(54) Title: A METHOD OF TREATING GLASS SURFACES WITH COUPLING AGENTS AND RESINS TO PROVIDE AN IMPROVED SURFACE FOR BONDING A FINAL RESIN

(57) Abstract

Use of synthetic resins with glass and glass fibers to produce composite glass structures. In particular, the present invention provides a method for coating glass surfaces with a combination of a reinforcement resin and a coupling agent to produce composites which resist electrical, chemical and mechanical stresses before the incorporation of a final resin. These final coated glass fibers exhibit enhanced stability and resistance to electrical, chemical and mechanical stresses and can be layered and pressed into glass laminate products.
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A Method of Treating Glass Surfaces with Coupling Agents and Resins to Provide an Improved Surface for Bonding a Final Resin

5 Field of the Invention

The present invention relates to the use of synthetic resins with glass and glass fibers to produce composite glass structures. In particular, the present invention provides a method for coating glass surfaces with a combination of a reinforcement resin and a coupling agent to produce composites which resist chemical and mechanical stresses before the incorporation of a final resin. These final coated glass fibers exhibit enhanced stability and resistance to chemical and mechanical stresses and can be layered and pressed into glass laminate products.

Background of the Invention

20 A large number of useful products ranging from automobile windshields to boats, fishing rods, computers and printed circuit boards depend on the adhesion of polymeric resin to glass surfaces in order to withstand
heat, light, mechanical stress, moisture, oxidizing conditions, and other stresses that can affect the use of these products.

From the earliest use of fibrous glass as a reinforcing material, the effects of moisture have been particularly difficult to prevent. Early attempts to reduce the debilitating effects of moisture used waterproofing agents such as silanes and silicones. Later attempts included removing starch-based sizes necessary for handling during processing of yarns into fabrics. Partial removal, caramelizing, and complete removal, coronizing, were investigated.

Later advances consisted of using coupling agents such as reactive silanes and complexes of trivalent chromium to increase the durability and strength of the bonding resin to glass in the presence of moisture and other stressful conditions. A number of theories evolved to explain the mode of action of these coupling agents and processes; most of these theories involved formation of covalent bonds between the coupling agent and the glass surface.

Wetting of the glass surfaces by the resin was considered the necessary step in producing moisture resistant glass composite structures. Heat cleaning was used during this step to increase the wettability of the glass surface, and increased wetting accounted for much of the improved strength obtained by using epoxy laminates in place of unsaturated polyester composites. Today, the generally accepted procedure for producing
stable polymeric glass layered products or glass laminates is to bind the polymeric resin through a coupling agent to form covalent bonds to the glass surface. The wetting requirement has not been reduced, but that procedure alone is not sufficient to give the ultimate strength and permanence desired for today's end use requirements.

A number of dispersed polymers have been used with glass for coatings to bind, protect, color, or adhere glass materials. Examples of such polymers include: polyvinyl alcohol, polyvinyl acetal or butyral, polyvinyl chloride, polyvinylidene chloride, polyvinyl acetate or butyrate, acrylonitrile polymers and copolymers, acrylic ester polymers and copolymers, melamine formaldehyde, phenol-formaldehyde, urea-formaldehyde, silicone polymers and copolymers, both inert and with reactive functional groups. A large number of coupling agents and wetting agents have been used with glass. These have included a number of titanate compounds, chromium complexes, silanes, siloxanes, and polymers thereof, and silicones. In general, these coupling agents are most useful when the processing conditions used are consistent with the formation of hydrolytically stable covalent bonds between the silanol groups of the glass surface and the coupling agent, and between reactive groups at other positions of the coupling agent and reactive groups in the intermediate resin.

Because the final product is preferably linked through a series of covalent bonds, the preservation of reactivity during processing and storage to provide sufficient
reactivity for the final linking step presents a problem. This problem is considered acute because of the instability of the coupling agent to moisture, oxygen, carbon dioxide, high temperatures and external contaminants. This reactivity has been responsible for the deleterious impact that chemical stresses occurring during processing and storage have had on glass laminates of the prior art.

Mechanical stresses have also had a negative impact on the stability of glass laminates in the prior art. Current theories for the failure of composite structures caused by mechanical stress indicate that the interaction between the final or pre-preg resin and the first or reinforcement resin determines much of the response of the material to stress. The layer which provides reinforcement for the final resin should either be highly compliant to reduce localized stresses, or extensible and of intermediate modulus of elasticity (E) to withstand the localized stresses without failure. Both approaches have been shown to improve specific properties in particular circumstances.

There is, therefore, a definite need in the art for a method to produce highly stable intermediate polymeric coated glass surfaces which provide versatility during processing and enhanced stability during storage. There is also a need to develop glass laminate products from these intermediate coated glass surfaces having superior properties for resisting chemical and mechanical stresses during end use.
Summary and Objects of the Invention

In view of the foregoing, it is an object of the present invention to provide a method for producing a storage-stable intermediate resin coated glass product layered with a coupling agent and a reinforcement resin in which the ability to resist the effects of chemical and mechanical stresses during storage and processing into multi-ply laminated glass products has been optimized.

It is also an object of this invention to provide a method for producing a final glass laminate product with superior resistance to electrical, chemical and mechanical stresses that occur during end use.

It is an additional object of this invention to provide a method for introducing onto glass surfaces a layer of coupling agent and reinforcement resin which promotes the stability of active functional groups of the coupling agent and the reinforcement resin for long periods during processing, storage, and transport and aids the pre-preg resin in wetting, so that the coupling agent and the intermediate resin can preferably both react with the pre-preg resin to produce a superior multi-ply laminate glass product.

It is a further object of this invention to provide intermediate resin coated glass products which are storable for periods of at least about 24 hours and can produce multi-ply laminated glass products exhibiting superior characteristics to those of the prior art.
It is a further object of this invention to modify the boundary layer between the pre-preg and reinforcement resins to provide an improvement in the ability of multi-ply laminated glass products to resist mechanical stresses by selecting the type of reinforcement resin and pre-preg resin depending on end use requirements.

It is a further object of this invention to provide multi-ply laminated glass products with superior resiliency to the effects of chemical and mechanical stresses during end use.

