Preparing Substrates for the Application of MEGUM™, THIXON™ and ROBOND™ Water-borne Bonding Agents.

Substrate pretreatment

MEGUM™, THIXON™ and ROBOND™ bonding agents are used to bond natural and synthetic rubbers to a variety of rigid, semi-rigid and flexible substrates.

MEGUM W, THIXON and ROBOND TR describe, or in the case of THIXON can describe, water-borne bonding agents. Therefore, cleaning and preparing the substrate surface before the application of these bonding agents is particularly critical for the bonding process. This is based on the fact that water needs an organic-free surface to be able to wet and create an intimate connection with the substrate chemistry. It is impossible to achieve consistent bonding performance between the substrate, the bonding agent, and the rubber unless the substrate is both physically and chemically clean and able to be wetted with water. Hence, it is necessary to create a high surface energy of at least ~45 dyne. Importantly, once the substrate has been cleaned, it must be protected from physical and chemical recontamination before application of the bonding agent.

The purpose of the substrate preparation process is to:
- Provide and maintain a clean, stable substrate bonding surface before the application of two-coat bonding agent primer and cover-cement or single-coat bonding agent system
- Remove oil and grease that could prevent the bonding agent from properly wetting the substrate surface
- Remove contamination, such as oxidative rust, which may fracture and cause bond delamination during the in-service application of the bonded component
- Prevent re-oxidation or recontamination of the freshly prepared substrate bonding surface

Substrates used for bonding

Steel is the most commonly used substrate for rubber-to-metal bonding. Other materials include stainless steel, aluminum, brass, plated metals and alloys. MEGUM, THIXON and ROBOND bonding agents are also used to bond rubbers to plastics including glass reinforced nylons, phenolic and epoxy resins.

Other specialized bonding substrates include natural and synthetic fibers and fabrics, etched PTFE, glass and ceramics, vulcanized and unvulcanized rubbers.

Choice of preparation method

Substrate preparation methods can be either mechanical or chemical, or a combination of both methods. The choice between using mechanical or chemical methods is influenced by considering a number of factors. These include substrate composition, size, number and configuration of components and the in-service application of the bonded component. The resistance of the bonded component to adverse environments and to under-bond corrosion can be affected by the substrate pretreatment process used.

Steel substrates that have been phosphated before bonding agent application, using recommended pretreatment methods, provide the potential to produce bonded components that are resistant to severe in-service environmental conditions. Recommendations for suitable pre-bond and post-bond phosphate treatments can be obtained from DuPont.

This guide gives detailed recommendations as to the preparation of substrates for the successful application of MEGUM, THIXON or ROBOND bonding agents, specifically if water-borne bonding agent systems are of interest.

Substrate Preparation Methods

Process outline

The stages, in regard to using solvent and/or water-borne bonding agents, are pretty similar, although water-borne bonding agents are less forgiving in regard to the insufficient removal of organic contaminants.

The first stage in the pretreatment process is degreasing. This will ensure that the bonding agent primer or single-coat bonding agent will thoroughly wet the substrate surface.

The second stage is removal of contamination – including the oxide layer – from metallic substrates, exposing a fresh, relatively oxide-free surface. Failure to remove an accumulated oxide layer, or a time delay between removal of the oxide layer and subsequent bonding agent primer or single-coat application (allowing re-oxidation of the prepared surface), may lead to in-service delamination of the bond within the oxide layer; the weakest spot in the lamination of rubber, bonding agent layer and substrate. Both mechanical and chemical pretreatment methods are suitable.
Removal of oil and grease

Steel parts for rubber-to-metal bonded components are usually supplied to the user with a protective oil or grease coating to prevent corrosion (rusting) during transport and storage. The first stage in the substrate preparation process is to remove this protective oil or grease layer, thereby ensuring that the MEGUM™, THIXON™ or ROBOND™ bonding agent achieves intimate contact, or, more specifically, is able to “wet” the substrate surface. This step needs to be very thorough when using water-borne bonding agents due to the high surface tension of the ‘solvent’ water.

