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(54) Title: METHOD AND COMPOSITION OF PREPARING ENCAPSULATED CERAMIC METAL OXIDES (57) Abstract Described is a method of preparing an encapsulated ceramic metal oxide and/or silicon oxide precursor comprising the steps: providing a ceramic metal oxide and/or silicon oxide precursor composition; providing a heat resistant resin composition; blending the compositions; encapsulating the ceramic metal oxide and/or silicon oxide precursor by the resin; and recovering the encapsulated ceramic metal oxide and/or silicon oxide. Also described are products of the process and the method of bonding fiber glass substrates by utilizing the encapsulated ceramic metal oxide precursor.		

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METHOD AND COMPOSITION OF PREPARING ENCAPSULATED CERAMIC METAL OXIDES

TECHNICAL FIELD

5 The present invention is concerned with encapsulated materials and the manufacture of ceramic metal oxides utilizing sol gel technology as it pertains to delivery systems of the ceramic metal oxide to end uses such as in the fiber glass field.

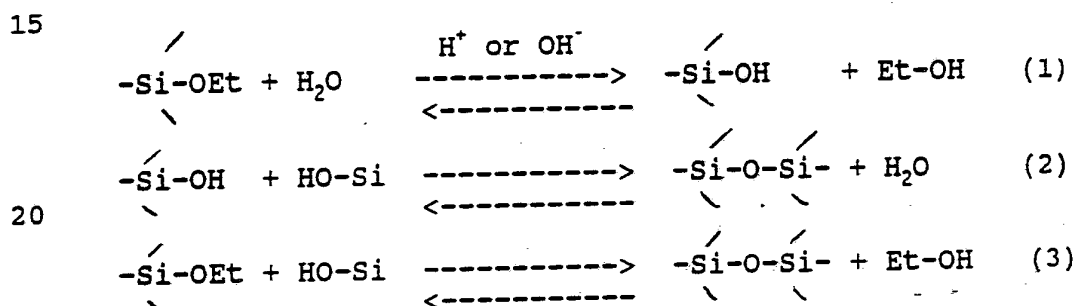
BACKGROUND ART

10 Metal and non-metal alkoxides have limited application as binders for glass or ceramic fibers and as a matrix material for fiber reinforced composites. Such limitation is inherent due to their sensitivity towards moisture, air and ambient temperature and
15 pressure. They tend to become powder or brittle material during or after processing and sintering by loss of solvent and have low flash point, low vapor pressure. For example, tetraethylorthosilicate (TEOS), $\text{Si}(\text{OEt})_4$, has flash point of 103°F, 1-4 mm Hg vapor pressure at
20 20°C, 28.5% SiO_2 and is insoluble in water.

However, these alkoxides have special applications when applied as coating or films on glassy or plastic substrate which has a chemically reactive surface. Ideally, such coatings/films are refractory,
25 corrosive and thermal resistant, electrically insulating and superconducting. In practice, the coating process is typically done in controlled environment such as closed chamber, non-oxidizing atmosphere and at ambient temperature and pressure.

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Typically, these metal or non-metal oxide based coatings are made by the so-called sol-gel process. In this process, alkoxides of network forming cations, e.g., Si, Zr, Al, Ti, B, Ba, etc., are used as glass or ceramic precursors. According to the typical process, silicon alkoxide represented by the general formula $[\text{Si}(\text{OR})_4]$ wherein R typically represents an alkyl radical, are dissolved first in an alcohol solvent and then hydrolyzed by adding water, usually in stoichiometric molar excess amount. Furthermore, the hydrolysis is followed by condensation reaction. The typical hydrolysis (partial or full) and the subsequent oligomerization can be represented by the following equations using silicon alkoxide (e.g., ethoxide) as an example.



Elaborate changes need to be made to accommodate such low flash point monomeric or oligomeric alkoxide materials when applied as a binder or coating on hot glass or ceramic surface, such as in fiber glass manufacturing operation. Such changes seem to be uneconomical and often the product cannot be sprayed, as in conventional spraying of fiber glass with water based organic binders, on hot glass surface in existing environment because of obvious smoke and fire hazards.