**Brief Description of the Invention**

In accordance with the foregoing objectives, this invention provides a method for producing glass surfaces coated with reinforcement resin that are storage-stable. A reinforcement resin coated glass surface which is storage stable is that which can react with a pre-preg resin after being stored for a period of at least about 24 hours under conditions that occur during normal storage and shipping and form a multi-ply laminated glass product exhibiting superior characteristics. The method comprises applying a coupling agent to a glass surface concurrently with, or followed closely by, a compatible reinforcement resin dispersion which can wet and cover, react with, and protect the coupling agent while the surface is in an intermediate stage during processing, transit or storage. Further, the reinforcement resin and coupling agent should also be able to aid in wetting the pre-preg resin for reaction and curing into a finished composite
structure. This invention further provides a superior multi-ply laminated glass product produced by this method. This multi-ply laminated glass product finds particular use in the manufacture of printed circuits, as printed circuit substrates, or as structural or decorative panels.

In the method of the present invention, a glass surface is first coated with a coupling agent that covalently links to the glass surface and either concurrently or shortly thereafter, a first or reinforcement resin is applied to the glass surface and bonded thereto, at least in part, through covalent linkages with the coupling agent to produce a storage-stable intermediate product. Thereafter, a second or pre-preg resin is applied to the intermediate product and covalently linked at least partially to the reinforcement resin, and preferably, also to the coupling agent to produce a final resin product. This final pre-preg resin product may then be stacked and cured to produce a multi-ply laminated glass product. Surprisingly, the pre-preg resin can be strongly bonded to the coupling agent and the reinforcement resin even after long periods of storage of the intermediate product. It is especially surprising that the pre-preg resin can be bonded to the coupling agent and to the reinforcement resin in a manner which provides laminated products of superior strength and quality.

In embodiments of the present invention, the glass substrate may be comprised of glass fabric, filamentous glass or nonwoven fiberglass. A particularly suitable
substrate is Fiberglass OCF™. The surface of the glass substrate may be any dimension that enables coupling agent and polymeric resin to bind to it.

5 The coupling agent in embodiments of the present invention comprises a silane compound containing one or more hydrolyzable groups, or a basic or hydrous derivative of a polyvalent metallic element. The coupling agent can be deposited on the glass surfaces directly when feasible, and can be deposited by exposing the glass surfaces to solutions or suspensions of coupling agent in water or water and organic solvents. It has been found that when the coupling agents of this invention are used in appropriate proportions in the method of the present invention, the resulting product obtained is considerably more stable and resilient to chemical and mechanical stresses than products which do not contain the appropriate quantities of coupling agents.

20 A water or water/organic solvent dispersable reinforcement resin which functions to provide enhanced stability and resilience to the final product may be deposited concurrently with or shortly after the coupling agent onto the glass surface. This reinforcement resin is selected to aid in preserving the coupling agent for subsequent reactions with the pre-preg resin, and for its ability to bind to the pre-preg resin during final processing steps.

25 After the deposit of the coupling agent and reinforcement resin, the storage-stable intermediate
glass products can be processed immediately or stored before final processing. Preferably, the intermediate glass products should be storable under normal conditions of storage and shipping for at least about 24 hours and most preferably, such products should be storable for at least about one week. The coupling agents and reinforcement resins are chosen to provide stability during storage and processing and maximum reactivity of the coupling agent with the pre-preg resins in the final processing stages. During storage, the coupling agents and reinforcement resin are subject to the harmful effects of moisture, light, and atmospheric gases (oxygen and carbon dioxide), oftentimes resulting in a decreased reactivity of the coupling agent with the pre-preg resin and weaker linkages with the reinforcement resin already deposited on the glass surfaces. The reinforcement resin is therefore chosen for its ability to be readily dispersible in water or a combination of water and an organic solvent to protect the coupling agent from the deleterious effects of moisture, heat, atmospheric gases, and external contaminants during storage, and processing, and for its potential to covalently bind with the pre-preg resin during final processing.

The pre-preg resin can be any resin that can form covalent bonds with the reactive groups of the reinforcement resin and/or coupling agent. Of course, the resin can be chosen to elicit the desired physical and aesthetic characteristics of the laminated product, so long as these characteristics are consistent with covalent bonding to the reinforcement resin and/or the
coupling agent.

The various detailed aspects of the present invention are presented in the sections that follow.

Detailed Description of the Invention

In the method of the present application, a glass surface is treated with a coupling agent and a first or reinforcement resin to produce a storage stable intermediate product in which the coupling agent is covalently coupled to the glass surface and the reinforcement resin. The reinforcement resin serves to promote the stability of the coupling agent before reaction of the final or pre-preg resin to form a final pre-preg resin product, and to provide structural integrity to the multi-ply laminated glass product to resist the effects of mechanical and chemical stresses.

Any glass surface reactive with silicon-containing or polyvalent metallic coupling agents can be used in the present invention. A glass surface useful in this invention is any surface containing silicon, silicate, borate, or phosphate or combinations of these units capable of covalently binding to chemical compounds through silanol chemical groups. Preferably, the glass surface is comprised of glass fabric, filamentous glass or Fiberglass OCF™, one or more dimensions of which is about .01 microns to about 100 microns in size.

The silicon-containing or polyvalent metallic compounds which are capable of functioning as the coupling agents
in the method of the present invention should have the following three characteristics:

1) chemical reactivity with the surface of glass under conditions of application and an ability to bond to the glass;

2) selective chemical reactivity with the reinforcement resin and, preferably, with the final or pre-preg resin at the appropriate step in conversion to final product; and

3) formation of chemical bonds at early stages which may be maintained through adverse conditions of storage or further processing as well as in adverse environments encountered by the multi-ply laminated product.

A number of silanes and polyvalent metallic compounds can be used as the coupling agents in the present invention. In general, the coupling agent should contain at least one chemical group reactive with the glass surface directly, or preferably, after this group is hydrolyzed, and one group reactive with the reinforcement resin. The coupling agent, therefore, preferably contains at least two reactive chemical groups, and may contain at least three reactive chemical groups, each chemical group being reactive at a different stage in the formation of the finished product.

