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(19) **United States**(12) **Patent Application Publication** (10) **Pub. No.: US 2006/0029787 A1****Wang et al.**(43) **Pub. Date: Feb. 9, 2006**(54) **GYPSUM BOARDS HAVING A TITANATE OR ZIRCONATE COUPLING AGENT WITH GLASS FIBER REINFORCEMENTS****Publication Classification**(51) **Int. Cl.**
D04H 3/00 (2006.01)(52) **U.S. Cl.** **428/292.1**(76) Inventors: **Lance Wang**, Parker, CO (US); **Klaus Gleich**, Littleton, CO (US); **Thomas G. Grassl**, Gross-Gerau (DE)(57) **ABSTRACT**

A bond is created between gypsum crystals and between gypsum crystals and glass fiber reinforcement in a gypsum board during cure by incorporation of titanium or zirconium based coupling compositions incorporated in the gypsum slurry. The commercially available titanium or zirconium based coupling has a generic formula of the type $[\text{RO}-]_n\text{Ti}[-\text{OXR}'\text{Y}]_{4-n}$ or $[\text{RO}-]_n\text{Zr}[-\text{OXR}'\text{Y}]_{4-n}$. These coupling compositions chemically bond to glass fibers by replacing the $-\text{OH}$ groups present on the glass fibers in aqueous solutions with $\text{Ti}-\text{O}$ or $\text{Zr}-\text{O}$ bonds. The X functionality of the coupling composition is selected to be a phosphato or pyrophosphato group to form bond with calcium ions of the gypsum crystal. The bond created by the titanium or zirconium based coupling composition results in load transfer between gypsum crystals in the gypsum matrix and between the glass fibers and gypsum matrix, resulting in improved flexure strength and nail pullout resistance.

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(63) Continuation-in-part of application No. 10/910,113, filed on Aug. 3, 2004.

