We
THE GOODYEAR TIRE & RUBBER COMPANY

of 1144 East Market Street, Akron, Ohio, United States of America

hereby apply for the grant of a Patent for an invention entitled

"PRIMER SYSTEM FOR FRP BONDING"

which is described in the accompanying complete specification. This application is a Convention Application and is based on the application numbered 960,898

for a patent or similar protection made in United States of America

on 15th November, 1978

Our address for service is:

Care: SPRUSON & FERGUSON
PATENT ATTORNEYS
ESSO HOUSE, 127 KENT STREET
SYDNEY, NEW SOUTH WALES.
AUSTRALIA.

Dated this TENTH day of OCTOBER, 1979,
THE GOODYEAR TIRE & RUBBER COMPANY

Per
Signature of Applicant
Registered Patent Attorney

To:
The Commissioner of Patents
COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952-66

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION
FOR A PATENT OR PATENT OF ADDITION

In support of the Convention Application made for a patent for an invention entitled:
"PRIMER SYSTEM FOR FRP BONDING"

I, Carl Henry Krukow,
in care of The Goodyear Tire & Rubber Company of 1144 East Market Street, Akron, Ohio, United States of America, do solemnly and sincerely declare as follows:

1. I am authorized by The Goodyear Tire & Rubber Company, the applicant for the patent, to make this declaration on its behalf.

2. The basic application as defined by section 141 of the act was made in the United States of America, on the 15th day of November, 1978, by Richard Lee Cline and Alvin Jay Kieft.

3. Richard Lee Cline and Alvin Jay Kieft, U.S. citizens, residing at R D 5, Box 83, Ashland, Ohio 44805 and 1092 Oak Hill Circle, Ashland, Ohio 44805, U.S.A., respectively, are (are) the actual inventor(s) of the invention and the facts upon which said Company is entitled to make the application are as follows:
By virtue of an assignment from the inventor(s) to the said Company.

4. The basic application referred to in Paragraph 2 of this Declaration was the first application made in a Convention country in respect of the invention the subject of the application.


THE GOODYEAR TIRE & RUBBER COMPANY

By Carl Henry Krukow
Administrator, International Patents
1. A method for improving the adhesion between an adhesive of the isocyanate class and a composition selected from the class consisting of polyester, ABS resin and acrylate, comprising treating the surface of the composition with a treating agent composed of a mixture of an organic isocyanate and a tertiary amine and then applying an adhesive of the isocyanate class and curing said adhesive.
THE GOODYEAR TIRE & RUBBER COMPANY

1144 East Market Street, Akron, Ohio
United States of America

RICHARD LEE CLINE and ALVIN JAY KIEFT

Spruson & Ferguson, Patent Attorneys, Esso House,
127 Kent Street, Sydney, New South Wales, 2000 Australia.

"PRIMER SYSTEM FOR FRP BONDING"

The following statement is a full description of this invention, including the best method of performing it known to me/us:
Abstract

An improved adhesion between polyester compositions and using the isocyanate type adhesive is obtained by first treating the composition with a treating agent obtained by mixing an organic polyisocyanate and with a tertiary amine.
Primer System for FRP Bonding

Technical Field

This invention relates to a method of obtaining improved adhesion between compositions such as polyester or acrylate per se and/or metals. More specifically this invention relates to a method of treating the surface of a polyester composition which may contain glass fiber reinforcement to enhance the effectiveness of an isocyanate adhesive.

Background Art

Heretofore, in making laminates between compositions such as polyesters per se and/or metals, it has been customary to clean the surface to be bonded with a suitable solvent to remove greases and other contaminants. This treatment has frequently resulted in a surface that would not give satisfactory bonds for some unknown reason. Therefore, to insure that a satisfactory bond is obtained under all conditions the better practice has been to sandblast the surface of the polyester composition or otherwise abrade it away and then give the surface a solvent wash. It should be readily evident that the use of a sandblasting treatment increases the cost and also presents problems due to the contamination of the surrounding area with the fines from the sandblasting treatment.

The molders of polyester compositions in recent years have tended to add compounding agents such as waxes, polyethylene, polypropylene, or, more broadly stated, unsaturated to saturated polymers or copolymers of olefins of 2 to 20 carbon atoms to give a finished molded polyester composition frequently referred to as a "low profile" molded part. Also, the so-called "low profile" molded polyester composition responds to treatment with the treating agent of this invention to give improved laminates.

In response to these developments it has become
customary to treat the composition of polyester or acrylate with primers of the type disclosed in U. S. Patents 3,703,426, 3,935,051 and 4,004,050.

5 Disclosure of Invention

We have discovered that the first and second treating agents of U. S. Patent 4,004,050 can be mixed together to form a primer that is superior to those customarily used. Therefore it is an object of this invention to provide an improved primer and a method for obtaining improved adhesion between compositions such as polyesters or acrylates per se and/or metals and said composition. This object and other advantages may be obtained by the practice of this invention as will be evident from the ensuing discussion.