The coupling agents are preferably deposited onto the glass surfaces so that the coupling agent comprises
about 0.001% to about 2% of the total weight of the final glass laminate product and most preferably comprises about 0.002% to about 0.3% of the total weight of the final product. The coupling agents can be coated onto the glass surfaces directly where feasible (e.g., if the coupling agent is itself a liquid) or by immersing the glass surface in a solution or suspension of the coupling agent in water or a combination of water and a water miscible solvent. Preferably this solution or suspension is comprised of about 0.05% to about 5% by weight of coupling agent, and most preferably about 0.05% to about 2.0% by weight. At concentrations of less than about 0.05%, the amount of silane is frequently found to be too small to promote adequate binding and structural integrity to the final laminate products, and at concentrations above about 5.0%, coupling agent tends to bond with coupling agent (self-couple) instead of to the glass surface, thus reducing the ability of the coupling agent to bind the glass surface and reinforcement resin.

The coupling agent should contain at least one chemical group which is reactive directly with the glass surface or is a precursor which can be easily manipulated by hydrolysis or other chemical techniques to form a group reactive with the glass surface. The coupling agent should also contain at least one group which is reactive with the reinforcement resin in addition to that which is reactive with the glass surface. The second group serves to covalently bond the reinforcement resin to the glass surface through the coupling agent. Advantageously, the coupling agent may contain at least
two reactive groups in addition to that which is reactive with the glass surface. These groups covalently link the reinforcement resin and the pre-preg resin to the coupling agent.

When silicon-containing coupling agents are used, the first and second chemical groups allow direct reaction of the glass surface and reinforcement resin with the silicon molecule. Preferably, some of these moieties are hydrolyzed to hydroxyl groups (silanol) which can in turn, react directly with the glass surface or may react with reactive groups on the reinforcement resin. These groups include, but are not limited to halogens, hydroxides, hydrogens (silanes) and alkoxide groups (silyl esters) which are easily displaced by the silanol groups on the surface of the glass forming a Si-O-Si bond, or are easily hydrolyzed with water to form a silanol group which can then react with the glass surface to form a Si-O-Si bond. It has been found advantageous to have silanol groups on the coupling agent for coupling to the glass surface, because silanol groups form strong bonds between the coupling agent and the glass surface. Hydrogen containing coupling agents are less preferred, at least in certain applications, because of their tendency to form hydrogen gas during reaction with the silanol groups on the glass surface. In other preferred embodiments the first chemical group is a halogen, hydroxide, hydrogen or alkoxide bound directly to the silicon atom, and the second chemical group is a vinyl, mercapto, halogenated alkyl, hydroxyalkyl, epoxide, or amine among other chemical groups. These groups have been found to be selectively
reactive with functional groups of the reinforcement resin.

In other preferred embodiments of the present invention, 5 the coupling agent contains a third group which does not react during application of the coupling agent or the first polymeric resin, and which is stable to the adverse chemical stresses that occur during storage and shipment before final processing. However, this group does react with or couples to the pre-preg resin during final processing. For these purposes, preferred groups include but are not limited to, amine groups, hydroxyl groups, sulfhydryl groups, halogen groups not bonded to silicon, epoxide groups, and groups containing olefinic unsaturation.

Examples of silicon-containing coupling agents useful in this invention include: vinyltrichlorosilane; vinyltris-(2-methoxyethoxy)silane; gamma-mercaptopropyltrimethoxysilane; gamma-aminopropyltriethoxysilane; Bis-acrylic acid-gamma-aminopropyl triethoxysilane; chloropropyltrimethoxysilane; gamma-methacyrloxypropyl-tris-(2-methoxyethoxy)silane; N-beta(amoineyl)-gamma-aminopropyl trimethoxysilane; Bis-hydroxy-ethyl-gamma-aminopropyl triethoxysilane; beta-(3,4-epoxycyclohexyl)-ethyltrimethoxysilane; vinyltriethoxysilane; methyl [2-(gamma-trimethoxysilylpropyl-amino) ethyl-amino] 3-propionate; gamma-methacyrloxypropyl trimethoxysilane; vinyltriacetoxy silane; gamma-glycidoxypropyl trimethoxysilane; vinyltrimethoxysilane; gamma-
aminopropyl trimethoxysilane; N[2 (Vinylbenzamino)-ethyl]-3-aminopropyl trimethoxysilane; N(beta-aminoethyl) gamma-aminopropyl trimethoxysilane; gamma-aminopropyl trimethoxysilane, beta-3,4(epoxy)cyclohexyl)-ethyl trimethoxysilane; gamma-glycidoxypropyl trimethoxysilane and gamma-methacryloxypropyl trimethoxysilane, among others.

Polyvalent metallic coupling agents preferred for practicing this invention include those compounds containing a trivalent metal ion selected from the group consisting of chromium, cobalt, nickel, copper, titanium and lead, at least one hydroxyl group bonded to the metal ion, and at least one anion of a strong mineral acid attached to the metal. A preferred coupling agent of this type is Volan™ a chromium complex of methacrylic acid. Also preferred in practicing certain aspects of this invention are coupling agents of the Werner type, in which a trivalent atom such as chromium is coordinated with an organic acid containing functional groups which can be used to bind the reinforcement resin or the pre-preg resin to the glass surface. Other Werner complexes of trivalent chromium having vinyl, amino, epoxy, sulfhydryl, hydroxyl or other functional groups, are also preferred in practicing aspects of this invention. Additional preferred coupling agents include titanium complexes containing functional groups capable of reacting with the reinforcement resin. These agents are described in U.S. Patent Nos. 2,611,718, 2,273,040, and 3,993,835 which are incorporated by reference herein.
The reinforcement resins that can be employed in practicing this invention include those resins that can provide protection to the coupling agent in minimizing the harmful effects of chemical stresses that occur during manufacture and storage and can provide structural resiliency to the final product in resisting chemical and mechanical stresses during end use. It is desirable that the reinforcement resins be maximally dispersible in water or water/organic solvent during deposition onto the glass surfaces. This will promote the formation of a thin moisture-proof film. It is preferred that a thin film of reinforcement resin completely coat the coupling agent and glass surface to reduce the effects of moisture, atmospheric gases, and external contaminants as well as insulate the coupling agent from the effects of heat during processing and storage. The coating of reinforcement resin, therefore, must be thick enough to prevent the adverse effects of stresses that occur during processing and storage, yet preferably, be thin enough to allow the pre-preg resin to penetrate filament bundles of the intermediate resin coated glass product to form covalent bonds to the reinforcing resin and the coupling agents during final processing.

