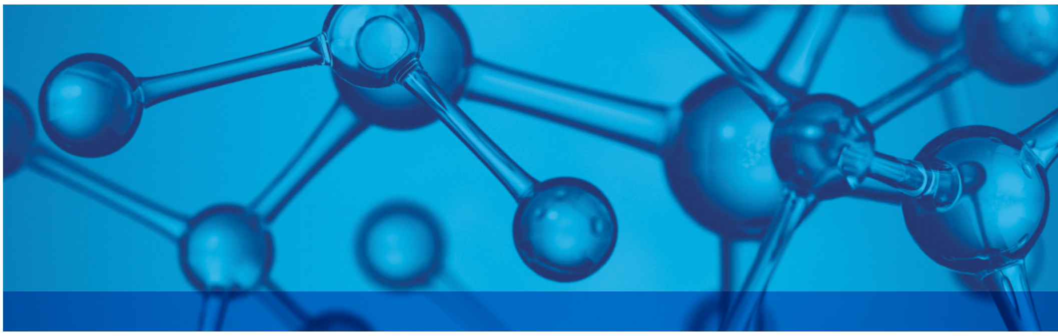

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Bonding Adhesives and Paints to Ryton® PPS

Introduction

Adhesive bonding is a versatile technique for joining like or dissimilar materials. Holes, rivets, clamps and screws have a tendency to cause stress points in concentrated areas which, under certain conditions, can lead to failure of the part. Adhesives, however, tend to distribute the load over a greater area, significantly reducing localized stresses. There are many adhesives that will bond Ryton® PPS (polyphenylene sulfide), providing the surface is properly prepared for good surface wetting by the adhesive. Adhesives should be selected to best meet the needs of the end product application.

Many paint systems can also be used with Ryton® PPS if the surface has been suitably prepared. When selecting the paint, the end use environment must be considered.

This information has been compiled to address inquiries about types of adhesives and paints that may be used with Ryton® PPS compounds, as well as surface treatment techniques to improve their performance.

Adhesive Bonding

For each adhesive bonding situation, the following should be considered:

- The characteristics of the materials to be joined
- Surface preparation required
- Type of joint design
- Type of adhesive and handling requirements
- Application methods
- Method of curing the adhesive
- Strength and environmental performance requirements of the adhesive bonded assembly

With adhesive bonding applications, careful consideration should be given to the part configuration, production requirements, and type of adhesive. The specific natures of various adhesive bonding techniques makes detailed discussion of individual applications impractical. Proper surface preparation to achieve good surface wetting by the adhesive is essential when bonding Ryton® PPS.

Surface Preparation

When bonding one part to another, a high strength bond is necessary to withstand the tensile or shear stresses involved. Likewise, for parts that require painting, a strong bond between the paint and the substrate is needed to prevent peeling. The condition of the Ryton® PPS surface is of primary importance. An "as molded" smooth, shiny surface offers the lowest bond strength, whereas a surface prepared using the various surface treatment methods described herein offers improved bond strength. For a strong bond to Ryton® PPS, contaminants must be removed from the surface, wetting of the surface with the adhesive or paint system is needed, and the viscosity characteristics of the adhesive or paint must be considered.

Surface treatment methods that can be used on Ryton® PPS include mechanical, flame, corona, plasma, and acid. All contaminants, such as grease, mold release agents or oils must be removed from the surface, because they act as weak boundary layers and decrease the strength of the adhesive bond. Solvents such as methyl ethyl ketone (MEK), trichloroethylene, toluene, and acetone may be used to remove such contaminants, but solvents that leave a film residue upon evaporation should be avoided.

Mechanical Treatment

Abrasion (sanding), grit blasting, or bead blasting can be used to roughen a surface for improved adhesion. Unlike chemical treatments that change the wetting ability of the surface, abrasion or grit blasting is strictly a mechanical aid. The roughened surface increases the overall area for adhesive contact, resulting in higher bond strengths. When used in conjunction with one of the treatment methods described below, abrasion or grit blasting will further improve adhesion.

Surface Oxidation

Surface oxidation methods chemically modify the part surface (increase surface energy) to provide better surface wetting and adhesion of whatever adhesive, coating, or paint is subsequently applied. There are a variety of widely used methods of surface oxidation. Flame treatment offers the advantages of ease of operation and economy. Duplicate passes of a part through an optimized flame treatment system will ensure a uniformly high degree of treatment. Corona treatment is not always as effective as flame treatment can be, but is adequate for many applications. Plasma treatment offers a highly effective, long lasting surface treatment. Precautions should always be taken to ensure the surface treatment is protected and maintained until the adhesive, paint, or coating is applied. The effectiveness of surface oxidation may be evaluated by wetting the surface with water. A properly treated surface will wet evenly and hold a film over the entire surface for at least 30 seconds, whereas if the water "beads" and does not coat the entire surface the treatment was inadequate.

