Surface Treatment

(Contributed by The ChemQuest Group)

Introduction

For effective bonding, the adhesive must completely wet the surface of each substrate being joined together. In addition, strong attractive interactions must form between the adhesive and the substrates. To satisfy these conditions, the surface of the substrate must be clean, reasonably smooth, and chemically receptive to the chosen adhesive. Surface treatment is the process whereby the adherend surface is cleaned and/or chemically treated to promote better adhesion.

To a large extent the surface treatment determines how well and for how long a bond will hold, Figure 1. If the chosen adhesive can withstand the service conditions to which the bond will be subjected, then the life and service expectancy of that bond will be directly proportional to the degree of surface treatment

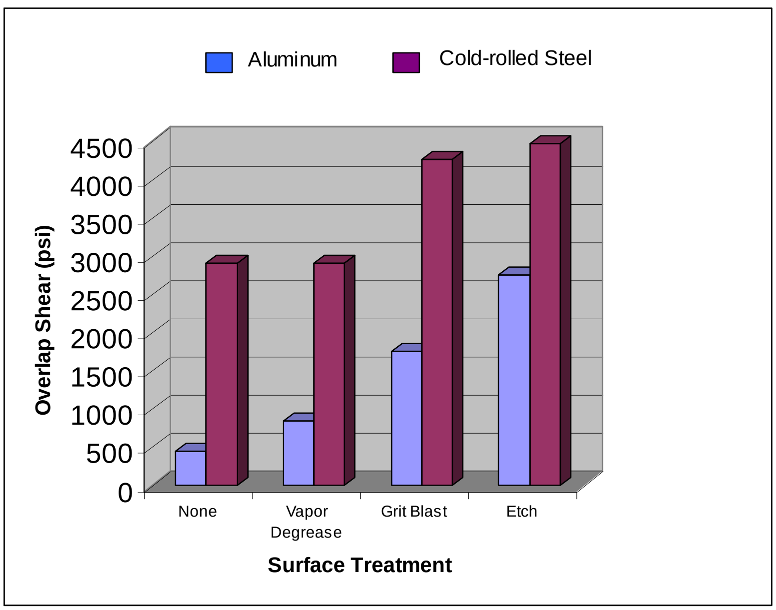

Figure 1. The effect of surface treatment on overlap shear strength (epoxy adhesive).

Since surface treatment adds another step (and additional expense) to the bonding process there is a tendency to reduce or even eliminate it all together. However, in general, the level of surface treatment used should be the minimum amount that gives a reproducible bonded part having the desired level of performance.

Surface treatment promotes adhesion by making it possible for the adhesive to wet the actual surface of the substrate, rather than its apparent surface. In many cases, what appears to be the surface is, in reality, a layer of grease, dirt, oil, or some other contaminant, Figure 2. The method used to prepare such surfaces for adequate wetting will depend on the type of contaminant and the nature of the adherend.

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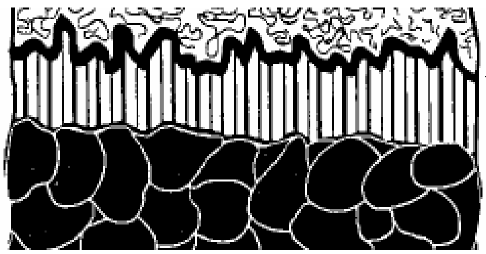

Figure 2. Typical surface layers on a metal substrate.

As a general rule the adhesive should be applied immediately after the surface treatment. If this is not possible the treated surface should be protected, for example by covering with kraft paper. Avoid putting finger prints on the newly prepared surface. If the substrate is left for more than a day before applying the adhesive it may be necessary to repeat the surface treatment.

Metal Surfaces

Contaminants that create bonding problems on metal surfaces include grease, dust, dirt, oil and oxide caused by air corrosion. Grease and oil not only interfere with bonding, but also make certain types of preparation operations, such as chemical surface modification ineffective.

Whether a metal adherend requires solvent cleaning, abrasive blasting, priming, or a combination of preparation methods depends upon how strong and durable the bond must be.

Wood Surfaces

Common wood contaminants include resin and wax. Wood also contains absorbed moisture that can lead to large dimensional changes. Before bonding, wood should be dried to the level of moisture content appropriate to its service use when bonded. Surface contamination should be sanded, planed, or machined away. Debris from such mechanical cleaning operations can be removed by compressed air, vacuuming or brushing, or it can be wiped away with a solvent moistened cloth.

Plastic Surfaces

Plastic surfaces are subject to many of the same sorts of contamination as wood and metal. In addition, components in the plastic may migrate to the surface. The basic methods of surface treatment involve solvent cleaning, abrasion and chemical surface modification. Surface modification, by chemical or physical methods is particularly important in the case of low surface energy plastics. The introduction of polar groups at the surface dramatically improves adhesion to these surfaces.