The reinforcement resin preferably comprises from about 0.001% to about 6.0% by weight of the final glass laminate product and most preferably comprises about 0.1% to about 2.0% by weight of the solids comprising the final glass laminate product. These proportions are based on coupling agent, reinforcement resin, pre-preg resin and glass being the solids comprising the final
product. Where desirable, cross-linking agents also comprise part of the solids used to form a final product. In general, below about 0.001% by weight of the final glass product, the amount of reinforcement resin is too small to assure protection of the coupling agents during storage, and above about 6.0% by weight solids the amount of resin may be too great to provide mechanical resiliency to the final product or to allow effective penetration of the pre-preg resin into the filament bundles.

The reinforcement resin must be maximally dispersible in a solvent that allows a uniform thin layer to be coated onto the glass surface and coupling agent. Preferably, the solvent is water or a mixture of water and an organic solvent. The type and amount of solvent mixed with water depends on the dispersibility of the resin in water, and the polarity of the resin. Organic solvents that can be used to aid in dispersing the reinforcement resin include any solvent that does not interfere with the reaction with the coupling agent, for example dimethylacetamide, dimethyl formamide, methyl cellosolve, 1,4 dioxane, acetone, tetrahydrofuran, toluene, methylene chloride, and petroleum ether, among others. Dispersions of reinforcement resin are generally comprised of about 0.01% to about 5% resin by weight and are preferably comprised of about 0.1% to about 2% resin by weight.

Any polymeric resin that is dispersible in water or a water/organic solvent mixture and contains functional groups which can react with the coupling agent and the
second or pre-preg resin can be used as a reinforcement resin in applications of the present invention. Preferably, however, the resin is synthetic. The reinforcing resin can be applied to the glass surface after the coupling agent has been coated onto the glass, or can be applied concurrently with the application of the coupling agent.

When silane coupling agents are used, the agents may be coated directly onto the glass surfaces where practical, or may be diluted by solvent and coated onto the glass surface. Any solvent that can solubilize the coupling agent and does not interfere with the glass surface - coupling agent reaction can be used. Preferably, water is used, but other preferred solvents include dimethylformamide, dimethylacetamide, and ether containing solvents such as diethylether, cellosolve solvents, 1,4 dioxane, tetrahydrofuran, and ketones such as acetone, and methyl ethyl ketone, and miscellaneous solvents such as toluene, methylene chloride, and petroleum ether, among others.

The final glass laminates of this invention are produced in three steps. First, the glass surface is reacted with the coupling agent. Second, the glass surface with covalently bonded coupling agent is reacted with the reinforcement resin to form an intermediate product which can be processed immediately or stored. Third, the intermediate product is reacted with the pre-preg resin to produce a final pre-preg resin product comprised of a coupling agent which binds the reinforcement resin to the glass surface, and a pre-preg
resin which binds to the reinforcement resin and preferably, also to the coupling agent. The final pre-preg glass product of this invention can then be stacked and pressed into multi-ply laminated glass products.

It is preferred that the silane-containing coupling agent be treated with water or water/organic solvent prior to and during application of the coupling agent to the glass surface. It is found that the water will hydrolyze silicon-halogen and silicon-alkoxide groups to reactive silicon-hydroxyl (silanol) groups rather readily. It is quite favorable during application of the coupling agent onto the glass surface to have hydroxyl groups bonded to silicon because the hydroxyl groups aid coating of the coupling agent and promote formation of Si–O–Si bonds between the glass surface and the coupling agent. It is apparent that the coupling between a Si–OH containing coupling agent and the Si–OH containing glass surfaces occurs more readily than the reaction between the glass surface and other functional groups on coupling agents. For example, laminates formed from Si–OH containing coupling agents exhibit superior characteristics over laminates formed from coupling agents containing silicon-halogen, silicon-hydrogen or silicon-alkoxide groups which directly react with glass.

Reinforcement resin can be added to the solution containing the coupling agent and reacted concurrently with the reaction of coupling agent. Alternatively, a dispersion of reinforcement resin in water or a combination of water and an organic solvent can be added
to the glass surface to which is already bound coupling agent, and then reacted under the appropriate conditions. Preferably, the coupling agent contains an amino group and the reinforcement resin contains an epoxide group. It is believed that reaction occurs by the amino group opening the epoxide, generally at room temperature or slightly elevated temperature. Conditions depend on the chemistry of the coupling agent and the reinforcement resin, but these conditions are well-known in the art.

The concurrent application of coupling agent and reinforcement resin can be achieved using water or water/organic solvent dispersions, depending on the nature of the reinforcement resin. Wetting agents are sometimes incorporated onto the glass surface along with the coupling agent and reinforcement resin. These agents are useful for wetting during introduction of the pre-preg resin and for softening the products. Examples of such wetting agents that may be employed include, but are not limited to, dioctyl sodium sulfosuccinate (Trade name GR5M from Rohm and Haas), octylphenoxypolyethoxyethanol (Trade name Triton X100 from Rohm and Haas), and alkylarylpolyether alcohol (Trade name Triton X155 from Rohm and Haas).

As previously mentioned, the type of reinforcement resin used in the method of the present invention depends on the nature of the coupling agent used, but is preferably a synthetic resin. It is preferred that the reinforcement resin contain at least two functional groups; one capable of reacting with the coupling agent
and the other capable of reacting with the pre-preg resin. Preferably, the reinforcement resin used in the present invention is a water dispersed/polyepoxy resin containing at least two epoxide functionalities or other reactive functional groups, for example hydroxyl groups. Examples of such polyepoxide dispersions include dispersions of epoxidized phenolic ethers such as the dispersion of the Diglycidyl Ether of Bisphenol A (Tradename CMD 35201 from Celanese Corporation), a dispersion of a urethane epoxide (Tradename W60-5520 from Celanese Corporation), an epoxy dispersion of a polyfunctional, polyaromatic epoxide (Tradename CMD W55-5003 from Celanese Corporation), and water dispersions of difunctional diepoxides for example the diglycidyl ethers of 1,4 butanediol and neopentylglycol (Tradenames WC-67 and WC-68, respectively, from Wilmington Chemical Corporation, Wilmington, Delaware). It is noted that the epoxides are preferred because they are generally dispersible and stable to the solvents employed to provide the most preferred reinforcement layers. The epoxides can also function to bind to the pre-preg resin in subsequent processing steps and are preferred because they are stable to moisture, atmospheric gases, and heat for long periods of time in the absence of catalysts. At a later stage, these epoxide groups can be reacted directly or cross-linked with functional groups on the pre-preg resins.