Acid Treatment

Acid treatment has been found to be the most effective method of improving adhesive bonding. Chromic acid or nitric acid will etch the surface and effect surface oxidation, providing mechanical and chemical enhancements for adhesive bonding. The disadvantage is that these acids are hazardous materials requiring conscientious safety measures and environmental considerations.

While all of these surface treatment methods may be suitable for adhesive bonding, only the surface oxidation methods are generally practical for painting. Mechanical treatment and acid treatment will likely result in an unacceptably rough surface finish after painting. Further information about these surface treatment methods is provided in Appendices I through V.

Adhesive/Paint Selection

Several factors should be considered when selecting the most suitable adhesive or paint. These include:

- The substrates to be bonded or painted
- Whether the surface is porous or non porous
- The service environment: chemical, thermal, mechanical
- The cure conditions: heat, pressure, time
- Techniques required for application
- Application and handling costs
- Other factors such as color or electrical and thermal properties

Adhesives

Listed below are types of adhesives that may be used for bonding Ryton® PPS, along with some suggested suppliers. Contact information for the suppliers is provided in Appendix VI. When bonding Ryton® PPS to itself or other materials with an adhesive, the strength of the bond is directly related to the method of surface treatment. Careful production control measures to ensure consistent and effective surface treatment procedures will help ensure effective bonding on an on-going basis. Consultation with an adhesive supplier is strongly recommended because the suppliers can help select, modify, or specially formulate adhesive bonding methods for specific applications. The following types of adhesives have been found to be most effective with PPS:

Two-part epoxies

- Best Thermal Stability; up to 121 °C (250 °F)
- Solvent and Moisture Resistant
- Inconvenient Handling and Slowest Curing
  - 3M DP-190 Gray
  - Emerson & Cuming Eccobond 104
  - Lord Corp. Fusor®
  - Three Bond

Two-part and UV curing acrylics

- Less Thermal Stability; up to 100 °C (212 °F)
- Good Moisture Resistance
- Inconvenient Handling, but Fast Curing
  - Loctite Depend 330
  - Loctite 3030
  - 3M DP-8005, DP-8010

Cyanoacrylates

- Least Thermal Stability; up to 80 °C (176 °F)
- Least Moisture and Solvent Resistance
- Low Viscosity and Most Rapid Curing
  - Loctite Prism 401
  - Loctite 4204
  - Loctite Super Bonder 414

Paints

Proper surface preparation allows a variety of paints to be used with Ryton® PPS compounds. Listed below are types of paints that may be used on Ryton® PPS, along with some suggested suppliers. Contact information for the suppliers is provided in Appendix VI. While surface treatment methods will improve adhesion, these paints may sometimes be used with no more surface preparation than a solvent wipe. When selecting a paint system, it is important to consider the service environment of the final part. Many paints can not withstand the environmental conditions for which Ryton® PPS compounds are the materials of choice. The paint manufacturer should be consulted regarding these issues. The following types of paints have been used on PPS:

- Solvent Borne Baking Enamel
  Rohm and Haas Q596
- Water Borne Baking Enamel
  W. C. Richards WKSB-19-601

- Solvent Borne Polyurethane Enamel
  DuPont Imron®
- Solvent Borne Acrylic Enamel
  DuPont Centari®
- Solvent Borne Lacquer
  Rohm and Haas N874
  Red Spot AE type
- Water Borne Lacquer
  Red Spot 296 WLE

Appendix I

Grit Blasting

Grit blasting is an effective method of improving adhesive bonding by pitting the surface to increase overall bonding surface area. The bonding surfaces should be cleaned with a solvent, such as MEK or acetone, prior to grit blasting with the desired grit. Aluminum oxide grit ranging from No. 54 to No. 400 grit size has typically been used. The air pressure should be maintained at or near 2.75 bar (40 psi), and the blast nozzle held 10 to 13 cm (4 to 5 inches) from the part. The blast nozzle should be moved across the part at a rate of 3.8 to 6.4 mm/sec (0.15 to 0.25 inch/sec). To ensure complete and uniform surface treatment, two or more passes can be made across the surface at 90° angles. After the grit blasting is complete, the part should be first blown with pressurized air, then wiped clean with a solvent and dried.