Water-borne bonding agents are not forgiving in regard to any organic contaminant and will not be able to wet the surface consistently, leaving an uncoated area which creates future metal failure after bonding.

Most mechanical surface pretreatment processes include a vapor degreasing unit in which the oil or grease is removed by contact with the vapor of a suitable organic solvent. The solvent vapor condenses on the part, and the grease or oil is dissolved and removed as the condensed solvent drips back into the liquid degreasing bath.

Chemical pretreatment methods use alkali wash tanks to remove oil or grease, followed by a water rinse to prevent carry-over of contamination into the chemical conversion process tanks. Here, the oil skimmer needs particularly thorough monitoring to ensure close control of the organic contaminants not to be pulled through the complete pretreatment process.

Chemical pretreatments

Chemical pretreatment methods generally use alkali wash tanks to remove oil and grease, followed by a water rinse to prevent carry-over of contamination into the chemical conversion process tanks. For certain types of grease (like animal greases) which resist alkali treatment, alternatives include the solvent degreasing by carbon hydrates or the perchloroethylene degreasing in fully-encapsulated units. Run a lab trial before deciding which degreasing treatment to use. The use of water-borne bonding agents requires a thorough rinsing to ensure all remaining alkaline is removed. Contact DuPont for further recommendations.

Mechanical pretreatments

Mechanical pretreatment methods involve abrasion of the degreased substrate surface to reveal a fresh, clean surface for bonding. The abrasion treatment is used to roughen the area to be bonded, thus increasing the surface area and providing a better anchor for the MEGUM, THIXON or ROBOND bonding agent. Once the surface has been mechanically abraded, it will react very rapidly with atmospheric oxygen, especially in the presence of high humidity. It is important to apply the bonding agent as quickly as possible to reduce the effects of oxidation and possible contamination.

Methods of mechanical pretreatment include wheel abraders or air blast using chilled iron, alumina, silica or corundum grits. Chilled iron or steel grit are not recommended for the preparation of stainless steel or other non-ferrous substrates. Other methods of abrading the metal surface include grinding, wire brushing or emery cloth.
Checklist for Substrate Pretreatment Before MEGUM™, THIXON™ or ROBOND™ Water-borne Bonding Agent Application

Clean and prepare the metal

Clean and prepare the metal by chemical, mechanical or a combination of chemical and mechanical surface pretreatment methods. Certain substrate types require special pretreatment processes. Ensure that the correct and the most appropriate pretreatment method is being used and monitor its performance.

Non-ferrous substrates like stainless steels and plastics should be grit blasted with non-ferrous grits.

Ensure that the prepared substrate surface is degreased before the bonding agent application. If grit blasting pretreatments are used, it is recommended that the substrate bonding surface be degreased before and after grit blasting. The first degreasing operation reduces contamination of the abrasive grit with oil or grease reducing the risk of incorporating oil or grease into the surface during the blasting process. The second degreasing operation finally removes residual oil or grease and remaining dust contaminants resulting from the grit abrasion process.

Handle carefully

Pretreated, degreased components must be handled carefully to avoid recontamination of the bonding surface before applying the MEGUM™, THIXON™ or ROBOND™ bonding agent.

Degreased components should be handled with clean, lint-free gloves to prevent contaminating the bonding surfaces (refer to Pictures 5a–5d for explanation).

Prevent degreased components being contaminated with oil, grease or dust before the bonding agent application. Avoid moisture condensation and ensure that prepared metal substrate components are kept at ambient temperatures. Avoid transferring cold metal components into relatively warm humid atmospheres where condensation of atmospheric moisture vapor is likely to occur.

Avoid delays

One of the crucial stages in the preparation of parts for rubber bonding is the time delay between the end of the pretreatment process and the application of the MEGUM, THIXON or ROBOND bonding agent. It is often during this stage that the final quality of the bonded component is determined. Both mechanically and chemically prepared metals are subject to oxidation and contamination.