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Microencapsulation is described in U.S. Patent No. 3,516,941 (June 23, 1970) by acid catalyzing a urea formaldehyde precondensate and forming the microcapsule cell wall.

5 U.S. Patent No. 4,874,667 describes a micro-encapsulated platinum group metal wherein the encapsulating wall is one or two layers of thermoplastic organic polymers. The microcapsules can be incorporated into storage stable one part polyorganosiloxane composi-
10 tions that cure by platinum catalyzed hydrosilation reaction.

The objective of this invention is to develop a process for the preparation and production of an application of microencapsulated monomeric or oligomeric
15 alkoxide comprising from cations of Si, Al, Zr, Ti, and the like, suitable for use as polymer matrix for fiber reinforce composite and preferably for use as inorganic binder/coating for fiber glass material to enhance thermal resistance of insulated product.

20 The object of the invention is, furthermore, to use high temperature resistant resins, preferably formaldehyde based resin, to encapsulate monomeric or oligomeric metal or non-metal alkoxides. It is impor-
25 tant that such microencapsulated alkoxide based materials could be sprayed in current industrial environment and using the existing machinery without any fire hazard.

It is further important that the controlled release of inorganic binder could be achieved by the
30 application of desired heat or pressure to the sprayed substrate.

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It is an object of the present invention to produce microcapsulated ceramic oxides wherein the encapsulated wall is comprised of heat resistant resins as thermosetting or thermoplastic compositions.

5 It is also an object of the present invention to bind fiberglass compositions utilizing the microencapsulated ceramic metal oxide composition whereby the ceramic metal oxide escapes from the encapsulated wall to thereby coat the individual fibers of the fiber glass
10 composition so that where the coated fibers intersect, the coating forms a bond, thereby binding the fibrous matrix together.

SUMMARY OF THE INVENTION

Described is a method of preparing an encapsu-
15 lated ceramic metal oxide and/or silicon oxide precursor comprising the steps:

providing a ceramic metal oxide and/or silicon
oxide precursor composition;
providing a heat resistant resin composition;
20 blending the compositions;
encapsulating the ceramic metal oxide and/or
silicon oxide precursor by the resin; and
recovering the encapsulated ceramic metal
oxide and/or silicon oxide.

25

DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention is concerned with microencapsulated ceramic metal oxide precursor compositions wherein the encapsulating wall is of a heat resistant resin, e.g., thermoset or thermoplastic