The surface of the composition is subjected to a treatment with the treating agent of this invention more fully described hereinafter, or preferably dissolved in a solvent. A suitable adhesive of the isocyanate type is applied to the surface of the composition to be bonded or laminated and the adhesive is allowed to set or cure.

More specifically the polyester compositions are those utilized for constructing panels or built-up objects of substantial rigidity, for instance, the use of solid polyester compositions containing glass fiber reinforcements such as those used in making automobile bodies or parts, boats and related objects are the ones to which this invention has its primary benefit. These polyester compositions may be made by reacting suitable polycarboxylic acids or their anhydrides with suitable glycols such as ethylene, propylene, butylene and higher. For these purposes the polycarboxylic acids of the aromatic type are particularly suitable as they tend to give a more rigid composition. Specific examples of these aromatic polycarboxylic acids are phthalic, isophthalic and terephthalic. Also, unsaturated polycarboxylic acids such as maleic and fumaric are utilized where it is desired to introduce a small to a relatively large amount of unsaturation in the polyester composition, especially
where the composition is to be cured or set by peroxide curing, either alone or in conjunction with an unsaturated monomer or alpha olefin such as styrene or acrylonitrile, etc.

The glass fiber reinforced polyester compositions are well known and are in wide commercial use, but in general these compositions are prepared by forming a copolymer containing maleic anhydride or related unsaturated polycarboxylic acids and one of the phthalic acids or lower aliphatic dicarboxylic acids with ethylene glycol or the other glycols such as di or triethylene glycol.

As indicated heretofore the objects and advantages of this invention are obtained by applying a treating agent composed of a mixture of an organic isocyanate and a tertiary amine to the clean surface of the polyester composition and/or metal, followed by application of the polyurethane adhesive, bringing the polyester composition or metal into laminating contact with another polyester composition until the adhesive has set or cured.

Any of the organic polyisocyanates may be used in combination with a tertiary amine, the treating agent to pre-treat the polyester surface to enhance the adhesion. Representative classes of these are the aromatic, aliphatic and cycloaliphatic diisocyanates and the triisocyanates such as those listed in U. S. Patents 2,917,489 and 3,102,875.

Since the organic polyisocyanates of higher molecular weight and higher isocyanate content are more viscous or even solids the use of a solvent as a vehicle to dissolve, dilute or lower the viscosity aids the control application during the pretreatment to the polyester or metal surface. Suitable and representative vehicles for the organic polyisocyanates are the ketones such as methyl ethyl ketone, acetone, the hydrocarbon distillates, chlorinated solvents such as hydrocarbons and other solvents boiling below about 121° C. and preferably below 150° C.

The second component for forming the treating agent for treating the surface of the composition in accordance with this invention is a tertiary amine of the aliphatic,
cycloaliphatic or heteroaromatic hydrocarbon class. Representative tertiary amines are triethylene diamine, alkyl piperazines, alkyl morpholines and dialkylated lower amines such as triethylamine. The resulting agent or treating agent is preferably dissolved in a suitable solvent such as the ketones or halogenated hydrocarbon solvents although any of the low boiling inert organic liquids in which the amine is soluble may be used. Usually about 0.5 to 5 or more parts of the agent is dissolved in 100 parts of solvent, and depending on the specific activity of the tertiary amine about one to three parts is preferred. This concentration of the treating agent or primer in the solvent allows adhesion to be obtained with the usual application methods. Of course it should be appreciated that higher concentrations, viz., preferably 5 or 10 parts can be used, but difficulty will be experienced in getting a uniform application of the primer to the surface at concentrations above 10 percent, and the cost of the treatment tends to become too expensive.

In general washing of the polyester or acrylate or the metals, for example, steel, copper, aluminum, magnesium and related alloys, is not necessary since the solvent in the treating agent can function to loosen the grease and other contaminants to permit the isocyanate to bond to the solid composition, viz., an FRP or acrylic panel.

An adhesive of the isocyanate class can be prepared by reacting the reactive hydrogen containing materials of about 500 to 4000 with an organic polyisocyanate, a low molecular weight polyamine containing material and preferably an inert filler. The adhesive of the isocyanate class is prepared by forming a prepolymer and then mixing the prepolymer with a curative, the prepolymer being formed by the reaction of the reactive hydrogen containing material. Preferably a polypropylene ether polyol of about 1000 to 3000 molecular weight and an organic polyisocyanate containing at least two and preferably more than an average of two isocyanates per molecule. This prepolymer can contain about five to as much as 70 percent by weight
of a filler based on the reactive hydrogen containing material. One of the prime functions of the inert filler such as clays, silica, etc., is to act as a viscosity increaser and also to hasten the building of green strength or tack in the adhesive. The curative may contain polyhydroxyl terminated materials of relatively low molecular weight, usually less than about 600. Representative of these materials are N,N,N',N'-(2-hydroxylpropyl) ethylene diamine or the adduct formed by reacting a material such as pentaerythritol, trimethylol, propane, trimethylol ethane and the hydroxylated sugars with alkylene oxides such as propylene oxide. These curatives may also contain in addition to the low molecular weight hydroxyl terminated or amine terminated materials a small amount of catalysts such as the tertiary amines or the organic tin compounds. Usually the adhesives of the isocyanate class of a relatively high isocyanate to reactive hydrogen material ratio is in excess of 2.5 and preferably about 5 to 7 mols per mole. The nature of the isocyanate adhesive and the treating agents of the prior art are adequately described in U. S. Patents 3,647,513, 3,703,426 and 4,004,050.