Mechanically-prepared metals

Mechanically pretreated metal surfaces oxidize rapidly after treatment due to the dramatically increased surface area. Aluminum, brass and stainless steels oxidize more rapidly than mild steel. Metal substrates will oxidize more quickly in humid and/or acidic atmospheres. Mechanically pretreated components that are subject to atmospheric moisture condensation (typically when relatively cold metal parts are brought into a relatively warm atmosphere in conditions of high relative humidity) will oxidize more quickly.

For steel substrates, a time delay of two hours is acceptable between the pretreatment and the bonding agent application. Some oxidation of the steel substrate will have occurred during this two-hour delay period; however, it should not have progressed to such an extent as to be detrimental to the bonding performance of the component, as long as the recommended precautions on handling, storage and transport have been observed.

The oxidation of mechanically pretreated non-ferrous metals and stainless steel substrates can be extremely rapid. A maximum time delay of 30 minutes should be allowed between pretreatment and MEGUM, THIXON or ROBOND bonding agent application.

For steel parts, as long as the handling, storage and transport conditions are dry and the parts are protected from contamination by oil, grease, dust and other contaminants, it may be possible to exceed the two-hour delay between pretreatment and bonding agent application. For details on metal treatment, see Table 1.
<table>
<thead>
<tr>
<th>Metal</th>
<th>Degreasing and mechanical pretreatment</th>
<th>Chemical pretreatment</th>
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<tbody>
<tr>
<td>Mild steel</td>
<td>Degrease, abrade, degrease and apply MEGUM™, THIXON™ or ROBOND™ bonding agent within two hours.</td>
<td>Phosphate: Aqueous degrease and phosphate.³ Apply MEGUM, THIXON or ROBOND bonding agent as quickly as possible after treatment. Acid pickle: with nitric acid-water rinse, dry and apply MEGUM, THIXON or ROBOND bonding agent as quickly as possible.</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>Degrease, abrade, degrease and apply MEGUM, THIXON or ROBOND bonding agent within 30 minutes. Non-ferrous grits should be used.</td>
<td>Acid pickle: with hydrochloric acid, nitric acid, oxalic acid or chromic acid pretreatments. Apply MEGUM, THIXON or ROBOND bonding agent as quickly as possible after pretreatment.</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Degrease, abrade, degrease and apply MEGUM, THIXON or ROBOND bonding agent within 30 minutes. Non-ferrous grits should be used.</td>
<td>Anodizing or alkali cleaning followed by chromic/sulfuric acid etching.</td>
</tr>
<tr>
<td>Brass or copper</td>
<td>Degrease, abrade, degrease and apply MEGUM, THIXON or ROBOND bonding agent within 30 minutes. Non-ferrous grits should be used.</td>
<td>Acid pickle, or use ammonium persulphate or ferric chloride pretreatments.</td>
</tr>
<tr>
<td>Zinc</td>
<td>Degrease, abrade, degrease and apply MEGUM, THIXON or ROBOND bonding agent within 30 minutes. Non-ferrous grits should be used.</td>
<td>Phosphate or acid pickle, apply MEGUM, THIXON or ROBOND bonding agent as quickly as possible.</td>
</tr>
<tr>
<td>Plated metal</td>
<td>Degrease, lightly abrade, degrease</td>
<td>Etch with dilute acid. Contact DuPont for recommendations.</td>
</tr>
<tr>
<td>Sherardized (Zinc)</td>
<td>Degrease, oil and/or grease may be absorbed into the porous sherardized surface. Ensure thorough degreasing. Lightly abrade.</td>
<td></td>
</tr>
</tbody>
</table>