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composition. The starting point for the encapsulated ceramic metal oxide is to prepare ceramic metal oxide compositions, e.g., precursor solutions, that can be inserted within the microencapsulated wall utilizing sol gel technology and encapsulation technology. In general, the metal oxide can be a dispersion, e.g., colloidal, solution or emulsion of one or more ceramic metal oxides which include zirconium oxide, TiO_2 , Cr_2O_3 , WO_3 , ThO_2 , Fe_2O_3 , MgO , Y_2O_3 , ZrO_2 , HfO_2 , V_2O_5 , Nb_2O_5 , UO_2 , BeO , CoO , NiO , CuO , ZnO , In_2O_3 , Sb_2O_3 , Al_2O_3 , SnO_2 , and mixtures thereof such as ZnO--TiO_2 , $\text{TiO}_2\text{--Fe}_2\text{O}_3$, $\text{SnO}_2\text{--TiO}_2$, $\text{Nd}_2\text{O}_3\text{--TiO}_2$, $\text{Al}_2\text{O}_3\text{--Cr}_2\text{O}_3$, $\text{MgO--Al}_2\text{O}_3$, MgO--TiO_2 , MgO--ZrO_2 , $\text{ThO}_2\text{--UO}_2$, $\text{ThO}_2\text{--CeO}_2$, $\text{Bi}_2\text{O}_3\text{--TiO}_2$, $\text{BeO--Al}_2\text{O}_3$, $\text{TiO}_2\text{--Fe}_2\text{O}_3\text{--Al}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{--Cr}_2\text{O}_3\text{--Fe}_2\text{O}_3$, $\text{PbO--ZrO}_2\text{--TiO}_2$, $\text{ZnO--Al}_2\text{O}_3\text{--Cr}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{--Cr}_2\text{O}_3\text{--Fe}_2\text{O}_3\text{--TiO}_2$, and $\text{ThO}_2\text{--Al}_2\text{O}_3\text{--Cr}_2\text{O}_3\text{--Fe}_2\text{O}_3\text{--TiO}_2$. It is also within the scope of this invention to use dispersion or sols of said ceramic metal oxides in combination or admixture with dispersions or sols of one or more metal oxides which are unstable in normal air environment (such as Li_2O , Na_2O , K_2O , CaO , SrO , and BaO) and/or ceramic nonmetal oxides having an atomic number of 14 or greater (such as SiO_2 , As_2O_3 , and P_2O_5), representative combinations including $\text{Al}_2\text{O}_3\text{--Li}_2\text{O}$, $\text{TiO}_2\text{--K}_2\text{O}$, $\text{ZrO}_2\text{--CaO}$, $\text{ZrO}_2\text{--Al}_2\text{O}_3\text{--CaO}$, $\text{ZrO}_2\text{--SrO}$, $\text{TiO}_2\text{--BaO}$, $\text{TiO}_2\text{--ZrO}_2\text{--BaO}$, $\text{Al}_2\text{O}_3\text{--Na}_2\text{O}$, MgO--SiO_2 , $\text{Fe}_2\text{O}_3\text{--BaO}$, $\text{ZrO}_2\text{--SiO}_2$, $\text{Al}_2\text{O}_3\text{--As}_2\text{O}_3$, $\text{ZrO}_2\text{--P}_2\text{O}_5$, $\text{Al}_2\text{O}_3\text{--SiO}_2$, $\text{Al}_2\text{O}_3\text{--B}_2\text{O}_3\text{--SiO}_2$, $\text{Al}_2\text{O}_3\text{--Cr}_2\text{O}_3\text{--SiO}_2$.

A number of the above-described oxides useful in this invention are commercially available in the form of aqueous sols or dry powders which can be readily dispersed in water to form sols, such as Al_2O_3 , Cr_2O_3 and Fe_2O_3 sols sold under the trademark "Nalco", silica sols sold under the trademarks "Nalco," "Ludox," "Syton" and "Nyacol," and Al_2O_3 colloidal powder sold under the

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trademark "Dispal," aluminum oxychloride powder sold under the trademark "Chlorhydrol Micro-Dry," and the like.

Instead of using the precursor material in the form of dispersion or sols of said oxides, it is within the scope of this invention to use the precursor material in the form of water soluble or dispersible inorganic or organic compounds which are calcinable to the corresponding oxide. These compounds representatively include many carboxylates and alcoholates, e.g. acetates, formates, oxalates, lactates, propylates, citrates, and acetylacetonates, and salts of mineral acids, e.g., bromides, chlorides, chlorates, nitrates, sulfates, phosphates, and oxysalts of mineral and organic acids, e.g., oxybromides, oxychlorides, oxychlorates, oxynitrates and oxyacetates, selection of the particular precursor compound being dictated by availability and ease of handling. Representative precursor compounds useful in this invention include ferric chloride or nitrate, chromium chloride, cobalt nitrate, nickel chloride, copper nitrate, zinc chloride or carbonate, lithium propylate, sodium carbonate or oxalate, potassium chloride, beryllium chloride, magnesium acetate, calcium lactate, strontium nitrate, barium acetate, yttrium bromide, zirconium acetate, hafnium oxychloride, vanadium chloride, ammonium tungstate, aluminum chloride, indium iodide, titanium acetylacetonate, stannic sulfate, lead formate, antimony chloride, bismuth nitrate, neodymium chloride, phosphoric acid, cerium nitrate, uranium nitrate, and thorium nitrate. Representative compounds include aluminum oxychloride, aluminum oxynitrate, oxyacetates, and the like.