Classification of Surface Treatment

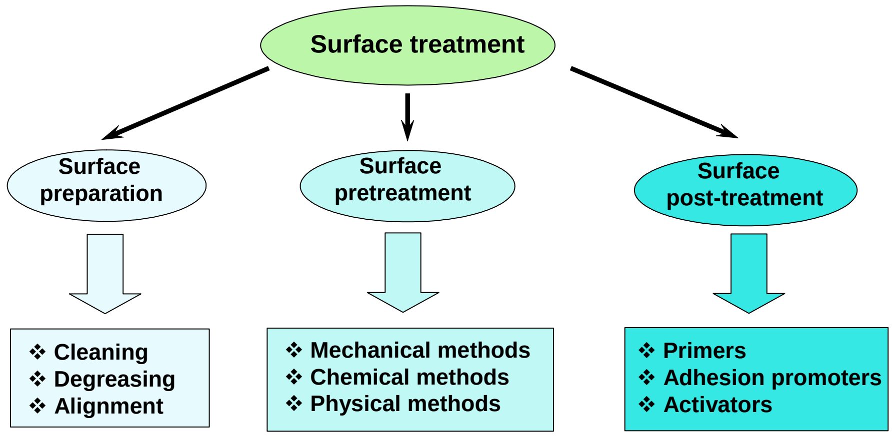

Figure 3. Possible steps involved in surface treatment.

Surface treatment may involve one or all of the following (Figure 3):

Surface Preparation – the removal of oil, grease and other surface contaminants, i.e. cleaning.

Surface Pretreatment – the use of mechanical, chemical or physical methods to remove strongly absorbed surface layers and activate the surface.

Surface Post-treatment – the application of adhesion promoters or primers to improve adhesion to the adhesive and/or protect the surface.

Surface Preparation

Surface preparation encompasses two main types of cleaning: a) detergent, b) solvent. The choice of cleaning method used will depend upon the type of substrate (metallic or nonmetallic) and the extent and nature of contamination. In some instances, it may suffice to merely dust or blow away loose dirt. In other cases, it may be necessary to remove all foreign material from the adherend surface.

Detergent Cleaning

Detergent, soaps, and caustic soda are the least expensive and easiest cleaning agents to handle. Applied by spraying, scrubbing, or immersing the part in an ultrasonically agitated solution, these cleaners can remove certain kinds of dirt and oil reasonably well. However, such cleaning agents may react with certain metals. After detergent cleaning it is necessary to rinse thoroughly with water and dry.

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Solvent Cleaning

Figure 4 summarizes the ability of different solvent types at removing the most common surface contaminants.

Contaminant	Hydrocarbons	Alcohols	Ketones, esters
Cutting oils	0	0	+
Protective oils	+	0	+
Waxes	+	0	0
Lubricants	+	0	+
Resins	+	+	+
Adhesives (not cured)	-	0	0
Fingerprints	-	+	+
Silicone oils	-	-	-

+ good removal 0 partial removal - poor removal

Figure 4. Cleaning and degreasing with solvents.

Solvent cleaning can be accomplished by wiping with a solvent-moistened cloth (or lint-free tissue), immersion in the solvent, or by exposure to the solvent vapor.

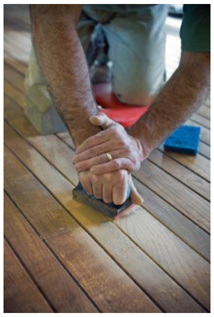
A ketone, such as methyl ethyl ketone, is generally a good solvent for cleaning metals, but it can be too aggressive for many plastics. An alcohol, such as isopropyl alcohol, is a better choice of solvent for use with plastic substrates.

Solvent cleaning should precede any chemical or abrasive surface pretreatment. Abrading a surface coated with oil, grease, or a release agent will serve only to drive the contaminants further into the substrate making it even more adhesion resistant. Further, grease and oil prevent the acid etch solution from reaching the adherend surface.

Surface Pretreatment

Following the preliminary surface preparation it may be necessary to pretreat the surface using one of variety of mechanical, chemical, or physical methods.

Mechanical Methods



Mechanical methods involve the use of handheld sandpaper or hand cleaning tools like wire brushes and scrapers. Such instruments are convenient to remove rust, scale, paint, and weld splatter. But they are too slow to use on large areas.

One drawback of the abrasion process is that it causes particles of debris to accumulate on the abraded surface. These particles come from the abrasive, the surface contaminants, and the surface material itself. All such particles must be removed before adhesive is applied. This may be accomplished with a clean cloth or brush, or with filtered compressed air.