Other reinforcement resins that can be employed in embodiments of this invention include polyimide resins, polyester resins (saturated or unsaturated) and aldehydic condensation resins, for example, the
condensation product of melamine and formaldehyde, urea and formaldehyde and similar polymers, among others.

After the reinforcement resin is applied to the glass surface, it is dried at elevated temperatures, between about room temperature and about 500°F, preferably between about 250° and 400°F and most preferably about 280-320°F. The intermediate product can then be stored or further processed by treating this intermediate product with a pre-preg or coating resin emulsion.

Pre-preg resins useful in embodiments of this invention include any resin that can covalently bind with the coupling agent, the reinforcement resin, or a cross-linking agent. The pre-preg resins may be solubilized or emulsified with a solvent, preferably a water soluble solvent. Preferred pre-preg resins may include epoxy containing resins, polyesters, polyimides, phenolic resins, vinyl esters, and melamine resins. Examples of such preferred resins include the polyglycidyl ethers, especially those of Bisphenol A, for example, the difunctional epoxide FR4™ of Dow Chemical Company (Commercial name DER -521), tetrafunctional epoxides, for example N,N,N',N'-tetraglycidyl-4,4'-methylenebis-benzenamine (Commercial name Araldite™ MY 720 of Ciba-Geigy), polyimide resins, for example the polyimide amide resin 1,1'-(methylene-di-4,1-phenylene) bismaleimide (Commercial name Keramid 601 of Rhone-Poulenc), polyesters, for example ortho phthalic polyester (Commercial name Polyite™ 31-006 of Reichhold Chemicals, Inc., Jacksonville, Florida), phenolic resins for example 105B4 Resin of Ironsides Company, Columbus,
Ohio and vinylesters, for example Derakane™ Resin of Dow Chemical.

The amount of pre-preg resin incorporated into the final product depends on the desired properties of the final product. Generally, the pre-preg resin comprises about 20% to about 95% by weight of the final product, and preferably about 22% to about 80% of the final product.

To introduce the pre-preg or coating resins onto the coupling agent containing glass surfaces, solutions of pre-preg resins are generally used, but emulsions may also be employed. The preferred solutions of the pre-preg resins generally contain water soluble solvents, preferably with boiling points higher than water. Solvents for solution and deposition of the pre-preg resin are chosen based on the solubility characteristics of the pre-preg resin, the coupling agent, and the reinforcement resin. It is most preferred that the pre-preg resin bind with both the coupling agent and reinforcement resin. To accomplish this, the pre-preg resin must penetrate the protective reinforcement resin layer and react with functional groups on the coupling agent. Thus, a solvent which maximally solubilizes the pre-preg resin, the coupling agent, and the reinforcement resin without affecting the covalent binding between these components will enable this preferred binding to occur. When epoxy resins such as the polyglycidyl ethers of Bisphenol A or the tetrafunctional epoxide Araldite™ MY 720 are used, the preferred solvents are acetone, methyl ethyl ketone, dimethyl formamide, methyl cellosolve, propylene glycol
and methyl ether. When polyimide resins such as Keramid 601 are used, the preferred solvent is N-methyl pyrrolidone. When polyester or vinylester resins such as Polylite™ or Derakane™ are used, the preferred solvent is styrene or methyl methacrylate.

When radical polymerization is used to bond the pre-preg resin with the coupling agent or the reinforcement resin, a radical initiator may be added to the pre-preg solution or may be incorporated within the intermediate resin product by adding the initiator to the reinforcement resin dispersion before depositing the dispersion onto the glass surface. Many of these initiators are not stable for long periods of storage however, and this may limit the length of time an intermediate product can be stored and still provide adequate reactivity for curing the pre-preg resins. Radical initiators useful to promote polymerization of ethylenically unsaturated groups include the peroxides, for example benzyol peroxide, butyryl peroxide, diacyl peroxides, ketone peroxides, perbenzoates, peracetates, among others, peroxy carbonates, for example di-n-propyl peroxydicarbonate, and azo compounds, among others.

Crosslinkers may also be employed to aid the bonding of the pre-preg resins. The cross-linkers are designed to link the pre-preg resin with the reinforcement resin and the coupling agent. Cross-linkers may be employed when the coupling agent or the reinforcement resin contain functional groups which can not form covalent bonds directly with functional groups of the pre-preg resin, for example when the only available functional groups on
the reinforcement resin and the pre-preg resin capable of reacting are hydroxyl groups or other nucleophiles. Similarly, coupling agents can be used when the only functional groups capable of reacting are electrophilic, for example epoxy groups. Cross-linkers used in bridging the functional groups of the reinforcement and pre-preg resins of this invention depend on the type of resins used.

When epoxy resins are to be cross-linked, a number of cross-linkers may be employed, for example metaphenylenediamine, methylenedianiline, and dicyandiamide. When epoxy resins are to be cross-linked through hydroxyl groups, other cross-linkers may be employed, for example, NMA (Nadicmethylnonhydride employed when the laminated products are to be used at high temperatures), pyromelliticdianhydride (also employed when the laminated product is to be used at high temperatures) and chlorendic anhydride (as a fire retardant), among others. The amount of cross-linker employed varies, and depends upon the reinforcement resin used. Ideally, as many of the free (non-reacted) functional groups of the reinforcement resin as possible should be cross-linked with functional groups of the pre-preg resin in the final product. Therefore, the amount of cross-linker used in the final product may vary from about 2% to about 120% by weight of the pre-preg resin used. Often, when cross-linkers are employed, an accelerator such as benzylidimethylamine or other amine is employed to enhance the cross-linking reaction. See, in general, Lee and Neville "Handbook of Epoxy Resins" published by McGraw Hill, 1967, Chapters
After the pre-preg resin has been bound to the reinforcement resin, coupling agent and glass surface, the final glass product of this invention can be stacked and pressed to produce multi-ply glass laminates. These laminates exhibit superior structural characteristics and are very resistant to electrical, chemical and mechanical stresses that may occur during use.