**Best Mode for Carrying Out the Invention**

The nature of this invention may be more specifically exemplified by the following examples wherein all parts are by weight unless otherwise indicated.

**EXAMPLE 1**

A suitable adhesive of the isocyanate class was prepared by reacting the following ingredients: 100 parts of a polypropylene ether glycol of about 2000 molecular weight having dispersed therein 60 parts of talc coated with zinc stearate and an organic polyisocyanate mixture comprising 28 parts of a polyisocyanate A and 32 parts of toluene diisocyanate where polyisocyanate A is the phosgenated mixture obtained by phosgenation of the rearrangement product of the reaction of aniline and formaldehyde as taught in U. S. Patent 2,683,730.

This prepolymer was then mixed in a two compartment
pressure adhesive gun with a curative comprising 30.8 parts N,N,N',N'-(2-hydroxypropyl) ethylene diamine and 13.2 parts of a propylene oxide adduct of pentaerythritol of about 400 molecular weight to form the adhesive.

**EXAMPLE 2**

Primer component A was prepared by mixing 100 parts of polymeric isocyanate (PAPI), 880 parts of methylene chloride, 0.20 part of an azo pigment (yellow) with 20.18 parts of a polypropylene ether glycol of 2000 molecular weight containing 0.18 part of a phenolic type antioxidant (The Goodyear Tire & Rubber Company's Wingstay L).

Primer component B was prepared by mixing 600 parts of methylene chloride, 0.01 part of Sudan Red dye, 0.20 part of triethylene diamine and 0.08 part of diphenyl guanidine.

Ten parts of primer component A was mixed with 40 parts of primer component B to form the primer. This primer was found to be stable for 96 hours at 24°C.

This primer was used to primer test specimens of FRP, ABS and metal by brush coating the surface of each specimen. Then a commercial isocyanate adhesive similar to the type described in Example 1 was applied over the primer coat and the test specimen brought into standard cross lamination position until the adhesive cured. Then cross laminated specimens were subjected to the adhesive pull test under the test conditions shown for the results shown in the table for the specimen listed.

<table>
<thead>
<tr>
<th>Test Condition</th>
<th>FRP to FRP</th>
<th>FRP to Steel</th>
<th>ABS to ABS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room Temperature</td>
<td>49.2 kg/cm²</td>
<td>52.7 kg/cm²</td>
<td>33.7 kg/cm²</td>
</tr>
<tr>
<td>-29°C</td>
<td>50.6 kg/cm²</td>
<td>54.8 kg/cm²</td>
<td></td>
</tr>
<tr>
<td>82°C</td>
<td>32.3 kg/cm²</td>
<td>33.7 kg/cm²</td>
<td></td>
</tr>
<tr>
<td>72 hours 97°C H₂O</td>
<td>38.7 kg/cm²</td>
<td>42.2 kg/cm²</td>
<td></td>
</tr>
<tr>
<td>14 days H₂O Imm.</td>
<td>62.6 kg/cm²</td>
<td>63.3 kg/cm²</td>
<td></td>
</tr>
<tr>
<td>14 days 88°C C.</td>
<td>59.8 kg/cm²</td>
<td>63.9 kg/cm²</td>
<td></td>
</tr>
</tbody>
</table>

All bonds had laminate failure except 83°C bond line test temperature which showed cohesive break in the adhesive. Parts primed with primer 24 hours old gave excellent improvement in adhesion values.

While certain representative embodiments and details
have been shown for the purpose of illustrating the invention it will be apparent to those skilled in this art that various changes and modifications may be made therein without departing from the spirit or scope of the invention.
The claims defining the invention are as follows:

1. A method for improving the adhesion between an adhesive of the isocyanate class and a composition selected from the class consisting of polyester, ABS resin and acrylate, comprising treating the surface of the composition with a treating agent composed of a mixture of an organic isocyanate and a tertiary amine and then applying an adhesive of the isocyanate class and curing said adhesive.

2. The method of Claim 1 wherein the treating agent contains 0.10 to 3.00 mol percent of a polyether polyol of 2 to 3 hydroxyls and a molecular weight of 500 to 4000.

DATED this TENTH day of OCTOBER, 1979

THE GOODYEAR TIRE & RUBBER COMPANY

Patent Attorneys for the Applicant
SPRUSON & FERGUSON