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GLASS FIBERS COATED WITH WERNER TYPE COMPLEX AND METHOD OF MAKING SAME

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This invention relates to reinforced synthetic resins or plastics, to a method of producing the same, and to fibrous products especially adapted as the reinforcing medium. More specifically, it relates to a method and product where plastic is reinforced by fibrous material incorporated in or bonded to the plastic.

The invention has as its object a reinforced resin or plastic article of high initial strength which will maintain the greater part of that strength after severe subjection to moisture.

In a patent to Ralph K. Iler for Chemical Process and Product, No. 2,273,040, granted February 17, 1942, there is disclosed the manufacture of complex compounds of the Werner type in which a trivalent nuclear chromium atom is coordinated with an acyclic carboxylic acid group having at least ten carbon atoms. These complexes are disclosed as being initially water soluble, but as becoming water insoluble when dried upon fabric, and as imparting marked hydrophobic characteristics to fabrics on which they are dried.

I have discovered that certain complexes of the Werner type properly applied to the surfaces of reinforcing fibers, such as glass fibers, employed to reinforce plastics greatly aids in maintaining the strength properties of the reinforced plastic in the presence of moisture.

More specifically, I have discovered that the tenacity of the bond between the fibers and plastic may be improved by employing certain unsaturated organic compounds in forming the complex, and that the beneficial results may be obtained with acid groups containing only 3 to 10 carbon atoms as well as with groups containing over ten carbon atoms.

In applications of the invention, complexes are formed by following either of the procedures described in Example IV and Example V of the above identified Iler patent, but employing, in place of stearic acid, various unsaturated acids including methacrylic, crotonic, furoic, furfurylacrylic and sorbic acid, and highly unsaturated acids derived from linseed oil and from oiticia oil, and other unsaturated acids in which the unsaturation is in the alpha to beta position.

A base solution of the complex in isopropyl alcohol was used in each case, the solution containing the complex in amounts equalling 6% of chromium, though other solvents such as ethyl, butyl, or propyl alcohol, and other concentrations, say 1 to 15% might be employed.

The reinforcing fiber may be in any of a number of fabricated forms. For instance, the fibers may be collected into short lengths of strands or yarns that are loosely associated together in masses, or in some cases bonded together by resinous binding materials into webs or mats. Yarns or strands of glass fibers may be interlaced to

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form interwoven or interknitted fabrics, or masses of separated or haphazardly arranged fibers may be bonded together into mats or webs.

Where the fibers are associated together in yarns or strands they are commonly provided with coatings or sizings of a material such as starch, gelatin, polyvinyl alcohol or the like to aid in holding the fibers together in the strand, and also with coatings of oil, waxes, fats or other materials that lubricate the fiber surfaces.

The complex of the present invention may be applied to the fibers of any of the fabricated forms mentioned either by spraying or dipping. Usually a dilute solution of the complex is employed, for example, two parts of the previously mentioned base solution in 98 parts of water, but other concentrations may be employed if desired. The fibrous material is then dried either by exposing it to the air for the necessary length of time or by heating it to temperatures of from about 200° F. for approximately 15 minutes to about 225° F. for two or three minutes. The drying renders the complex insoluble in water.

In most instances it has been found that better results are accomplished if the binder and lubricant ordinarily present on the fiber surfaces is removed prior to application of the complex. This removal may be accomplished by washing the fibrous material with water containing detergents or by cleaning the fibrous material with solvents depending upon the particular type of sizing present on the fiber surfaces. In all cases the sizing is easily removed by heating the fibrous material to temperatures in the neighborhood of 400° to 700° F. for several minutes to decompose and burn off all organic material on the surfaces of the fibers.

The fibrous material treated as just described is then combined with synthetic resins or plastics in conventional manner. Fabrics such as cloth or mats of fibers may be impregnated with resins in liquid state and then superposed in a mold and the resin impregnated cured under heat and pressure. Masses of loosely associated fibers or strands may be collected into preforms by usual practice and the preforms in turn impregnated with the resinous material which is then cured under heat and pressure.

The invention has been found particularly valuable in connection with resins of the low pressure thermosetting, non-condensing type. Resins that may be used with the invention are allyl type resins such as those disclosed in United States Patents Nos. 2,318,959, 2,385,911, and 2,401,549; styrene alkyd resins, for instance those disclosed in Patents Nos. 2,381,969, and 2,397,240; allyl copolymers, for example those disclosed in Patent No. 2,373,067 polymerized mixture of an unsaturated acid such as maleic anhydride with an olefinic compound such as dimethylallyl ether; and

dimethacrylates, for instance, the resins disclosed in Patents Nos. 2,332,461 and 2,379,246. Styrene copolymers, bimethacrylates and styrene-methacrylate copolymers may also be used. Low pressure phenolic resins of the conventional kind are also usable with the present invention. The invention also displays some benefit where natural rubber and synthetic rubber, such as a butadiene acrylonitrile copolymerization product is vulcanized in place on glass fiber surfaces.