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The Al_2O_3 precursor can be aluminum alkoxide. The aluminum alkoxides can be those of the aluminum containing materials further comprising hydrocarbyl containing lower alkyl radicals from 1 to 15 carbon atoms, preferably isopropyl. Illustrative materials are aluminum tri-sec-butoxide, aluminum tri-tert-butoxide, aluminum triethoxide, aluminum n-butoxide, aluminum sec-butoxide stearate, aluminum t-butoxide, aluminum di-(sec-butoxide) acetoacetic esterchelate, aluminum di(iso-propoxide, aluminum phenoxide, and the like.

The most preferred material is aluminum oxychloride which on sintering gives the aluminum oxide. Controlled amounts of additives and/or mineralizers are added as sintering aids to reduce the higher temperatures required for grain-growth inhibitors and toughening agents. The additives added most frequently include Fe_2O_3 , Cr_2O_3 , TiO_2 , ZrO_2 , Ga_2O_3 , MgO , Na_2O , K_2O , B_2O_3 and V_2O_3 . ZrO_2 increases the toughness by a grain-boundary-strengthening mechanism by adding up to 0.05 wt% ZrO_2 . The Na_2O , Fe_2O_3 and B_2O_3 reduce the temperature, e.g., of mullite formation and crystallization. B_2O_3 is a preferred mineralizer (concentrations <2%) added to the precursor solution in the form of boric acid.

It is well known to produce ceramic metal oxides utilizing the sol gel technique which techniques need not be reproduced herein.

A preferred sol gel technique to produce the ceramic metal oxide is described in assignee's copending application, U.S. Serial No. _____, Attorney's Docket No. MAN 0199 PUS, filed December 3, 1990. In that application, ceramic metal oxide materials are prepared from a silica containing aqueous

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material which is modified to adjust the ph to acidic ph and then that composition is homogeneously blended with ceramic metal oxide solution or dispersion as described above.

5 The silicon that may be employed either alone or with metal oxides as identified above can generally be characterized as silicon oxides or alkoxides. The silicon oxides can be silicon dioxide or oligomers or polymers thereof. The silicon alkoxides can be those
10 comprised of the silicon containing materials further comprising hydrocarbyl containing lower alkyl radicals from 1 to 6 carbon atoms, preferably ethyl. Illustrative materials are tetramethoxysilane, tetraethoxysilane, methyltrimethoxysilane, ethyltriethoxysilane and
15 amyltriethoxysilane, and the like.

 It is most preferred that the silicon material be colloidal silica which has an acidic ph, preferably a ph of 3-5 when it is reacted with the above identified metal oxides. The colloidal silica is preferably in an
20 aqueous state with a particle size less than 50 nanometers, preferably 0.5-25 nanometers.

 The ph is adjusted from the normal ph of colloidal silica which is basic, usually about 8 to 10 by the use of acidic materials. Any acidic material
25 that does not interfere with subsequent processing steps may be employed whether it be organic or inorganic, although preferably organic acids of less than 6 carbon atoms and even more preferably acetic acid is employed.

 It is preferred that the colloidal silica be
30 a very fine particle size. The silica concentration should be less than 50% and preferably approximately 10-

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30%, and even more preferably, about 20% by weight. The purpose in adding the acidic material is to produce a negative electrostatic charge on the silica particles. Colloidal silica particles exhibit a significant negative electrostatic charge in the ph range of from 3 to 5 and a value within this range is selected for matching with the ph of the aqueous metal oxide solution.

The ph adjusted colloidal silica solution are added to the slurry containing the metal oxide and the mixture is stirred, preferably in the presence of ultrasonic treatment to facilitate the reaction. The colloidal silica particles with a negative electrostatic charge are attracted to the positively charged metal ion (for example the zeta potential for zirconia at a ph of 3-5 is approximately 58-64 millivolts and for alumina at a ph of 3-5 is about 45-50 millivolts).

It is preferred that the ratio of silicon material to metal oxide is from 0.5 to 1.1 (silica calculated as silica dioxide) to 1 (metal oxide calculated as metal dioxide) mole ratio. Most preferably, the mole ratio is 1:1.

