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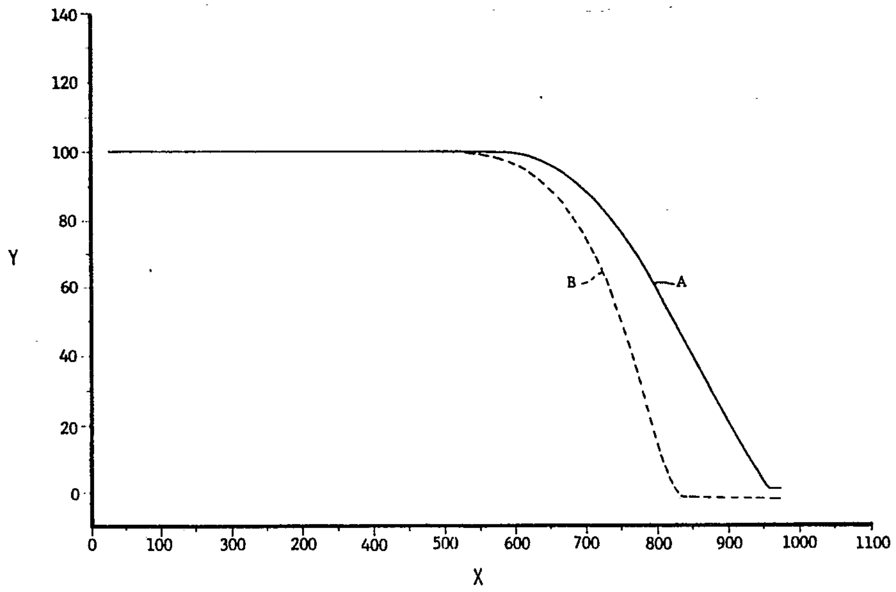
(71) Applicant: **UNITED TECHNOLOGIES CORPORATION**
United Technologies Building 1, Financial Plaza
Hartford, CT 06101(US)

(72) Inventor: **Pike, Roscoe A.**
55 Windmill Drive
Granby Connecticut 06035(US)

(74) Representative: **Schmitz, Jean-Marie et al**
OFFICE DENNEMEYER S.à.r.l. P.O. Box 1502
L-1015 Luxembourg(LU)

(54) Stable amorphous hydrated metal oxide sizing for fibres in composites.

(57) A method of using a polymeric composite wherein the composite exhibits greater oxidative stability. The fiber reinforcement has a layer of amorphous hydrated metal alkoxide formed by deposition onto the fiber and subsequent hydrolysis of metal alkoxides. The improvement comprises exposing the composite to temperatures of about 100° C to about 975° C.



Oxidatively Stable Amorphous Hydrated Metal Oxide Sizing for Composite Fibers

Technical Field

The field of art to which this invention pertains is methods for using composites.

Background Art

Weight saving and manufacturing cost benefits have led to the increase in use of organic matrix fiber reinforced composite structures in the aircraft and aerospace industries. In order to be a viable alternative to metal these composites should maintain the strength typical of conventional structural systems. In many applications composites are put under a variety of environmental and mechanical stresses. For example, frequently these composites are exposed over long periods of time to elevated temperatures which can result in a loss of composite properties. The loss of properties can result from heat induced microcracks that allow oxygen to attack the fibers. As a result of this deficiency, extensive research and development efforts have been undertaken to define methods and identify materials which improve composite performance in elevated temperatures. For example, it is known that surface preparation of fibers can be important in the formation of composites. Thus, the fiber can be coated with an organic primer or sizing agent to produce a surface which with improved handling (i.e., weaveability) and less subject to contamination when combined with the matrix resin develops the strengths which meet application requirements. A variety of sizing agents have been used to produce improved bondability including epoxy, polyimide and polyvinylacetate polymers. In particular, commonly assigned U.S. Patent No. 4,678,820 describes an amorphous hydrated metal oxide primer as a fiber size that provides improved wet strength to a fabricated composite. Although the above surface preparations have provided advantages, there is a need for new technology to aid in the advancement of lightweight aerospace-type composite structures.

Accordingly, there is a constant search in this field of art for new methods of providing lightweight, structurally sound composites.

Disclosure of Invention

The invention is directed to a method of using a polymeric composite wherein the composite exhibits greater oxidative stability. The fiber reinforcement has a layer of amorphous hydrated metal alkoxide formed by deposition onto the fiber and subsequent hydrolysis of metal alkoxides. The improvement comprises exposing the composite to temperatures of about 100° C to about 975° C.

This amorphous hydrated metal oxide sizing for composite fibers provides improved oxidation resistance at elevated temperatures. Thus, this invention makes a significant advance to the aerospace industry by providing new technology relating to structural composites.