The manner of making and using the present invention will be illustrated further by the following detailed examples. Test methods and materials are generally described in American Society for Testing Materials (ASTM) Publications. A list of certain applicable specifications might include the following documents and others referenced within those standards.

ASTM-D229  Test Procedures for Rigid Insulation
ASTM-D790  Flexural Tests
ASTM-D695  Compression Tests
ASTM-D257  DC Resistance
ASTM-D150  AC Loss Characteristics
ASTM-D149  Dielectric Strength

The machine used for physical strength testing is an Instron, model 1125 with suitable jigs, clamps, and fixtures as required by the specifications and sample types.
EXAMPLE 1

A piece of heat cleaned glass fabric, style 7781 (ASTM Standard), was treated with a silane finish, PAPT (N-phenyl-gamma-amino propyltrimethoxysilane), in the usual manner by dipping glass surfaces into a bath containing about 0.25% of the coupling agent in water at room temperature. The glass fabric was then dried at 325°C for approximately 2 minutes. This fabric was then padded with a 1% by weight solution of polyimide resin (LMB-2429 resin from Ciba-Geigy, Switzerland) in a 70:30 methyl cellosolve: water solvent. The fabric was dried at 300°F for five minutes in an air circulating oven.

The treated fabric was impregnated with a 60% solution of Kerimid 601 in N-Methylpyrrolidone and dried to give a pre-preg. Twelve plies of pre-preg were then stacked and pressed between plates in a heated hydraulic press for 30 min. at 250°F and 1 hr. at 360°F to give a glass-polyimide composite. The composite was post cured for 48 hrs. at 200°C, to produce a material suitable for use in high temperature structural applications.

Other fabrics were treated before impregnation with PAPT without a resin coating and with A-1100 (gamma-amino propyltrimethoxysilane) to show the effect of both the coupling agent change and the resin interlayer effect.
Table 1: Polyimide Laminates Glass Fabric Style 7781 in Kerimid 601 resin

<table>
<thead>
<tr>
<th>Finish</th>
<th>A-1100</th>
<th>PAPT</th>
<th>PAPT with Protective Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plies</td>
<td>12</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Thickness, in.</td>
<td>0.119</td>
<td>0.124</td>
<td>0.118</td>
</tr>
<tr>
<td>Flexural strength, dry, psi After 72 hour boil</td>
<td>58,823</td>
<td>76,756</td>
<td>92,658</td>
</tr>
<tr>
<td>After 88 hrs. @ 250°C</td>
<td>72,275</td>
<td>62,549</td>
<td>80,231</td>
</tr>
<tr>
<td>Compressive strength, dry, psi After 72 hour boil</td>
<td>55,476</td>
<td>56,137</td>
<td>72,442</td>
</tr>
<tr>
<td>psi</td>
<td>62,618</td>
<td>61,263</td>
<td>67,939</td>
</tr>
<tr>
<td>47,859</td>
<td>53,450</td>
<td>60,515</td>
<td></td>
</tr>
</tbody>
</table>

**EXAMPLE 2**

Heat cleaned glass fabric, style 7628 (ASTM Standard), was treated with a dispersion of silane and resin prepared by dissolving 0.5% by weight of A-187 (gamma-glycidoxypropyltrimethoxysilane) in 0.01% acetic acid solution and adding 0.75% resin dispersion in the final bath. A urethane epoxy dispersion (CMD-W-60-5520 from Celanese), was used as the resin dispersion.

The treated fabric was prepregged with Dow Epoxy Resin (DER 521-A-80), dicyandiamide crosslinker and benzylidimethylamine accelerator, stacked, and pressed, a normal procedure for FR-4 laminate production.

A second laminate was produced with the same procedure except a polyfunctional aromatic epoxy dispersion (CMD-W55-5003 from Celanese) was substituted for the urethane epoxy of the earlier trial.
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A third laminate was produced using the same procedure without adding a resin dispersion to the silane solution. The advantage of the resin additions is shown by the enhanced solder dip resistance of the laminates containing resin dispersions in the finish.

Table 2: Epoxy Laminate Data S/7628 DER 521, Dicyandiamide, BDMA Resin System

<table>
<thead>
<tr>
<th>Finish</th>
<th>A-187</th>
<th>Epoxy</th>
<th>A-187</th>
<th>Epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness, ins.</td>
<td>0.063</td>
<td>0.063</td>
<td>0.063</td>
<td></td>
</tr>
<tr>
<td>20 sec. solder dip @ 550°F after 45 mins. steam @ 15 psi delaminated</td>
<td>no effect</td>
<td>no effect</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

20

EXAMPLE 3

Laminates were prepared as in Example 2 with the exception of the drying temperature of the oven after padding of the finish on the fabrics. The critical nature of the drying conditions are shown by the results.

Table 3:

<table>
<thead>
<tr>
<th>Silane</th>
<th>Resin Addition</th>
<th>Drying Temp., °F</th>
<th>Thickness @ 510°F</th>
<th>45 Mins. 15 psi Steam Followed by 20 Sec Solder Dip @ 550°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5% A-187 0.75% CMD-W-60-5520</td>
<td>300</td>
<td>0.063</td>
<td>No damage</td>
<td>No damage</td>
</tr>
<tr>
<td>0.5% A-187 0.75% CMD-W-60-5520</td>
<td>400</td>
<td>0.063</td>
<td>Delaminated</td>
<td>Delaminated</td>
</tr>
<tr>
<td>0.5% A-187 0.75% CMD-W-55-5003</td>
<td>300</td>
<td>0.063</td>
<td>No damage</td>
<td>No damage</td>
</tr>
<tr>
<td>0.5% A-187 0.75% CMD-W-55-5003</td>
<td>400</td>
<td>0.063</td>
<td>Delaminated</td>
<td>Delaminated</td>
</tr>
</tbody>
</table>

40

Example 4
(a) Strips of heat cleaned S/7628 glass cloth were finished with a bath containing 0.125% Z-6032 N-[2(Vinylbenzamino) ethyl] 3-aminopropyltrimethoxysilane as recommended by Dow Corning and 0.75% CMD 35201 (dispersion of a Bisphenol A epoxy resin obtained from Celanese) and dried.