When a mullite composition is desired, the metal oxide to silicon dioxide corresponds to the moles of Al_2O_3 to the moles of SiO_2 . Ultrasonic treatment may be utilized for desirable blending. The processing parameters are at ambient temperature and pressure and that the frequency ranges from 0.01 to 1 kilohertz, preferably less than 0.1 kilohertz, e.g., 0.05 to 0.07 kilohertz.

After the silicon containing material and metal oxide containing material are blended together in

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a homogeneous mixture, the concentration ranges from 10 to 80° wt %. The viscosity of the solution or dispersion ranges from 1 to 40 Centipoise (CPS). Thereafter, the solution or mixture of materials which approaches the gel state may be dried prior to blending with the polymeric composition. Preferably, however, the metal oxide sol is blended in the liquid state with the liquid polymer composition.

Turning now to a discussion of the heat-resistant thermoplastic or thermoset compositions that are desired, it is to be appreciated that a wide variety of polymeric materials may be utilized. By "heat resistant" is meant a resin capable of withstanding temperatures of at least 350° F or higher. Lower temperature resins may not permit proper processing in the fiber glass field. Too low a temperature resistance may have the ceramic oxide and/or silicon oxide materials erupt from the ruptured resin wall because the resin could not withstand the heat. Suitable materials may be crystalline polypropylene, urea formaldehyde polymers, phenolformaldehyde polymers such as phenolic resins, melamine resins, e.g., melamine formaldehyde resins, melamine urea-formaldehyde resins, polyimides, polybenzimidazole, polyphenylquinoxaline, polyamide-imides, polyarylsulfone, poly(arylethersulfone), polyphenylene, aromatic polyester, polyamides as aromatic polyamide, polyphenylene sulfide, acrylic and methacrylic acid and esters and copolymers thereof with vinyl materials as styrene, vinylchloride, and the like. The most preferred however are the least expensive such as the formaldehyde resins and the phenolic resins.

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The thermoplastic or thermosetting compositions may be available as solutions, dispersions or emulsions of the various resinous compositions.

5 Encapsulation techniques are well known in the art. See, for example, U.S. Patent No. 3,516,941, describing encapsulation by acid catalyzing a urea-formaldehyde precondensate and forming the microcapsule cell wall.

10 In blending together the ceramic metal oxide and/or silicon oxide precursor solutions and the polymer composition, it is preferred that this be conducted at ambient temperature and pressure. It is to be appreciated, however, that in order to obtain suitable processing conditions, the temperatures may need to be in-
15 creased to less than boiling temperature of the various materials, and correspondingly, the pressure may need to be increased or decreased to above or below atmospheric pressure to improve the solubilizing/mixing processing conditions.

20 In the process of the present invention, the two liquids, the one being the aqueous metal oxide and/or silicon oxide precursor solution and the second being the resinous composition are blended together. Due to the relative immiscibility or insolubility of the
25 metal oxide liquid, the wall of the polymeric material forms about the metal oxide precursor solutions. Thereafter, the encapsulant is cured and solidified. Curing by heating or by other mechanisms such as adjustment of ph of the solution or addition of cross-linking agents
30 may be utilized providing the agents have no detrimental effect on the ceramic metal oxide precursor solutions.

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Cooling of the thermoplastic material will solidify the wall about the ceramic oxide and/or silicon oxide. Thereafter, the product is obtained by evaporating to dryness the composition or by separating out by filtration or other separation techniques the encapsulated metal oxide composition. Once the materials have been separated, increasing the temperature will cause the thermosetting composition to cure further about the ceramic metal oxide materials. In general, due to the nature of the polymeric material, curing may be done by the application of heat. These materials have a curing temperature of at least 350°F.

While applicant does not wish to be bound to any theory, it is believed that due to the presence of labile hydrogen atoms (see equations (1)-(3) above) in the silicon containing ceramic compositions that there may be an affinity or a grafting or bonding of the ceramic material to a portion of the resinous encapsulating shell.

Once the oligomeric network of a least partially hydrolyzed metal alkoxide is formed, it is most likely that the reactive functional groups of polymeric microcapsule cell wall may further react with it to form a graft polymer.