While the preferable manner of applying the complex to the fiber surfaces is by the after-treatments referred to above, it is also possible to apply the complexes to the fibers immediately after their formation and as they are collected into strands or mats. In these cases it is desirable to combine the complex with a sizing or binding material for the fibers that is in aqueous solution or dispersion, and to apply the resulting mixture as by spraying or wiping it onto the fibers as they are collected into a strand or by spraying or flowing the mixture onto the fibers as they are collected into a mat. A size or binder of this type may include about 2 to 15% synthetic resin such as methyl methacrylate, polystyrene, phenol formaldehyde, or other resin such as any of those previously mentioned, and .2 to 5% of the 6% base solution of the chromium complex. Examples of fiber-treating compositions of this type are as follows:

Example I

	Per cent
Polyvinyl acetate emulsion (50% solids) -----	5
Methacrylato chromic chloride (6% base solution) -----	2
Water -----	93

Example II

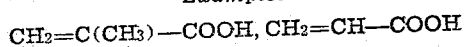
	Per cent
Polybutyl methacrylate (50% water dispersion) -----	15
Furfurylacrylato chromic chloride (6% base solution) -----	5
Water -----	80

This composition is wiped onto the fiber surfaces as they are collected into a strand. The resulting strand may then be twisted and plied with other yarns, the plied yarns woven into cloth, and the cloth employed as the reinforcing fibrous material in a plastic laminate.

The adhesion of the plastic to the fibers, and the consequent initial strength of the laminate or fiber-reinforced article, was found to be increased by each of the complexes employed; but a far greater advantage was the fact that the treatment mitigated the deterioration in strength due to exposure to moisture, and the longer and more severe the exposure to moisture, the more marked became the superiority of the treated laminates.

It is believed that the conjugated group in the complex aids in obtaining a good bond. All unsaturated organic acido groups available for test gave positive results, but preference is given to the monovalent aliphatic acido group with unsaturated carbon-to-carbon linkage adjacent the alpha carbon atom therein.

Examples



Reference is made to my copending application Ser. No. 741,939, filed on April 16, 1947, now Patent 2,552,910 which describes and claims the

broad concept of treating glass fiber surfaces with a Werner type complex compound having an acido group of 1 to 6 carbon atoms which contains a functional group to improve the adhesion of certain materials for the glass fiber surfaces.

While the ultimate object is a strong and moisture-resistant reinforced plastic, it will be readily understood that the fiber of glass or the like, treated with the chrome complex so as to be ready for use as reinforcement for plastics, is likewise an article of commerce, usable for manufacture with plastics into any desired articles.

I claim:

1. An article of manufacture comprising glass fibers and a coating insolubilized on the glass fiber surfaces to render the surfaces more receptive to polyester resins, said coating comprising a complex compound of the Werner type in which a trivalent nuclear chromium atom is coordinated with an unsaturated acido group having from 3 to 7 carbon atoms in which the unsaturated group is between the alpha and beta carbon atoms.

2. An article of manufacture comprising glass fibers and a coating of a copolymer of maleic anhydride and dimethyl ether on the glass fiber surfaces and a complex compound of the Werner type in which a trivalent nuclear chromium atom is coordinated with an alpha, beta unsaturated acido group having from 3 to 7 carbon atoms to improve the adherence of the resinous material to the glass fiber surfaces.

3. An article of manufacture as claimed in claim 1 in which the acido group is a methacrylate.

4. A method of modifying glass fiber surfaces to make them more receptive to polyester resin comprising treating the glass fiber surfaces with a complex compound of the Werner type in which a trivalent nuclear chromium atom is coordinated with an alpha, beta unsaturated acido group having 3 to 7 carbon atoms and insolubilizing the Werner complex compound on the glass fiber surfaces by drying.

5. The method of modifying glass fibers to make their surfaces more receptive to polyester resins comprising treating the glass fibers with a complex compound of the Werner type in which the trivalent nuclear chromium atom is coordinated with an acido group unsaturated between the alpha and beta position and having from 3 to 7 carbon atoms, and baking the treated glass fibers at a temperature of about 225° F. to insolubilize the Werner complex compound on the glass fiber surfaces.

6. The method of modifying glass fiber surfaces to make them more receptive to polyester resins comprising treating the glass fibers with a complex compound of the Werner type in which the trivalent nuclear chromium atom is coordinated with a methacrylate group.

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REFERENCES CITED

The following references are of record in the file of this patent:

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Number	Name	Date
2,273,040	Iler -----	Feb. 17, 1942
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2,544,666	Goebel et al. -----	Mar. 13, 1951