The foregoing, and other features and advantages of the present invention will become more apparent from the following description, claims and accompanying drawings.

Brief Description of the Drawings

The Figure graphically depicts the oxidation resistance of unsized graphite fiber and fibers having the sizing of this invention.

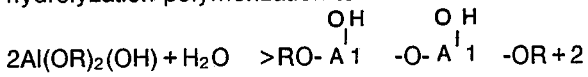
Best Mode for Carrying Out the Invention

Any metal alkoxide that hydrolyzes to give an amorphous hydrated metal oxide (i.e. a monohydroxy metal oxide) may be used in the practice of this invention. Metal alkoxides having the formula $M_x(OR)_y$ where x is 1 and y is 3 or 4 are preferred in forming the metal oxide primer of this disclosure, y being determined by the particular valence of the metal. Typically, a valence of at least 3 is preferable to form a monohydroxy metal oxide. However, alkoxides where y is 2 are preferably combined with alkoxides having higher y values. M is any metal capable of forming a stable alkoxide, which can be purified by, for example, distillation or crystallization without decomposition; as y is defined above essentially all metals meet this requirement. It is preferred that the metal is selected from the group consisting of titanium, zirconium, silicon, nickel, iron and aluminum. It is especially preferred that M is aluminum. Typically, R can be any organic radical that can be distilled at temperatures below about 300° C. Since the alkoxide (-OR moiety) is not incorporated into the primer, the important criteria associated with it is that the resultant alcohol can be volatilized at temperatures that are not high enough to damage the primer or substrate. It is preferred that R is an alkane radical from C_1 to C_{10}. It is especially preferred that R is methyl, ethyl, propyl or sec-butyl as these radicals are volatilized as alcohols at relatively low temperatures. In addition, the alkoxides can be modified by incorporation of varying amounts of additives such as phosphate, silicate or magnesium oxide without affecting the sizing properties. Mixtures of the above metal alkoxides may also be used in the practice of this invention. In addition, partial hydrolyzates of the metal alkoxides can also be used as starting material, i.e., dimers, trimers, etc. of the monomeric alkoxides.

The above metal alkoxides hydrolyze to amorphous hydrated metal oxides (sizing) when exposed to moisture such as atmospheric moisture or moisture on the fiber substrate surface and optionally heat as described below. An exemplary reaction believed to occur is that of aluminum alkoxide to alumina. The initial hydrolyzation reaction of aluminum alkoxides is empirically illustrated as

$Al(OR)_3 + H_2O\ Al(OR)_2(OH) + R(OH)$ (1)

This reaction proceeds rapidly with further hydrolyzation-polymerization to



$2Al(OR)_2(OH) + H_2O \quad > RO\text{-}\overset{OH}{\overset{|}{A1}}\ \text{-}O\text{-}\overset{OH}{\overset{|}{A1}}\ \text{-}OR + 2\ ROH$, etc. (2)

to incorporate n aluminum ions, i.e. $Al_nO_{n-1}(OH)_{(n+2)-x}(OR)_x$ assuming linear polymerization for simplicity. As the reaction proceeds the number of OR groups, i.e. x, relative to n decreases to a value depending on the hydrolysis temperature and available moisture concentration. Under normal application conditions, the ratio of residual OR groups as designated by x is less than 4 and n is 28 or greater. Such low levels of -OR do not impede the performance of the primer. In contrast, zirconium alkoxide is believed to hydrolyze to a hydrated oxide, i.e. $ZrO_2 \cdot 1.7\ H_2O$ having no residual -OR or -OH groups.

The thickness of this primer layer can vary effectively from about 1.5 nanometers (nm) to about 1000 nm. Above about 1000 nm, the layer can be so thick as to create stress risers and to form a weak boundary layer. Below about 1.5 nm, the layer does not provide the properties such as crack propagation resistance and stress transfer at the levels typically required. In addition, it is preferable to apply the primer to the fiber surface with a plurality of layers of metal alkoxide as this facilitates removal of volatiles and solvent which can be more difficult to achieve from a single thick application.

Any fiber may be used in the practice of this invention that is useful for making composite articles. Examples include amide, carbon, metal, boron, glass, silicon carbide, alumina and KEVLAR™ fibers (DuPont DeNemours, E.I., Co., Wilmington, Delaware). Preferably graphite or glass fibers are used as these provide the properties most desired of composites such as strength and light weight. It is especially preferred to use graphite available from BASF as it resists environmental stresses and produces lightweight composites having good strength.