Thus, in accordance with a preferred embodiment of the present invention, the resulting polymeric network of at least partially hydrolyzed metal alkoxide may be further reacted with a reactive substance of the resinous material represented by the general formula:

$$R'_n X_n$$

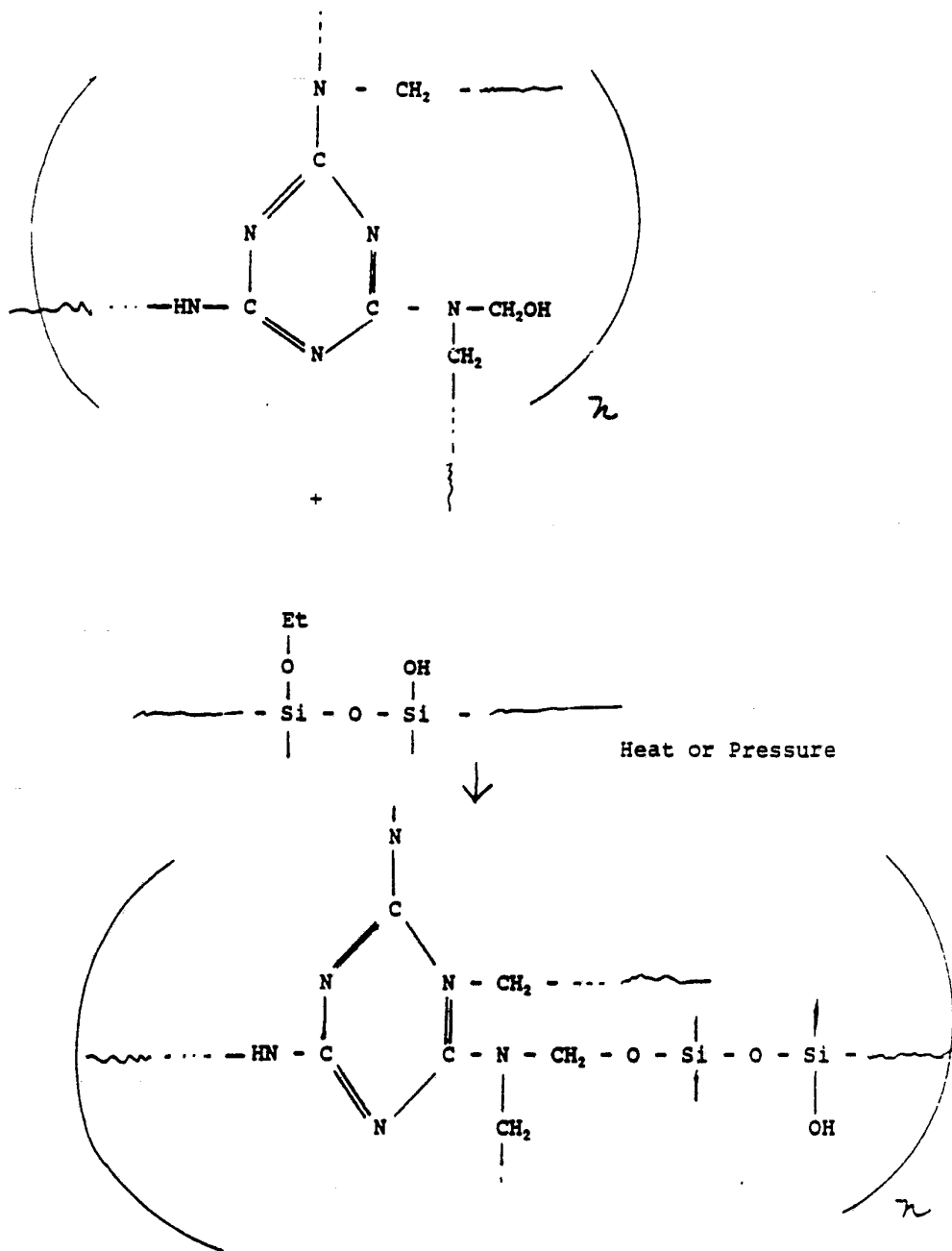
wherein R' represents a reactive functional group, such as - OH, -COOH, halide, aldehyde, hydrolyzable ester

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and/or ether, hydrocarbonyl, alkene, alkyne, or an alkoxy radical, X represents entity on which R' radicals are substituted, and n is an integer of 1 or greater.