After the abrasion debris has been removed, it is usual to give another solvent clean before bonding. A solvent-moistened cloth is convenient for this, but as the cloth will become contaminated during this operation, it should be renewed frequently.

Mechanical cleaning also includes a number of much faster abrading methods such as sandblasting, tumbling, and abrading with power tools.

Chemical Methods

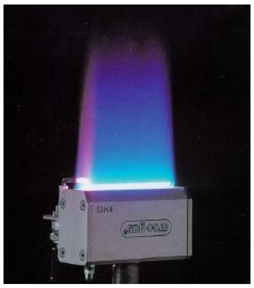
In chemical treatments that alter the surface of the adherend, the part is dipped into a chemically active solution. This solution either dissolves part of the surface or transforms it, making it more chemically active and thus more receptive to adhesive bonding.

Acid etching involves immersing a metal substrate in an aqueous acid solution to remove a loose layer of oxide from its surface. The particular acid used depends upon the metal and type of oxide being treated. In many cases acid etching may provide enough surface preparation for bonding - depending, of course, upon the degree of adhesion desired. Acid etching can also be effectively used with certain plastics, for example chromic acid is used to treat polyolefins.

Anodization involves the electrochemical modification of the surface. The process deposits a porous and stable oxide layer on top of the oxide layer formed after etching of the substrate.

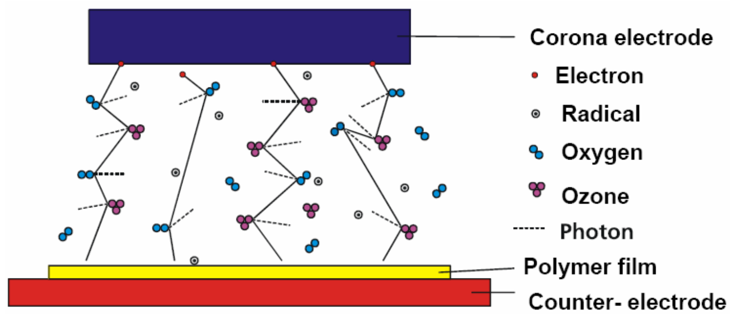
Physical Methods

These are techniques where the surface is cleaned and chemically modified by exposure to highly energetic charges or other ionic species. The most common methods are flame treatment, corona discharge and plasma. These pre-treatment methods have been applied to metals and, in particular, composites and plastics.



Flame treatment of the substrate surface for just a few seconds with an oxygen-containing (blue) propane or acetylene gas flame leads to the incorporation of oxygen-containing groups at the surface. This improves the wetting properties and hence the adhesion. Flame treatment is used almost exclusively for polyethylene and polypropylene substrates. The effect of the pretreatment subsides within a short time so that flame-treated substrates must be bonded immediately.

A corona discharge is essentially a plasma generated in air at atmospheric pressure by applying a high frequency and high voltage between two electrodes. It contains a number of energetic species that can clean and introduce polar groups, mostly oxidation products, at the substrate surface. The corona discharge may also lead to crosslinking of the polymer surface. The pretreatment effects are short lived so bonding should be carried out immediately. It is used mainly for polyolefin films and is capable of high processing speeds.



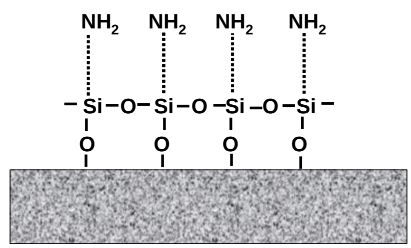
A plasma is usually generated in a low pressure chamber and so is best suited to batch processing. Commercial units of various sizes are available. The advantage of this method is that it allows treatment of substrates by plasmas of gasses other than oxygen, for example argon, ammonia, or nitrogen. Plasmas created from inert gases are generally used to clean substrate surfaces.

Surface Post-Treatment

It may be necessary to further treat the substrate surface following surface pretreatment by the application of a primer or adhesion promoter. These are materials that are adsorbed strongly onto the substrate surface and that also interact strongly with the adhesive. A primer or adhesion promoter is applied to achieve one or more of the following:

- **Modify the surface energy of the substrate.**
- **Promote chemical reaction between adhesive and substrate.**
- **Activate the adhesive.**
- **Inhibit corrosion of the substrate.**
- **Protect the surface after pretreatment.**

Organo-functional silanes, for example 3-aminopropyl trimethoxysilane, are widely used to improve adhesion. The silane substituent at one end reacts with hydroxyl groups on the surface to give a polysiloxane polymeric layer. The organic substituent on the other end reacts with the adhesive providing a covalent link.



Proprietary Surface Treatments

In recent years a number of proprietary surface treatments have been introduced that combine both physical and chemical treatments.