Any conventional resin matrix can be used for the practice of this invention that is useful for making composite articles. Preferably epoxides, bis-maleimides or polyimide resins are used as these provide the properties most desired such as good strength. It is especially preferred to use 3501-6™ resin available from Hercules, Inc. (Wilmington, Delaware) 5208 resin available from Narmco,Arimide N™ resin (E.I. DuPont DeNemours) and LARC-TPI resin (Nasa) as they resist environmental stresses, are strong and are commercially readily available.

Any method of making a composite may be used for the practice of this invention that provides composites having reinforcing amorphous hydrated metal oxide coated fibers. For example, a chopped fiber composite can be made by mixing chopped fibers coated with amorphous hydrated metal oxide and resin in a mold under pressure and optional heat. However, it is preferred to apply a coating of metal alkoxide to the carbon fibers by drawing the fiber through a solution of metal alkoxide. The metal alkoxide coated composite fibers are then maintained at a temperature of about 25°C to about 300°C as below 25°C the reaction kinetics are typically too slow and above 400°C loss of desirable fiber properties or crystallization of the coating may occur with an accompanying loss of mechanical strength. It is especially preferred to heat the aluminum alkoxide coated fibers to a temperature of about 100°C to about 200°C as the lower temperatures minimize the risk of mechanical property degradation of fibers and morphological transformation of the coatings leading to shrinkage and embrittlement. Surprisingly, an increase in temperature from room temperature (R.T.) to about 325°C does not affect an increase in metal alkoxide conversion to amorphous hydrated metal oxide.

Once coated with amorphous hydrated metal oxide, the reinforcing carbon fibers (tows) are dipped into the resin solution to form a tape prior to the molding step. Typically, the resin impregnated fibers are allowed to dry so that any solvent will evaporate. The graphite tape can then be cut into plies (layers of impregnated fibers) of the desired dimensions of the article to be fabricated. The plies are then stacked to create the desired thickness, typically in metal molds coated with mold release agent such as Micro Spray♦ (Micro-Spray Products Inc.). The assembled ply layup is then placed in a press and exposed to pressures and temperatures conventional for the resin system used and application desired.

Example 1

Inorganic primer was applied to unsized, surface treated, Celion 6000 graphite fiber available from BASF Corporation by drawing the fiber tow through a 1% toluene solution of Stauffer Chemical Company aluminum alkoxide, E-8385, and drum winding the coated tows. The resulting wound tape was heated at 200-325° C in an air oven to dry and thus produce the amorphous alumina coating.

The coated fibers and uncoated fibers as controls were tested for high temperature oxidation resistance using thermogravimetric analysis (TGA). The results are depicted in the Figure. In the Figure, percent weight loss (Y) is graphed against temperature in degrees centigrade (X). There is a significant difference in the thermal oxidative stability as shown by curve (A) (treated graphite) in comparison to curve (B) (untreated graphite).

This primer may be used to advantage in a wide range of composites. For example, chopped fiber, filament wound and ordered fiber composites benefit from this primer. While this invention has been described in terms of a metal alkoxide, a mixture of various metal alkoxides can be used.

This sizing coating provides improved oxidation resistance at elevated temperatures. At temperatures of about 100° C to about 975° C, this sizing results in more oxidatively stable fibers and hence composites. The resulting properties such as tensile and flexural strengths of composites made with the inorganic fiber sizing are believed at least equivalent or better than composites made using conventional organic fiber sizing. Yet the inorganic sizing agent can be utilized at thinner layers than the 1.0 wt. % loading of fibers typical of organic sizing. Thicker layers tend to set up stress risers and to form a weak boundary layer as the components segregate. Also, because of its oxidation resistance the inorganic sizing can be used equally as well with high temperature resins such as polyimides or with low temperature resins such as epoxy systems unlike organic sizing agents which are typically temperature specific.

It is also believed that composites using the inorganic sized fibers will have improved wet strength retention, be less subject to microcracking and exhibit improved fracture toughness and impact strength properties. Also, the inorganic insulating sheath will have little, if any, deleterious effect on electrical equipment (e.g., cause shorting) should such a composite disintegrate.

This invention provides an amorphous hydrated metal oxide sizing for fiber reinforced composites resulting in improved oxidation resistance. Thus, it makes a significant advance in the aerospace industry by providing new technology relating to composites.

It should be understood that the invention is not limited to the particular embodiments shown and described herein, but that various changes and modifications may be made without departing from the spirit and scope of this novel concept as defined by the following claims.