- 5 Given below for illustrative purposes only and not to limit the present invention is an illustration of the mechanism of how melamine formaldehyde polymer is bonded to the partially hydrolyzed silicon alkoxide oligomer.



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The use of the capsulated ceramic metal oxide and/or silicon oxide is for refractory purposes, e.g., utilizing the ceramic metal oxide in usual refractory purposes but delivered to a site under the protective envelope of the microencapsulated wall. In particular, the microencapsulated spheres are applied to glass fibers to bind the fibers together. In the application of binding the glass fibers together, the temperature, that the encapsulated ceramic metal oxide is subjected to, is such that it will exceed the temperature of stabilization of the polymeric material preferably in excess of 350°F. The temperature of degradation will vary with the type of polymer used to encapsulate. For many fiber glass applications, an activation temperature would be as low as 350°F - 400°F. At this point, the polymeric material will degrade and release the ceramic metal oxide and/or silicon oxide contained therein which will coat the fiber glass. Where the coated fibers intersect, the coating forms a bond thereby binding the fibrous matrix together.

The ceramic metal oxide and/or silicon oxide is applied to the fiber glass in any desired technique such as by spraying from an aqueous containing composition such as a dispersion or emulsion of same. The amount of encapsulated metal oxide in the aqueous composition ranges from 1 to 75% by weight.

The fiberglass substrates to which the encapsulated ceramic metal oxide is applied are well known fiber glass compositions such as those that contain silica, aluminum and/or iron oxide, calcium oxide, magnesia, and optionally, other materials such as alkali oxide such as potassium or sodium oxide, boron oxides and the like. Generally, the fiberglass materials can

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be made from pure or natural ingredients or from mineral or slag wool or the like.

While the forms of the invention herein disclosed constitute presently preferred embodiments,
5 many others are possible. It is not intended herein to mention all of the possible equivalent forms or ramifications of the invention. It is understood that the terms used herein are merely descriptive rather than
10 limiting, and that various changes may be made without departing from the spirit or scope of the invention.

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WHAT IS CLAIMED IS:

1. A method for preparing an encapsulated ceramic metal oxide and/or silicon oxide precursor composition comprising the steps:
 - 5 providing a solution or dispersion of ceramic metal oxide and/or silicon oxide precursor composition;
 - providing a heat resistant resin composition;
 - blending the compositions;
 - encapsulating the ceramic metal oxide and/or
 - 10 silicon oxide precursor composition by the resin; and
 - recovering the encapsulated ceramic metal oxide and/or silicon oxide.
2. The method of claim 1 wherein the ceramic metal oxide composition is comprised of a silicon
- 15 containing composition.
3. The method of claim 1 wherein the metal oxide is comprised of aluminum oxide.
4. The method of claim 1 wherein the metal oxide is comprised of zirconia.
- 20 5. The method of claim 2 wherein the mole ratio of metal oxide ranges from 0.5 to 1.1 moles of silicon (calculated as silicon dioxide): 1 mole of metal oxide (calculate as metal oxide).
6. The method of claim 1 wherein the solu-
- 25 tion or dispersion is of silicon oxide materials without ceramic metal oxides.
7. The method of claim 1 wherein the resin has a temperature resistance up to about 350°F.

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8. The method of claim 1 wherein the resin is a thermosetting resin.

9. The method of claim 1 wherein the resin is a thermoplastic resin.

5 10. The method of claim 1 wherein the resin is selected from the group consisting of crystalline polypropylene, urea formaldehyde, melamine, melamine-urea formaldehyde, phenolic, polyimide, polybenzimidazole, polyphenylquinoxaline, polyamide-imide, polyarylsulfone, poly(arylethersulfone), polyphenylene, aromatic
10 polyester resins, polyamide, polyphenylene sulfide, acrylic, methacrylic, and mixtures thereof.