¹Mechanical treatment methods: abrade to remove surface oxidation and other contaminants. Degrease to remove oil, grease and residual dust from the abrasion process. Recommended abrasives include chilled iron (0.6 to 1.0 mm particle size), alumina (brown, angular 0.7 to 0.9 mm particle size) silica or carborundum grits. Other methods include surface grinding, wire brushing or emery cloth.²Degreasing agents include chlorinated solvents such as perchloroethylene and other high boiling point degreasing solvents. Vapor degreasing processes are preferred.³Chemical treatment methods for mild steel substrates: 1. Aqueous degrease: using acid or alkali treatments 2. Activation 3. Phosphate treatment: zinc or iron phosphate Contact DuPont for specific advice on chemical cleaning and pretreatment processes.
Chemically-prepared metals
Phosphate pretreatments recommended for MEGUM™, THIXON™ or ROBOND™ bonding agents used on bonded metal substrates produce a relatively thin phosphate layer (typically 3 to 5 micrometer). Localized areas of untreated metal can be vulnerable to oxidation. The oxidative process will be accelerated in conditions of high humidity and in the presence of other contaminants either in the atmosphere (acidic components) or as the result of ineffective rinsing of acidic components from the phosphating process itself.

The transport and storage of phosphated parts can be a decisive factor in determining whether oxidation of the bonding surface occurs. Phosphated components should be protected from moisture and other contaminants by being stored in sealed containers before use. If the phosphating process is remote from the bonding agent application location (for example when contract phosphating is being carried out), then particular care should be taken to protect the parts from moisture and other contamination during transport and storage. Phosphated parts should be kept in suitably sealed containers until required for use. A rigid inspection procedure should be adopted for incoming phosphated parts to ensure that corrosion of parts is not occurring.

If the quality of the phosphating process, transport and storage is maintained, and a rigid inspection before use is imposed, then generally a delay of 24 hours between phosphating and bonding agent application is acceptable.

As long as the parts have been correctly treated with phosphate, and they are stored in sealed containers protected from contamination by moisture, dust, oil, grease and other contaminants, then it may be possible to exceed the 24-hour delay period without affecting bonding performance.

Surface contamination
Contamination of the substrate surfaces is a problem common to mechanically and chemically pretreated parts. Protection of parts during storage and transport is important in maintaining the overall quality of the bonded component. The greater the time delay between substrate pretreatment and application of MEGUM, THIXON or ROBOND bonding agents, the greater the possibility of oxidation and/or contamination of the substrate surface by dust, dirt, oils, greases, moisture or mold-release agents.

The location of the pretreatment area can be significant. If possible, isolate the mechanical pretreatment area from the bonding agent application area and this area from the bonding area producing the final part. By adopting this compartmentalization technique, cross contamination of untreated, pretreated, and bonding agent coated parts can be reduced.

Effects of contamination in general
Bond failures can be caused by ineffective or inconsistent substrate pretreatment or due to faults in handling, transport and/or storage procedures.

By analyzing the performance of bonded components, it is usually possible to determine whether failure has occurred as the result of oxidation or contamination of the substrate. Delamination of the bonded component at the bonding agent primer/metal or bonding agent primer/plastic substrate interface could indicate a surface contamination problem. However, substrate contamination can also occasionally affect the bond between the bonding agent primer and the cover-cement. Delamination at the bonding agent/substrate interface is usually associated with a reduction in the expected bond strength.

If bond failures persistently occur, then a full reassessment of the pretreatment process and environment, storage, transport and potential sources of contamination is essential. A reduction in the time delay between pretreatment and application of MEGUM, THIXON or ROBOND bonding agents may be required.

Plastics pretreatment
Plastic substrates often become contaminated with mold-release agents as part of their manufacture. This contamination is usually removed by degreasing, but, occasionally, this is not sufficient. A light grit blast with non-ferrous grit (such as alumina) followed by degreasing is recommended.