Claims

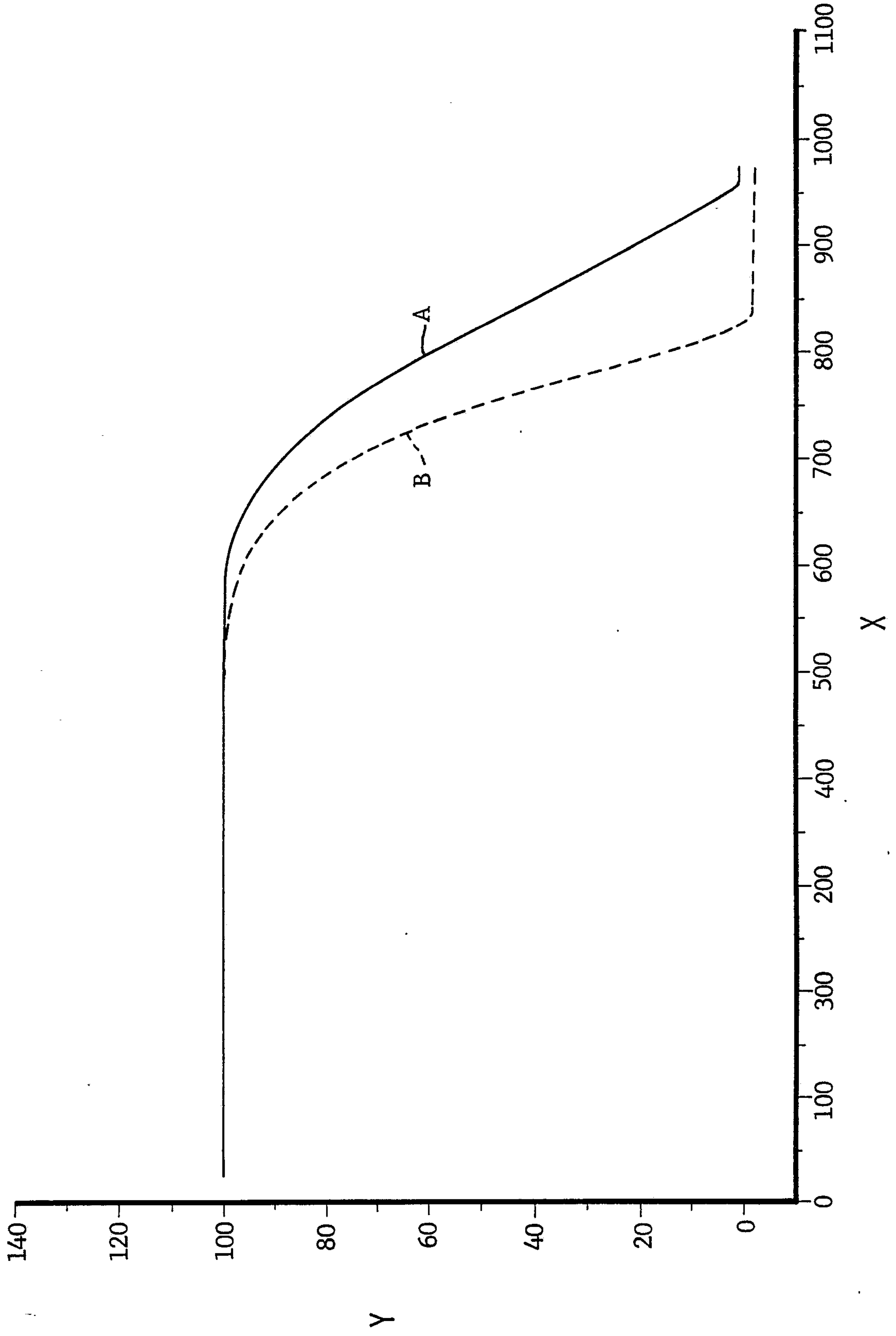
1. A method of using a fiber reinforced polymeric matrix composite material wherein the fiber reinforcement has a layer of amorphous hydrated metal alkoxide formed by deposition onto the fiber and subsequent hydrolysis of a layer of M_xOR_y or combinations thereof where
a) x is 1;
b) y is 2, 3 or 4;
c) M has a valence of 2, 3 or 4; and
d) R is an organic radical;
wherein the improvement comprises: exposing the composite to temperatures of about 100° C to about 975° C wherein the composite has greater oxidative stability.

2. The method as recited in claim 1 wherein M is selected from the group consisting of titanium, aluminum, and silicon and the fiber is selected from the group consisting of graphite, glass, silicon carbide, alulmina, boron and polyaramid.

3. The method as recited in claim 1 wherein the fiber is graphite and M is aluminum.

4. The method as recited in claim 1 wherein the composite is exposed to temperatures of about 500° C to about 975° C.

5. The method as recited in claim 1 wherein M_xOR_y is partially hydrolyzed prior to application of the fiber.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