Appendix II

Flame Treatment

Flame treatment accomplishes surface oxidation by exposure to a flame that is fed with excess oxygen. Automated systems for flame treatment are very efficient in cases where the surface requiring treatment is relatively flat and devoid of irregular features. However, the wide variety of applications for Ryton® PPS makes automated systems for flame treatment impractical in many cases. Deep recesses in the part, protruding areas, extreme tapers or other irregularities can prevent accurate control of the distance from the part to the flame tips. In other cases, the relatively small number of parts to be treated may not warrant automated equipment. In these instances, parts may be flame treated using a hand-held burner. To reduce the amount of time required to treat large areas, it is recommended that a burner with at least a 127 mm (5 inch) flame width be used. Burners having much greater flame widths (610 mm, 24 inches) may be used, especially in automated systems. Effective and consistent treatment requires careful control of four critical variables:

- The burner BTU output
- The air/gas ratio of the flame
- The distance from the part to the flame tips
- The burner travel over the part

The optimum burner BTU output and air/gas ratio of the flame are somewhat dependent on the equipment being used. As a general guideline, the optimum treatment levels with the least critical air/gas ratio occur when the burner is operated at about 75 % of its rated BTU output. At least 10 % excess oxygen is required in the air/gas mixture. An appropriate air/gas ratio generally produces pale blue (rather than dark blue) flame tips that extend about 12.7 mm (0.5 inch) from the burner face. The safest equipment employs a venturi mixer or mass flow control valves that will proportionally adjust the gas flow as the air flow is increased or decreased. This allows the BTU output to be easily adjusted without significantly affecting the air/gas ratio, and if the air flow is shut off the flame is instantly extinguished.

The best treating distance is about 12.7 mm (0.5 inch) from the flame tips. This distance can be increased to 50.8 mm (2 inches), but the flame must be moved more slowly. If the flame tips touch the part, streaking will occur and adhesion failures will result. The area should be retreated to remove the streaking. Operator skill is required to maintain the distance required, since the contour of the surface should be followed as closely as possible, just as in spray painting. The speed at which the flame is moved over the surface is the least critical variable. The optimum speed is typically about 9 – 15 m/min (30 – 50 ft/min) or roughly 152 mm/sec (6 in/sec).

After treating, the part should be moderately warm, not hot. Reliability of the treatment can be increased if the surface is treated in one direction, allowed to cool, then treated at an angle 90° to the first pass. This will form a crosshatch pattern. Considerable practice on test parts should be done until familiarity with the technique is developed.

Appendix III

Corona Discharge Treatment

Corona discharge treatment involves exposing the part surface to an ionized atmosphere, or corona, to increase the surface energy. The corona is generated between an anode and ground connected to a high voltage, low amperage generator. The anode and/or ground electrodes are coated with a dielectric material to prevent arcing between the electrodes, resulting instead in ionization of the atmosphere between them. The ionized atmosphere oxidizes the surface of materials in close proximity to the anode. The resin type, geometry of the part, end-use application, and type of treating equipment dictate the optimum treatment parameters, the most critical of which are the power level, treatment period, and physical orientation of the parts in relation to the anode. The assistance of the equipment manufacturer should be sought when establishing treatment parameters. This method requires that the part have a reasonably regular surface, because close proximity of the part surface to the anode (within 1 mm) is essential for effective treatment.

Most commercially available equipment is designed for treatment of film or sheet, however other equipment configurations are available. Cylindrical parts are typically rotated while maintaining the proper clearance between the anode and the part surface. Advantages over flame treatment include no heat generation, glossy surfaces remain intact, and fewer variables to control. Generally, surface oxidation is not quite as effective as with flame treatment.

Appendix IV

Plasma Treatment

Plasma treatment ablates and/or oxidizes the part surface by exposure to diffuse ionized gas (plasma). There is wide flexibility in the design and geometry of chambers for this process. Equipment for batch or continuous processing is available. For processing of small parts or components, the batch system appears more desirable. Since plasma diffuses throughout the system, shadowing effects, or other geometrical restrictions associated with vacuum evaporation or RF sputtering processes, are not of concern. Unlike corona treatment, where the distance from the part to the electrode is very important, plasma treatment is uniform over the entire surface. Since plasma treatment produces no visual effect on the treated surface, masking of parts to preserve aesthetic appearance is unnecessary. Only the material surface is affected, so bulk properties are unchanged, and simultaneous treatment of all surfaces occurs.