11. The method of claim 1 wherein the resins are selected from the group consisting of melamine
15 resins and phenolic resins.

12. The method of claim 1 wherein the blending of the metal oxide and/or silicon oxide precursor composition and resin composition is at atmospheric temperature and pressure.

20 13. An encapsulated ceramic metal oxide and/or silicon oxide wherein the capsulating wall is of a heat resistant resin wherein the particle size of the encapsulated material is less than 100 microns.

14. The encapsulated material of claim 13
25 wherein the ceramic metal oxide composition is comprised of a silicon containing composition.

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15. The encapsulated material of claim 13 wherein the metal oxide is comprised of aluminum oxide.

16. The encapsulated material of claim 13 wherein the metal oxide is comprised of zirconia.

5 17. The encapsulated material of claim 13 wherein the mole ratio of metal oxide ranges from 0.5 to 1.1 moles of silicon (calculated as silicon dioxide): 1 mole of metal oxide (calculated as metal oxide).

10 18. The encapsulated material of claim 13 wherein the solution or dispersion is of silicon oxide materials without ceramic metal oxide.

19. The encapsulated material of claim 13 wherein the resin has a heat resistance up to about 350°F.

15 20. The encapsulated material of claim 13 wherein the resin is a thermosetting resin.

21. The encapsulated material of claim 13 wherein the resin is a thermoplastic resin.

20 22. The encapsulated material of claim 13 wherein the resin is selected from the group consisting of urea formaldehyde, melamine, melamine-urea formaldehyde, phenolic, polyimide, polybenzimidazole, polyphenylquinoxaline, polyamide-imide, polyarylsulfone, poly(arylethersulfone), polyphenylene, aromatic polyester resins, polyamide, polyphenylene sulfide acrylic, methacrylic, and mixtures thereof.

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23. The encapsulated material of claim 13 wherein the resins are selected from the group consisting of melamine resins and phenolic resins.

24. A method for bonding fiber glass substrates comprising the steps of:

applying to the fiber glass substrate an encapsulated ceramic metal oxide and/or silicon oxide particle wherein the encapsulating wall is a heat resistant resin;

heating the treated fiber glass to degrade the resin, thereby releasing the ceramic metal oxide and/or silicon oxide; and

coating and binding the fiber glass with the released ceramic metal oxide and/or silicon oxide.

25. The method of claim 24 wherein the encapsulated ceramic metal oxide and/or silicon oxide particles are applied in an aqueous composition having from 1 to 75% by weight of encapsulated metal oxide particles.

26. The method of claim 24 wherein the temperature of the degradation step exceeds 350°F.

27. The method of claim 24 wherein the ceramic metal oxide composition further is comprised of a silicon containing composition.

28. The method of claim 24 wherein the metal oxide is comprised of aluminum oxide.

29. The method of claim 24 wherein the metal oxide is comprised of zirconia.

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30. The method of claim 24 wherein the mole ratio of metal oxide ranges from 0.5 to 1.1 moles of silicon (calculated as silicon dioxide): 1 mole of metal oxide (calculated as metal oxide).

5 31. The encapsulated material of claim 24 wherein the solution or dispersion is of silicon oxide materials without ceramic metal oxide.

32. The method of claim 24 wherein the resin has a temperature resistance up to about 350°F.

10 33. The method of claim 24 wherein the resin is selected from the group consisting of crystalline polypropylene, urea formaldehyde, melamine, melamine urea formaldehyde, phenolic, polyimide, polybenzimidazole, polyphenylquinoxaline, polyamide-imide, polyaryl-
15 sulfone, poly(arylethersulfone), polyphenylene, aromatic polyester resins, polyamide, polyphenylene sulfide, acrylic, methacrylic, and mixtures thereof.

20 34. The method of claim 24 wherein the resins are selected from the group consisting of melamine resins and phenolic resins.

35. The method of claim 24 wherein the blending of the metal oxide composition and resin composition is at atmospheric temperature and pressure.

25 36. The method of claim 24 wherein the particle size of the encapsulated material is less than 100 microns.

37. The product of the process of claim 24.