Silicone mold-release agents are particularly persistent and difficult to remove. It should be specified to the manufacturer of the plastic parts that silicone-release agents should never be used. For details on plastic pretreatment, see Table 2.
Table 2: Pretreatment of Plastic and Cured Rubber Substrates

<table>
<thead>
<tr>
<th>Plastic</th>
<th>Degrease and mechanical pretreatment</th>
<th>Chemical pretreatment</th>
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<tbody>
<tr>
<td></td>
<td>Vapor degrease</td>
<td>Dip/wipe degrease</td>
</tr>
<tr>
<td>Polyamide (including glass reinforced)</td>
<td>Yes</td>
<td>Acetone or MEK</td>
</tr>
<tr>
<td>Polyester</td>
<td>Yes</td>
<td>Acetone</td>
</tr>
<tr>
<td>Acetal</td>
<td>No</td>
<td>Acetone</td>
</tr>
<tr>
<td>Phenolic resins</td>
<td>Yes</td>
<td>Acetone or MEK</td>
</tr>
<tr>
<td>PTFE</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>No</td>
<td>Methanol or IPA</td>
</tr>
<tr>
<td>Epoxy resin</td>
<td>Yes</td>
<td>Acetone or MEK</td>
</tr>
<tr>
<td>ABS</td>
<td>Acetone</td>
<td>Yes</td>
</tr>
<tr>
<td>Polymide</td>
<td>Acetone or MEK</td>
<td>Yes</td>
</tr>
<tr>
<td>Polyethylene, polypropylene</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>

1 Degreasing agents: the choice of degreasing agent can be critical. Some organic solvents can cause crazing or dissolve certain plastics.
2 Vapor degreasing: perchloroethylene is recommended.
3 Dip or wipe degreasing: MEK is methyl ethyl ketone, IPA is isopropyl alcohol.
4 Grit blasting medium: recommended particle size is between 0.6 and 1.0 mm.
Substrate Cleaning for Application of Water-borne Bonding Agents

As seen in previous sections, it is obvious that for water-borne bonding agents, the cleanliness of the surface to be coated is critical for the success of the application. An easy way to get a first impression on the quality and completeness of the cleaning process is to utilize the ‘water-break-free’ test. Water tends to spread and wet a surface when the surface is clean and has a sufficient surface energy level. In Picture 1, this behavior is clearly seen. Glass or metal can usually be wetted easily. However, in the case of insufficient cleaning or contamination with organic material, it will immediately show insufficient water spreading.

![Contaminated Surface]  ![Clean Surface]

**Picture 1:** Water-break-free test. Insufficiently cleaned surface (left), well-cleaned surface with water film (right).

An additional method to determine surface cleanliness will be explained in more detail in the following paragraphs.

Evaluation of Cleaning Process Effectiveness

This section will cover the explanation of surface energy and surface tension and how they play a role in the application of water-borne bonding agents.

Surface energy and surface tension

In general, surfaces are very interesting, especially if looked at from the perspective of energetic phenomena between phases. Here especially, the surfaces between liquid and air provide very interesting aspects as all partners in each phase are very mobile throughout their own phase. Liquids usually have the tendency to keep their surface as small as possible because this is the only possibility to keep as many molecules as possible inside the bulk material so the amounts of neighboring molecules are maximized. Hence, if gravity is not the determining factor, each liquid will form a sphere, as this represents the smallest correlation between surface and bulk.

Looking at a drop of water on a water-repellent surface, (Picture 2) it becomes obvious how the molecules are energetically pulled to each other by trying to become a sphere. Here, only because of gravitational impact, the sphere is not perfectly shaped. To visualize the interaction of the molecules, especially at the surface of the different phases (water and air), the red and blue arrows indicate the different forces pulling on each molecule along the surface. As the forces within the water molecules overcome the forces applied by the air molecules, the droplet is built to account for the equilibrium of all forces for the optimum of bulk-to-surface correlation.

![Picture 2: Correlation of forces determining the shape of liquids – surface tension.](Picture 2)
For liquids, this phenomenon is called surface tension. It defines the surface energy for liquids. This behavior can be used to determine the surface energy of different materials and/or define whether a surface will be able to be wetted by a certain liquid. Only if the forces between the liquid and solid surface molecules are equal or in a certain range to each other, the forces of the solid material’s surface molecules will be able to stretch the liquid. This is seen as spreading or wetting the surface. One useful indicator of surface energy is to look for the measurement of contact angle between solid surface, air and liquid. If the surface tension of the liquid is known, the surface energy of the solid material can be determined.