Plasma treatment is conducted in a chamber operating at a few torr (mm Hg) pressure of the particular plasma gas to be employed. Fresh gas is continuously fed into the chamber, and waste gases are continually exhausted (in concentrations negligible from hazard and pollution considerations) through a mechanical pump. A plasma is created by irradiating the gas with radio frequency (RF) energy from electrodes properly situated (either internal or external to the chamber) remote from the material to be treated. A uniform atmosphere of ions, electrons, excited species, and free radicals diffuses through the entire volume of the treatment chamber, treating all exposed surfaces of the parts. Air, other oxygen-containing gas mixtures, or nitrogen-containing gases are used when more aggressive treatment is desired, whereas noble gases such as argon or helium will provide a milder treatment. Consecutive treatments with different gases are sometimes employed to achieve specific treatment objectives. Process gas consumption rates vary from a few hundred cubic centimeters per minute to a few liters per minute STP maximum, depending on the chamber size, capacity, and material being treated. Besides the gas or gases used, critical process parameters include the gas flow rates, RF power level, treatment period, and arrangement of parts in the chamber. The assistance of the equipment manufacturer should be sought when determining process conditions. Compared to other plastics, Ryton® PPS compounds generally require relatively severe treatment conditions.

This technique can be used to accomplish much the same results as various wet chemical treatments without the many disadvantages associated with using wet chemical treatments. To improve adhesive bonding, weakly bound polymeric fragments or contaminants on the surface are removed, and improvement of the cohesive strength of the remaining surface is accomplished through oxidation and/or cross-linking reactions. In addition, increasing available surface area through plasma etching further enhances bond strength, replacing mechanical roughening methods with a fine, dry plasma abrasion. Finally, chemical attachment of active functional groups to the polymer surface through free radicals liberated in the plasma can improve adhesion in certain cases.

Appendix V

Acid Treatment

Acid treatment of Ryton® PPS may be accomplished using chromic acid or nitric acid. A typical chromic acid solution is composed of 48.8 mL distilled water, 9.2 g sodium dichromate ($Na_2Cr_2O_7$), and 80 mL concentrated sulfuric acid (H_2SO_4). The sulfuric acid should be slowly added to the mixture of water and sodium dichromate. Nitric acid may be used at concentrations ranging from 5 % to 71 %. Dilution should be performed by slowly adding the acid to water (never pour water into concentrated acid). Lower acid concentrations will require longer immersion times or higher temperatures to effect adequate surface oxidation and etching. Extreme caution is imperative when handling such solutions.

Optimum acid bath temperature and immersion time will vary depending on what Ryton® PPS compound is used, part geometry, and acid strength. Optimum treatment conditions must be determined by trial and error, and caution must be exercised to prevent over-treatment (severe surface degradation due to excessive oxidation). Suggested initial conditions for the chromic acid solution described above are about two minutes at 71 °C (160 °F). Suggested initial conditions for concentrated (71 %) nitric acid are about 30 seconds at room temperature. These are only guidelines for initial trials, and if these conditions affect too little or too much etching, different conditions should be tried. If treatment is not adequate, immersion time, bath temperature, or acid concentration may be increased. If etching is too excessive, immersion time, bath temperature, or acid concentration may be decreased. Bath temperatures above 82 °C (180 °F) are not recommended, and chromic acid concentration greater than described above is not recommended. Proper agitation of the acid bath is essential for uniform treatment. When using chromic acid, agitation should be sufficient to prevent chromic acid crystals from settling. Acid strength will slowly decrease over time (as the reagents are consumed) and longer immersion times may be required when using older acid solutions. Chromic acid solution will turn green when it is completely spent, and should be discarded. In either case, the waste must be disposed of according to applicable safety and environmental regulations.

Parts must be thoroughly rinsed (15 seconds under running water) after treatment to remove all acid contamination from the surface. Treated and rinsed parts should never be wiped dry because it may destroy the surface treatment. Typically, treatment will remain effective for at least one year if the treated (readily wetted) surface is not abraded or contaminated with dust, grease, moisture, etc.

Appendix VI

Adhesive and Paint Suppliers

3M
St. Paul, MN
888-364-3577
www.3m.com

Bostik
Middleton MA
978-777-0100
www.bostik.com

DuPont Performance Coatings
Wilmington DE
248-583-4565
www.performancecoatings.dupont.com

Emerson & Cuming, Inc.
Canton MA
781-828-3300
www.emersoncuming.com

Loctite Corporation
Rocky Hill CT
1-800-LOCTITE
860-571-5100
www.loctite.com

Lord Corporation (Fusor®)
Cary NC
1-800-234-FUSOR
www.fusor.com

Red Spot Paint and Varnish
Evansville IN
812-428-9100
www.redspot.com

Rohm and Haas
Automotive Coatings
Lansing IL
708-474-7000
www.rohmhaas.com

Three Bond
Cincinnati OH
513-779-7300
www.threebond.com

W. C. Richards Company
Blue Island IL
708-385-6633

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