(b) Another group of strips were finished in a similar bath containing 0.5% Z-6032 and 0.75% CMD 35201 and dried.

Both sets of strips were impregnated with a resin solution containing 60% solids made from DER 521 A80 epoxy resin solution (Brominated epoxy resin from Dow Chemical Corporation) with dicyandiamide crosslinker and BDMA accelerator in the normal manner for preparing FR-4 laminates. "B" staging, stacking, and laminating follow well known procedures for high pressure laminating.

Table 4:

<table>
<thead>
<tr>
<th>Finish</th>
<th>% Resin Content</th>
<th>Thickness</th>
<th>@ 510°F</th>
<th>@ 550°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>44.9</td>
<td>0.064</td>
<td>No damage</td>
<td>Delamination</td>
</tr>
<tr>
<td>(b)</td>
<td>44.2</td>
<td>0.064</td>
<td>No damage</td>
<td>Minor measles</td>
</tr>
</tbody>
</table>

The concentration of silane obviously affects the characteristics of the laminate.

EXAMPLE 5

(a) Strips of heat cleaned S/7628 glass cloth were
treated with 0.5% Z-6032 solution (as recommended by Dow Corning) to which had been added 0.5% by weight of XU-238 water soluble hydantoin epoxy resin (from Ciba-Geigy).

(b) A second series of strips were finished as in 5(a) above except that WC-67, diglycidyl ether of 1,4 butanediol, was substituted for XU-238.

(c) A third set of strips was finished in a solution as in example 5(a) with the omission of the resin.

Each of the above strips of fabric was dried as in earlier examples and impregnated, "B" staged, stacked, and pressed by standard procedures.

Table 5:

<table>
<thead>
<tr>
<th>Finish</th>
<th>Resin</th>
<th>% Resin</th>
<th>Thickness</th>
<th>20 Sec. Solder Dip After 45 Mins. in 15 psi Steam @ 510°F</th>
<th>@ 550°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>5(a)</td>
<td>XU-238</td>
<td>39.1</td>
<td>0.063</td>
<td>No defect</td>
<td>No defect</td>
</tr>
<tr>
<td>5(b)</td>
<td>WC-67</td>
<td>43.9</td>
<td>0.063</td>
<td>No defect</td>
<td>No defect</td>
</tr>
<tr>
<td>5(c)</td>
<td>None</td>
<td>44.2</td>
<td>0.063</td>
<td>No defect</td>
<td>Delamination</td>
</tr>
</tbody>
</table>

EXAMPLE 6

Heat cleaned glass fabric, styles 1080 and 113 were treated with a solution of 2 quarts of N[2(Vinylbenzamino)ethyl]-3-aminopropyl trimethoxysilane solution in methanol in 50 gallons of water. The fabric was dried at 325°F for about 1 minute. To a similar finish solution was added 1 quart of XU238 Epoxy resin per 50 gallons. The same fabric styles were padded and dried to produce finished fabric.
Each of the fabric samples was impregnated, "B" staged, stacked and pressed by standard procedures.

5 Table 6: 2 Ply Laminates Electrical Resistivity

<table>
<thead>
<tr>
<th>Style</th>
<th>Resin</th>
<th>1080</th>
<th>1080</th>
<th>113</th>
<th>113</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>none</td>
<td>4.5x10^{15}</td>
<td>1.8x10^{15}</td>
<td>9.2x10^{14}</td>
<td>1.1x10^{15}</td>
</tr>
<tr>
<td>Surface Resistivity, dry, ohms</td>
<td>5.5x10^{13}</td>
<td>8.6x10^{13}</td>
<td>1.1x10^{14}</td>
<td>8.6x10^{13}</td>
<td></td>
</tr>
<tr>
<td>D2/100, ohms</td>
<td>5.5x10^{16}</td>
<td>8.5x10^{16}</td>
<td>1.6x10^{16}</td>
<td>5.2x10^{15}</td>
<td></td>
</tr>
<tr>
<td>15 Volume Resistivity, dry, ohm-cm</td>
<td>1.4x10^{15}</td>
<td>6.8x10^{14}</td>
<td>3.2x10^{15}</td>
<td>1.0x10^{15}</td>
<td></td>
</tr>
<tr>
<td>D2/100, ohm-cm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

This invention has been described in terms of specific embodiments set forth in detail herein, but it should be understood that these are by way of illustration and the invention is not necessarily limited thereto.

25 Modifications and variations will be apparent from the disclosure and may be resorted to without departing from the scope of this invention as those skilled in the art will recognize. Accordingly, such variations and modifications are considered within the scope of this invention.
We claim:

1. A storage-stable intermediate product suitable for the formation of a laminated glass composite comprising a glass substrate having a surface with a coupling agent bonded thereto, and a reinforcement resin bonded to said coupling agent and having reactive groups capable of thereafter reacting with a pre-preg resin so as to form a layer suitable for formation of a laminate, said product being functionally stable for a period of at least about 24 hours.

2. The product according to claim 1 wherein said glass substrate is selected from the group consisting of glass fabric, filamentous glass or non-woven fiberglass.

3. The product according to claim 1 wherein the weight ratio of said reinforcement resin and said coupling agent is about 1:1-10:1.

4. The product according to claim 1 wherein said coupling agent is a silicon-containing chemical compound.

5. The product according to claim 4 wherein said coupling agent is comprised of at least two chemical functional groups one of said groups being covalently bonded to silicon.

6. The product according to claim 4 wherein said group
bonded to silicon is selected from the group consisting of hydroxyl, halogen, alkoxide, and hydrogen.

7. The product according to claim 1 wherein said coupling agent is a hydrous derivative of a polyvalent cation.

8. The product according to claim 7 wherein said polyvalent cation is selected from the group consisting of chromium, titanium, cobalt, nickel, copper and lead.

9. The product according to claim 5 wherein said compound is a trialkoxy silane containing amine groups.

10. The product according to claim 1 wherein said reinforcement resin is selected from the group consisting of a polyepoxide, polyimide, polyester and aldehyde-condensation resin.

11. The product according to claim 10 wherein said polyester resin is unsaturated.

12. A final pre-preg resin product comprising the product of claim 1 and a pre-preg resin covalently bonded to said reinforcement resin and/or said coupling agent.