Silicoater™ This method has been mainly used with dental alloys, to improve adhesion to other materials. The sandblasted alloy is passed through an oxidizing flame into which a solution of tetraethoxysilane is injected. This results in a layer of silica embedded in the surface of the alloy. After cooling the surface is then treated with a solution of an organosilane coupling agent. The functionalized alloy surface is ready for adhesive bonding.

ATmaP™ This method is suggested for use with a variety of materials such as plastics, glass and metals. The surface to be treated is passed through a flame with a controlled amount of oxygen into which a solution of a diamine is injected. The vaporized solution produces a number of reactive species in the flame that impinge on the surface resulting in hydroxyl, carboxyl, and nitrogen species being chemically bonded to the surface. The functionalized surface enhances adhesion, immediately after treatment, or, after storage for several months.

Rocatec™ This is a tribochemical method for functionalizing surfaces that has been used mainly for dental applications. The part to be treated is first cleaned then blasted with aluminum oxide that has been treated with a surface layer of silica. After impact some of the silica is embedded in the surface. The surface is then treated with a solution of an organosilane coupling agent to give a functionalized surface ready for adhesive bonding.

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Surface Treatment in Practice

Some level of surface treatment is usually necessary before adhesive bonding.

Although a simple solvent wipe may be sufficient for some applications, the following basic surface treatment is generally found suitable for most materials. A silane coupling agent may be used to improve surface wetting and increase the bonded joint's long-term durability.

Basic Surface Treatment

1. Solvent wipe to remove oil or grease contamination.
2. Abrade or shot blast using medium grit (120 - 200 grit size) preferably alumina.
3. Remove coarse debris, if present.
4. Solvent wipe to Remove fine debris.
5. Ensure surface is completely dry.
6. Bond or prime immediately.

Additional Chemical Pretreatments

For some applications it may be necessary to follow the basic surface treatment with an addition pretreatment in order to achieve the level of performance required of the adhesively bonded joint. The following tables summarize chemical pretreatments for specific metals and plastics.

Table 1. Chemical Pretreatments for Metals

Substrate	Etching Solution (composition wt.%)		Pretreatment Conditions
Aluminum Stainless Steel	conc. Sulfuric acid	27.5	Immerse in etch solution 12 - 15 mins. @ 150 - 160F
	Sodium dichromate	7.5	Rinse in distilled water
	dist. Water	65	Air dry 150F 10 mins.
Carbon Steel	conc. Sulfuric acid	10	Immerse in etch solution 30 mins. @ 140F
	Oxalic acid	10	Rinse in distilled water
	dist. Water	80	Air dry 150F 10 mins.
Copper	Ferric chloride	2	Immerse in etch solution 2 mins. @ RT
	conc. Nitric acid	10	Rinse in distilled water
	dist. Water	88	Air dry at RT
Magnesium	Chromium trioxide	10	Immerse in etch solution 5 mins. @ 160F
	an. Sodium sulfate	0.03	Rinse in distilled water
	dist. Water	89.97	Air dry at 150F
Titanium	Chromium trioxide	1.6	Detergent wash, rinse, dry
	Sodium fluoride	3.2	Immerse in etch solution 5 - 10 mins. @ RT
	conc. Sulfuric acid	16	Rinse in distilled water
	dist. Water	79.2	Oven dry 10 - 15 mins. @ 170F

Notes: Perform the Basic Surface Treatment before the chemical pretreatment. Bond substrates immediately after the surface treatment. RT = room temperature.

Table 2. Chemical Pretreatments for Plastics

Substrate	Etching Solution (composition wt.%)		Pretreatment Conditions
ABS Acetal	conc. Sulfuric acid Sodium dichromate dist. Water	84.2 0.6 15.2	Immerse in etch solution 12 - 15 mins. @ RT Rinse in distilled water Warm air dry
Polystyrene Polyethylene	conc. Sulfuric acid Sodium dichromate dist. Water	88.8 1.5 9.7	Immerse in etch solution 12 - 15 mins. @ RT Rinse in distilled water Warm air dry
Polyester	Sodium hydroxide dist. Water	20 80	Immerse in etch solution 6 mins. @ 170 - 190F Rinse in distilled water Air dry at 150F
Polyamide Nylon	Ethyl acetate Resorcinol	91 9	Immerse in etch solution 8 secs. @ RT Air dry at RT (filtered compressed air)
PTFE	Tetrahydrofuran Naphthalene Sodium (available as a commercial etch)	85.5 12.3 2.2	Immerse in etch solution 15 mins. @ RT Wash in acetone Rinse in distilled water Warm air dry

Notes: Solvent wipe before the chemical pretreatment. Bond substrates immediately after the surface treatment. Physical pretreatment (flame, corona, plasma) are also effective on most plastics. RT=room temperature.

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