasticizers

Some paintable mold releases are available, but many other mold releases adversely affect paint adhesion. Various techniques may be required to remove these agents used to facilitate the separation of plastic parts from the molds. Wax type mold releases can sometimes be removed by solvent cleaning, but this type of release is not recommended for parts to be painted. Solvent use is almost automatically discouraged due to VOC emission restrictions and potential fire and health dangers with many solvents. Water-soluble mold releases are much preferred. Removal of these from the plastic surface is readily accomplished with ordinary aqueous detergent solutions.

Mold release agents may also be blended into plastic formulations; these are termed "internal" mold release agents. Internal mold releases must be avoided whenever possible. Paintability may or may not be impaired immediately, and QA adhesion tests may show excellent initial adhesion. In some cases, however, internal mold releases have slowly migrated to the part surface and caused paint adhesion failure months after a part was painted.

Plasticizers can be added to molding resins to increase impact strength, but often these can decrease paint adhesion just as mold releases do. Some plasticizers will slowly migrate to the surface and soften the interface between the plastic and the paint, resulting in adhesion loss. In this case, too, initial paint adhesion tests may be completely satisfactory, but subsequent lifting or separation of the paint film from the plastic surface occurs later. This can result in costly field failures and liability claims later, long after the part has been put into service.

Achieving Robust Paint Adhesion

Most plastic surfaces are not only low in surface energy but also inherently low in surface profile. Smooth surfaces will tend to give poor paint adhesion unless the surface is first roughened by chemical or mechanical means. Conversion coatings on metals contribute to paint adhesion in part by the micro-rough surface of the inorganic layer produced on the metal. The most common way of overcoming surface smoothness of plastics is to etch the surface with a chemical agent to generate micro-roughness and

anchoring sites that will provide adhesion for the paint. If possible, the etching is done by the solvents present in the paint being applied to avoid a separate processing step. The paint solvent selection is rather critical because different solvents etch plastics at varying rates. Both over-etching and under-etching are to be avoided. Insufficient etching will not provide proper adhesion; excessive etching can damage the plastic. It may warp the part, expose particles of additive fillers and extenders, and perhaps even create areas where materials in the plastic may bleed into the coating. Some plastics, such as polycarbonate or polystyrene, will crack or become overly surface-crazed from attack by solvents to which they are especially sensitive. If plastics have areas that are highly stressed from the molding process, solvents can form visible cracks in these areas due to stress-relief. So a measure of care is required when solvent etching is done.

When some part shapes are molded, there are areas where the rapid plastic injection flow produces significant frictional heating of the part inside the mold. In those areas a highly crosslinked (glazed) skin is formed that is resistant to solvent etching. Paint adhesion will be poor in these areas unless steps are taken to remove the overly hard plastic skin. These areas can be de-glazed enough to allow satisfactory paint adhesion by tumbling with a moderately abrasive media, or by blasting the surface with a mildly aggressive grit material. Brief hot solvent or solvent vapor immersion treatment is also effective for some parts. But creating micro-roughness with solvents is generally effective only if the plastic itself is at least somewhat polar in nature.

When de-glazing or solvent etching is not effective or otherwise undesirable, it may be necessary to use a chemical reaction to create polar oxidized groups on the surface. This is especially true for extremely non-polar plastic surfaces. Polypropylene and polyethylene are two examples of low polar plastics that are treated oxidatively. These resins and similar low-polar plastics may be briefly exposed to an open flame from a gas burner. This initiates an oxidative chemical reaction (incipient burning) that although it is not enough to be visible, forms enough polarity on the surface to provide excellent paint adhesion. Passing plastic parts through an electrical corona discharge that generates ozone has also been used to cause surface oxidation. The corona produces excited oxygen atoms that form ozone, which in turn oxidatively attacks the plastic to produce polar groups such as hydroxyl, carbonyl and carboxylic acid moieties.



Low polarity plastics can also be surface oxidized using light sensitive chemicals called photosensitizers, followed by exposure to ultraviolet light. The UV light "cracks" the molecules of photosensitive compounds to form free radicals. Free radicals are extremely reactive species that in this process combine with the oxygen present in air. Oxygen free radicals in turn react with the plastic to produce polar groups on the surface.

Cold gas-plasma technology can be employed to pretreat plastics and

oxidize the surface to dramatically improve surface properties for paint adhesion. When a gas is forced to absorb enough energy, it becomes ionized, or a "plasma". A radiofrequency generator provides excitation. Arc welding and fluorescent lighting are both examples of a phenomenon in which a "glow" is caused by excited ions falling back to their stable energy state. Within the safety limits of the system this process can use any single gas or mixture of gases. Oxygen, nitrogen, helium, argon, air, and ammonia have been used for this purpose.

Plasma conditioning allows plastics to be painted with good adhesion as well. The plasma reactor is typically a vacuum vessel fitted with a tightly sealable port for loading and unloading parts. A glow discharge can be observed when the reactor is operating. Gas-plasma treatment both micro-etches and activates the surface. A brief treatment will create a polar surface that has a high surface energy on an otherwise low-polar or non-polar plastic, enabling it to be "wet" completely and uniformly by paint. Plasma processes usually do not change the surface appearance, so materials can be treated without causing discoloration. Excellent adhesion can be achieved with the same paint used on metals. This can be an important feature to some manufacturers because an assembled unit that contains both plastic and metal can be painted simultaneously using the same coating.

Less effective is the use of chemical oxidizing agents in the paint itself to oxidize the plastic surface enough to generate better paint adhesion. Reflectance infrared spectroscopy has verified that these treatments produce the same oxygenated (hydroxyl, carbonyl and carboxylic acid) groups on the plastic surface as the other oxidizing processes, just not as much. Only in limited cases will oxidants in the paint itself cause polarity sufficient enough for durable paint adhesion.



Surface pretreatments increase (widen) processing windows. For example, "untreated" Polyolefins have surface energies in the range of 29-31 dynes/cm. For painting processes these surfaces require treatment levels in the range of 38-60 dynes/cm, depending upon the type of coating chemistry, e.g., solvent, waterborne or UV. Each pretreatment method is application-specific and has potential advantages, limitations and cost implications. Under certain circumstances, gas-phase oxidation processes can deleteriously affect down-

stream manufacturing operations such as heat sealing. A thorough evaluation prior to production implementation is critical.

Adhesion Testing

Numerous methods are used to measure paint adhesion and scratch hardness properties. Accelerated age testing is a technique that can help predict long-term product performance. The following experiment design is one example:

> Group 1: Five (5) days, 158°F, dry no humidity Group 2: Five (5) days, 90°F, 90% humidity Group 3: Control group, ambient conditions

A visual inspection should be performed immediately following testing and compared to the control group. Once the samples have stabilized, peel tests should be conducted in accordance to ASTM D3330. In many applications, a 180° peel test is most often used. For comparative purposes, a 90° peel is also suggested. This test may give a truer idea of adhesion performance although the values may be lower than those recorded at 180° peel. Extending Group 1 testing from 5 days to 10 days would not predict double field performance because the relationship is not a linear function; however it would indicate more robust results.

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