13. The product according to claim 12 wherein said coupling agent comprises about 0.001% to about 5%
by weight.

14. The product according to claim 12 wherein said coupling agent comprises about 0.002% to about 0.3% by weight.

15. The product according to claim 13 wherein said reinforcement resin comprises about 0.001% to about 5% by weight.

16. The product according to claim 14 wherein said reinforcement resin comprises about 0.1% to about 2% by weight.

17. The product according to claim 15 wherein the weight ratio of said reinforcement resin and said coupling agent is about 1-10:1.

18. The product according to claim 16 wherein said pre-preg resin is covalently bonded to said first resin and said coupling agent.

19. The product according to claim 16 wherein said pre-preg resin comprises about 20% to about 95% by weight.

20. The product according to claim 16 wherein said pre-preg resin comprises about 22% to about 80% by weight.

21. The product according to claim 20 wherein said pre-preg resin is selected from the group
consisting of an epoxide, polyester, polyimide, aldehyde condensation, phenolic or melamine resin.

22. The product according to claim 21 wherein said polyester resin is unsaturated.

23. A multi-ply laminated glass product comprised of the product of claim 12 which has been stacked and pressed.

24. A method of producing a storage-stable intermediate product suitable for the formation of a laminated glass composite comprising the steps of:

   1) covalently bonding a coupling agent to the surface of a glass substrate, and

   2) covalently bonding a reinforcement resin to said coupling agent, said bound reinforcement resin having sufficient unreacted functional groups thereon to enable subsequent reaction with a prepreg resin after periods of storage of at least about 24 hours.

25. The method according to claim 24 wherein said coupling agent is a silicon-containing chemical compound.

26. The method according to claim 24 wherein said bonding steps 1 and 2 occur in a water or a water/organic solvent bath.
27. The method according to claim 25 wherein said coupling agent comprises about 0.05% to about 2% by weight of said bath.

28. The method according to claim 25 wherein said reinforcement resin comprises about 0.1% to about 2% by weight of said bath.

29. The method according to claim 25 wherein said bonding steps 1 and 2 occur in the same bath.

30. The method according to claim 25 wherein the weight ratio of reinforcement resin to coupling agent in said bath is about 1-10:1.

31. The method according to claim 25 wherein said coupling agent is comprised of at least two different chemical functional groups one of said functional groups being covalently bonded to silicon.

32. The method according to claim 31 wherein said group bound to silicon is selected from the group consisting of acyloxy, hydroxyl, halogen, alkoxide and hydrogen.

33. The method according to claim 24 wherein said coupling agent is a hydrous derivative of a polyvalent cation.

34. The method according to claim 33 wherein said polyvalent cation is selected from the group
consisting of chromium, titanium, cobalt, nickel, copper, and lead.

35. The method according to claim 30 wherein said coupling agent is a trialkoxysilane containing amine groups.

36. The method according to claim 24 wherein said reinforcement resin is selected from the group consisting of a polyepoxide, polyester, polyimide and aldehyde-condensation resin.

37. The method according to claim 36 wherein said polyester resin is unsaturated.

38. The method according to claim 24 further comprising depositing a pre-preg resin onto said intermediate product said pre-preg resin covalently binding to said reinforcement resin to produce a final resin product.

39. The method according to claim 38 wherein said prepreg resin covalently binds to said reinforcement resin and to said coupling agent.

40. The method according to claim 38 wherein said coupling agent comprises about 0.001% to about 2% by weight of said final product.

41. The method according to claim 38 wherein said coupling agent comprises about 0.002% to about 0.3% by weight of said final product.
42. The method according to claim 40 wherein said reinforcement resin comprises about 0.001% to about 6% by weight of said final product.

43. The method according to claim 41 wherein said reinforcement resin comprises about 0.1% to about 2% by weight of said final product.

44. The method according to claim 42 wherein said prepreg resin comprises about 20% to about 95% of the total weight of the final product.

45. The method according to claim 42 wherein said prepreg resin comprises about 22% to about 80% of the total weight of the final product.

46. The method according to claim 38 wherein said prepreg resin is selected from the group consisting of a polyester, polyimide, phenolic, aldehyde-condensation, and melamine resins.

47. The method according to claim 46 wherein said polyester resin is unsaturated.

48. The method according to claim 38 further comprising the steps of stacking the final resin product and pressing the stacked product under pressure to produce multi-ply laminated glass products.
# INTERNATIONAL SEARCH REPORT

**International Application No:** PCT/US87/01805

## I. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both National Classification and IPC

<table>
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<tr>
<th>IPC4</th>
<th>B32B 17/04; B05D 7/00</th>
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<td>U.S. Cl.</td>
<td>428/391; 427/407.3</td>
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## II. FIELDS SEARCHED

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<tr>
<td><strong>U.S.</strong></td>
<td>428/288, 391, 426; 427/269, 389.8, 407.3</td>
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched:

## III. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<th>Category</th>
<th>Citation of Document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to Claim No.</th>
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<tr>
<td>Y</td>
<td>US, A, 2,563,288 (OWENS-CORNING FIBERGLASS CORP.) 07 AUGUST 1951. SEE COLUMN 1 TO 2.T</td>
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<td>Y</td>
<td>US, A, 2,720,470 (ERICKSON) 11 OCTOBER 1955 SEE COLUMN 4, LINES 12-34.</td>
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<td>Y</td>
<td>US, A, 3,972,765 (KITACHI CHEMICAL CO., LTD) 03 AUGUST 1976, SEE COLUMN 1, LINES 54-68 TO COLUMN 2, LINES 1-49.</td>
<td>12-23, 38-48</td>
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<td>Y</td>
<td>US, A, 3,993,835 (PPG INDUSTRIES, INC.) 23 NOVEMBER 1976, SEE THE ABSTRACT.</td>
<td>33-34</td>
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* Special categories of cited documents:
  - "A" document defining the general state of the art which is not considered to be of particular relevance
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  - "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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  - "Z" document member of the same patent family

## IV. CERTIFICATION

- **Date of the Actual Completion of the International Search:** 27 AUGUST 1987
- **Date of Mailing of this International Search Report:** 21 SEP 1987
- **International Searching Authority:** ISA/US
- **Signature of Authority Officer:** [Signature]

Form PCT/ISA/210 (second sheet) (May 1986)