Mathematically, this phenomenon of contact angle and the different interactions between the molecules of each area has been described by the Young’s equation (Picture 3):

\[
\cos \theta = \frac{\sigma_{sg} - \sigma_{sl}}{\sigma_{lg}} = \frac{\sigma_{c}}{\sigma_{lg}}
\]

Picture 3: Contact angle – the Young’s equation

\( \theta = \) contact angle  
\( \sigma_{lg} = \) surface tension of the used liquid  
\( \sigma_{sg} = \) surface energy of the solid  
\( \sigma_{sl} = \) energy of interphase  
\( C = \) critical surface energy

(The SI unit N/m for surface energy or J/m² refers to 1000 dyne/cm, which is the most common unit used to describe surface energy.)

To understand this more clearly, Picture 4 shows the contact angle measurement in two extremes. In Picture 4a, the surface energy difference between the liquid and the solid substrate is too high. The surface energy of the solid is lower than the liquid. Clearly, the cohesive forces inside the liquid, the forces which keep the liquid molecules together, are higher than the forces pulling on the liquid molecules when attached to the solid surface. Hence, the droplet is still intact. The contact angle is high, and no wetting is possible. Picture 4b, however, shows the situation where the surface energy of the solid is at a level very close to or higher than the interaction forces between the liquid molecules. Hence, in the contact to the solid, the liquid molecules are pulled towards the solid. The contact angle is small, and the liquid spreads on the surface or is able to wet the surface.

Picture 4a+b: Contact angle and wetting correlation

Using this behavior allows for an easy check on the quality of the surface in regard to being wetted by water, hence evaluating the function of the cleaning process overall.
Here, an additional method to determine surface cleanliness can be employed. The surface in question will show a certain behavior if immersed into water. A set-up is shown in Picture 5a. Using a container filled with water, slowly monitor the surface in question during immersion. Even when fully immersed, the surface will show potential inconsistency of cleaning.

A clean line along the meniscus of the water line can be observed. No irisation or inconsistency on the immersed surface is detected. In this case, the surface is wettable and clean. If the surface is clean and has a surface energy comparable to the surface tension of water (~68-73 dyne/cm; see Table 3) the meniscus will be pulled towards the surface, appearing to be pulled up from the water surface.

Contamination of this surface with a fingerprint, for example, which refers to organic (here fatty) contamination, will provide a different behavior when repeating this test (Picture 5b).

Now the contaminated area will create a surface which can no longer be wetted by water. Hence, the surface energy of that area is lower and cannot overcome the surface tension of water. This will keep the water molecules drawn to themselves, trying to keep a curved surface as seen in the picture/scheme above. It seems that the water surface in this area is pulled inside the bulk water underneath the actual water surface when immersing the metal plate. When fully immersed, depending on the direction of the light source, it will show a different appearance than the remaining (clean) surface. Additionally, little silver “pearls” might appear on the surface. This happens when air is still attached to the surface because water couldn’t wet the surface and replace the air (Picture 5c and 5d).
Looking at Table 4, the listed surface energies indicate the wide range of different potential substrates possible.

As a liquid will only wet surfaces with higher surface energies than their own surface tension, it is obvious that a particular focus on cleaning for high-energy surfaces, like metal or glass, is required to allow a good wetting of water. Conversely, if a low-energy surface is of interest, the surface energy needs to be increased to make it wettable with water. As mentioned above, most commonly, plasma treatment is used, created by either high electrical current or flames. Chemical etching is sometimes utilized to change the surface energy by incorporating oxygen into the surface chemistry.

### Summary

In summarizing the pretreatment guide for using water-borne bonding agents, the following items are critical:

a) As water is a very unique solvent, the pretreatment cleaning process needs to be thorough and controlled.

b) The potential surface to be coated with a water-borne bonding agent needs to be evaluated in regard to being suitable for wetting with water (at minimum 45-50 dyne).

c) Surfaces need to be thoroughly protected and carefully handled after the cleaning has been done to prevent contamination with organics; especially fingerprints (gloves to handle the parts are highly recommended).