Fig. 1a

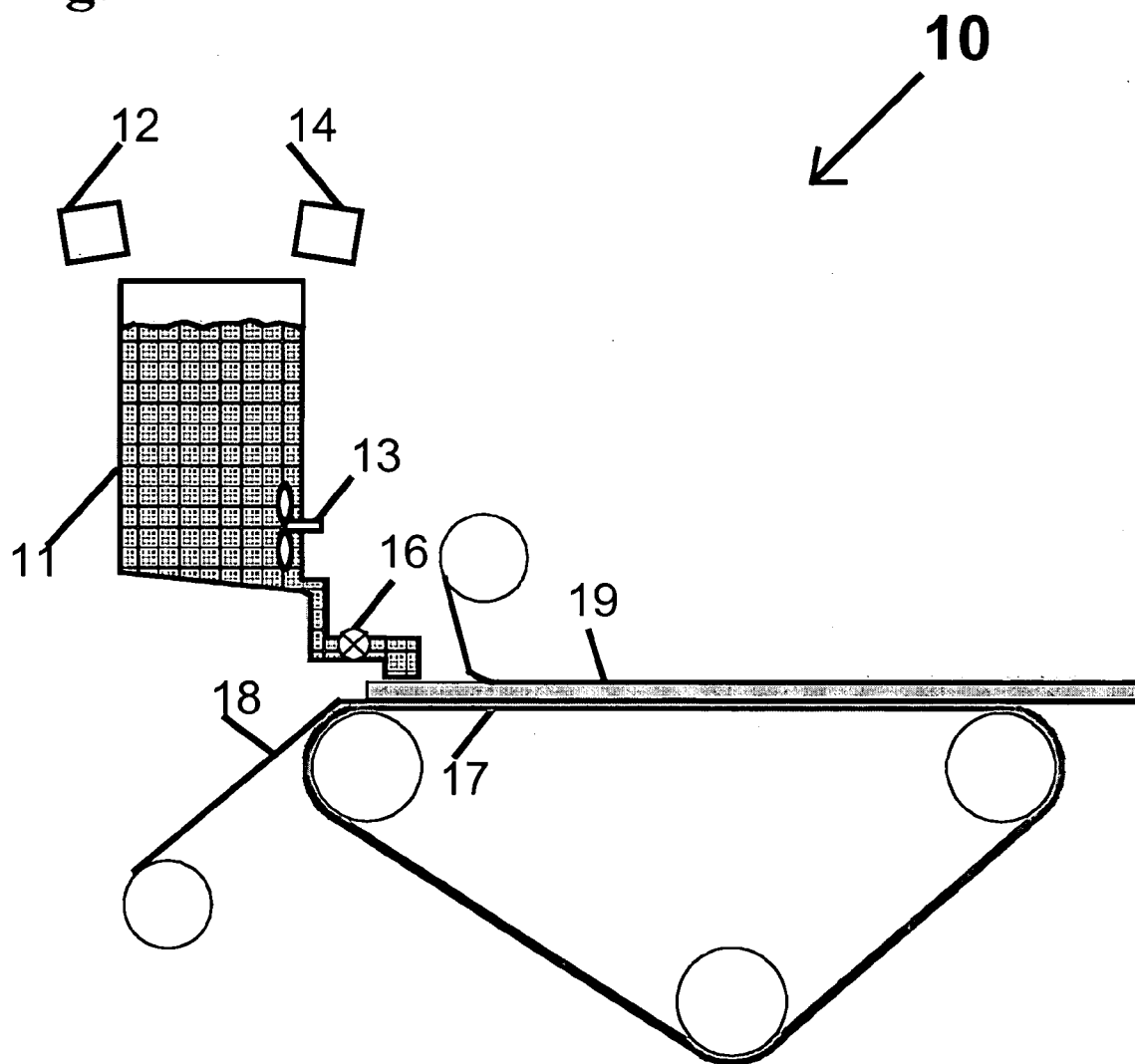


Fig. 1b

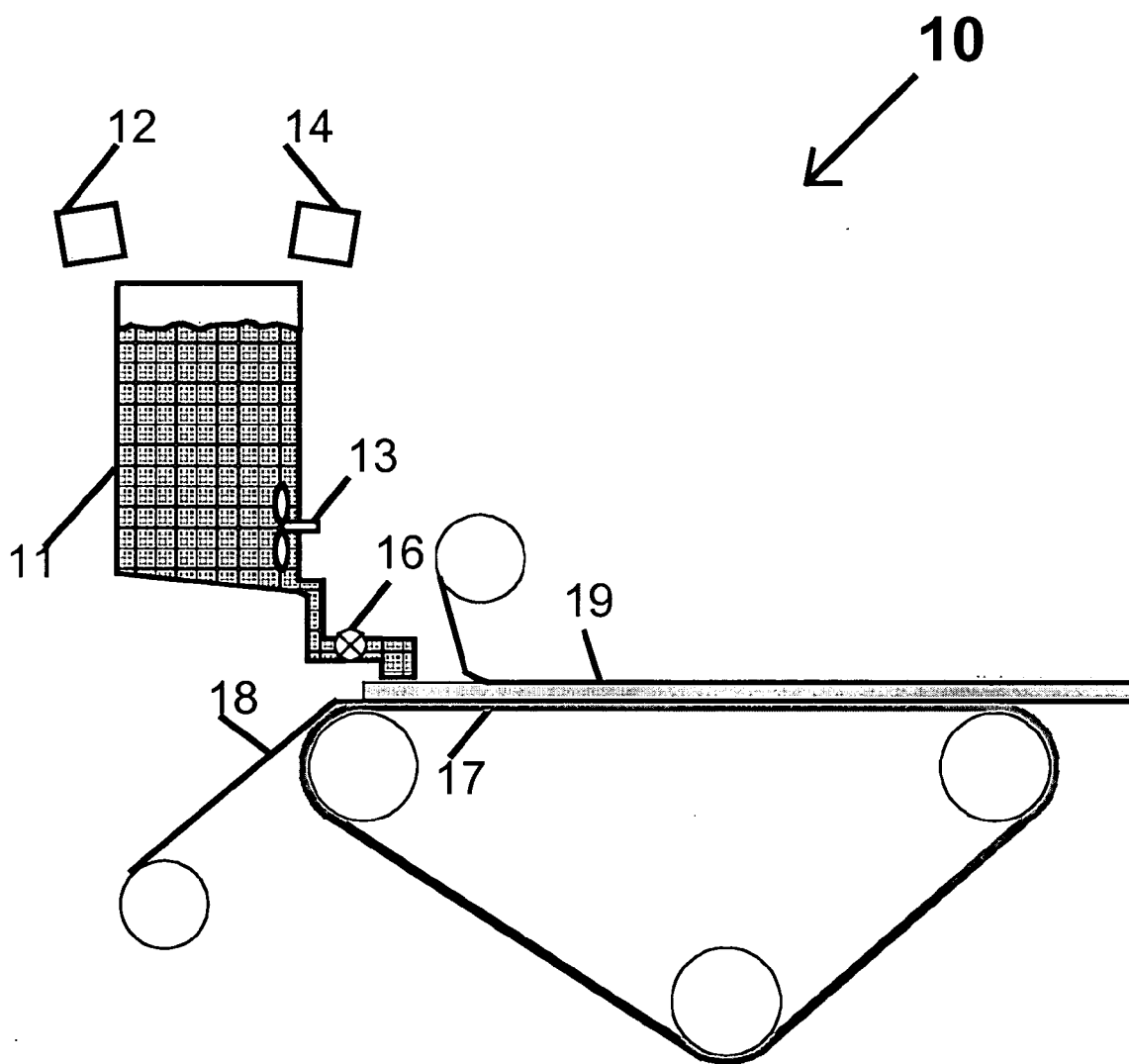


Fig. 1c

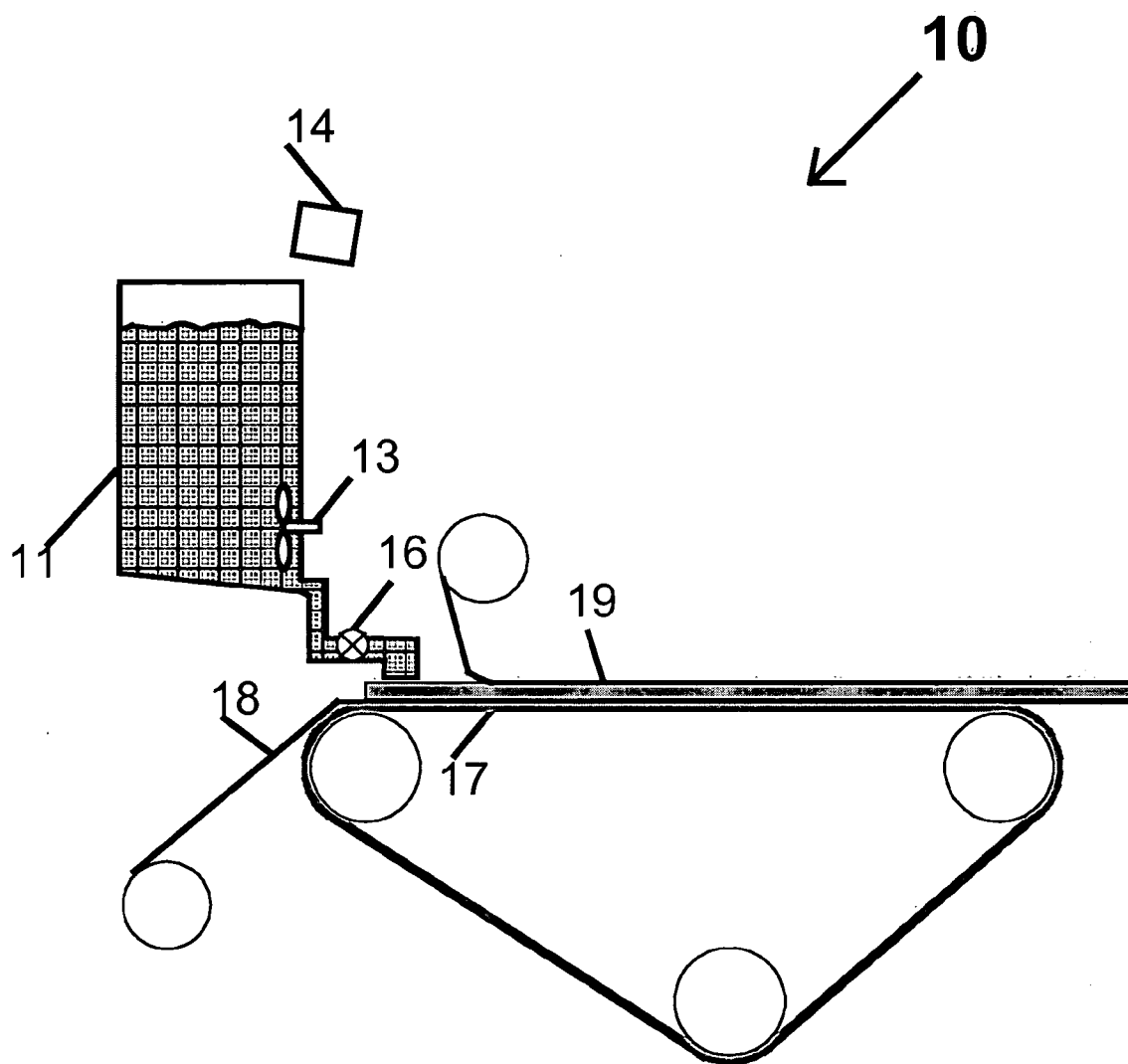


Fig. 2

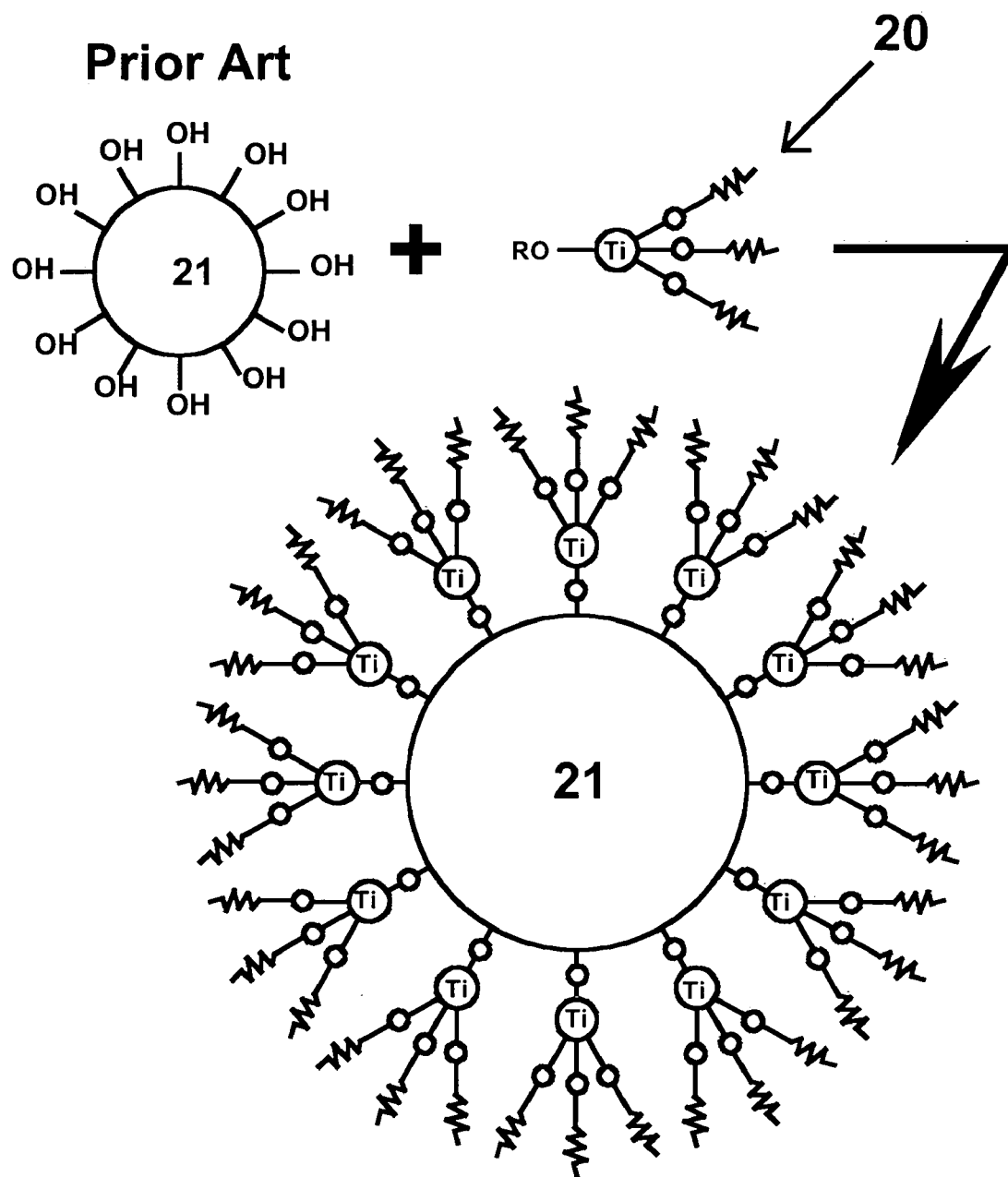


Fig. 3

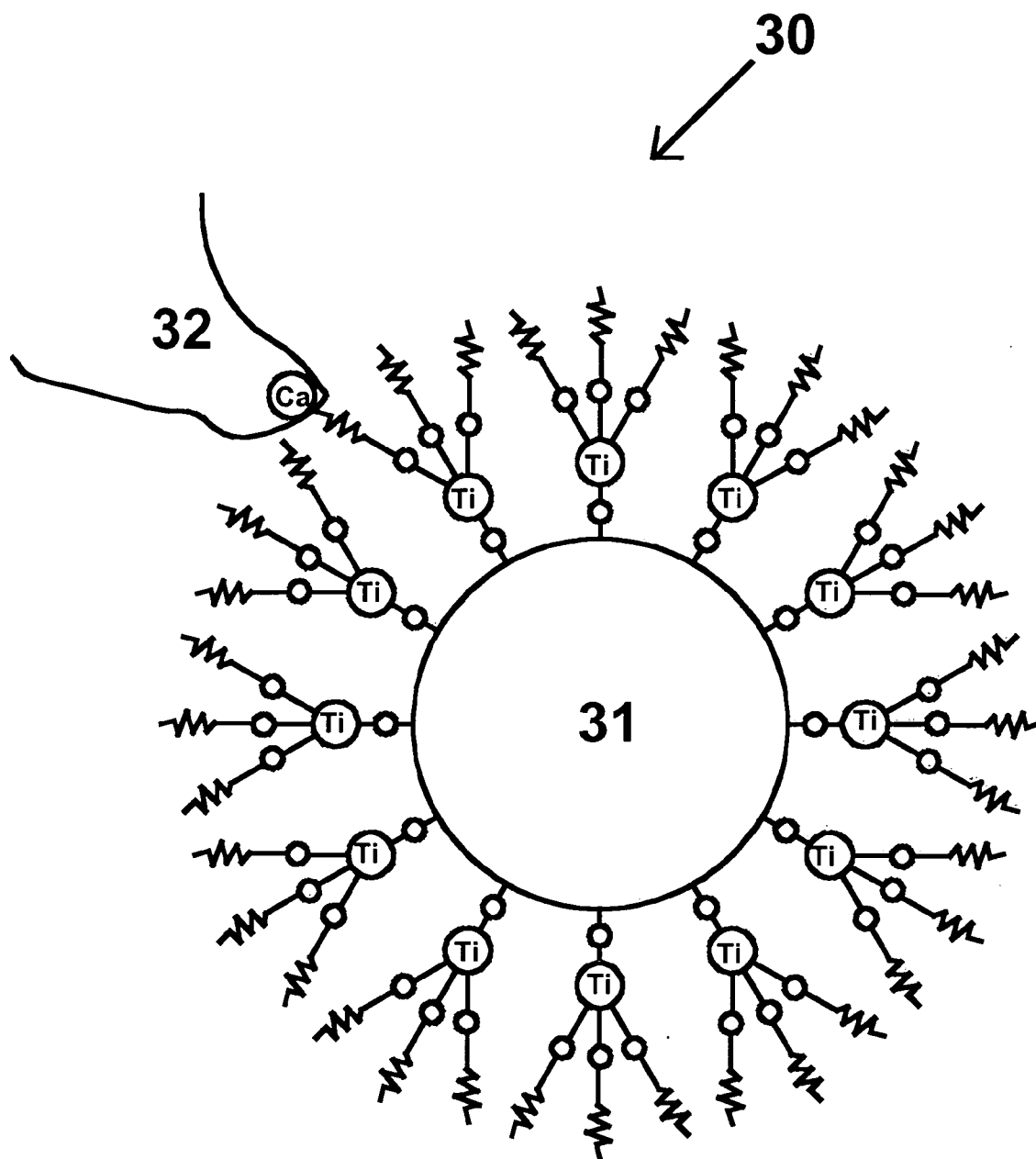
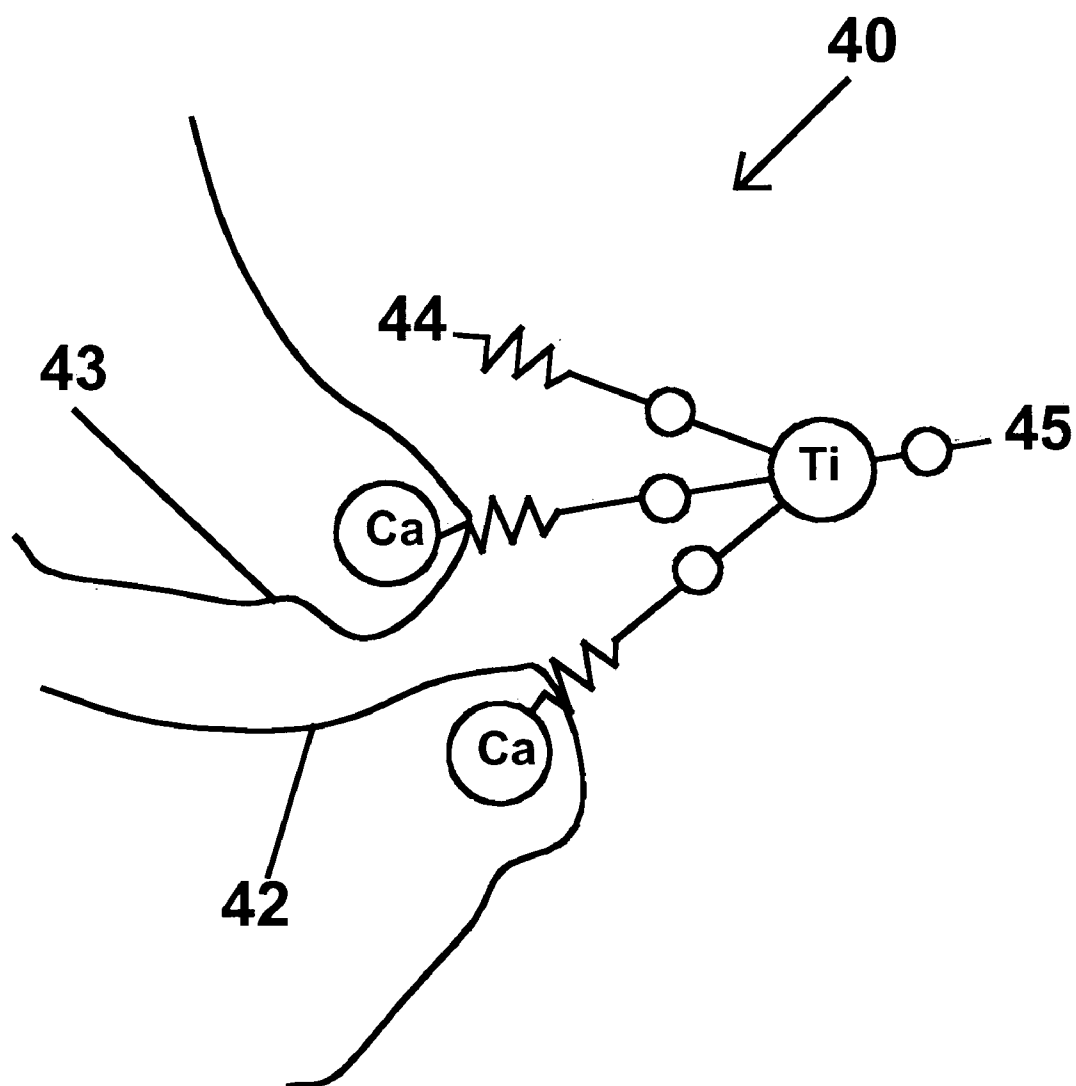


Fig. 4



GYPSUM BOARDS HAVING A TITANATE OR ZIRCONATE COUPLING AGENT WITH GLASS FIBER REINFORCEMENTS

[0001] This is a Continuation-In-Part of application Ser. No. 10/910,113, filed Aug. 3, 2004, the disclosure of which is hereby incorporated in its entirety by reference thereto.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to gypsum wallboard products for building construction; and more particularly, to wallboard products wherein use of a titanium or zirconium containing sizing or coupling composition in the gypsum matrix provides superior flexure strength and nail pullout resistance.

[0004] 2. Description of the Prior Art

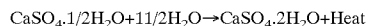
[0005] Gypsum boards have been manufactured with or without glass or other reinforcement fibers. Glass fibers are commonly used in the production gypsum wallboard to improve the tensile and tear strength of the product. The fibers are employed in many forms, including individual fibers, strands containing plural fibers, and rovings. These fiber products, in turn, may be used in discrete form or they may be assembled into woven and non-woven fabric or mats and incorporated into a gypsum matrix.

[0006] Glass fiber filaments or strands that are to be incorporated in a gypsum matrix, either as individual fibers or as woven or non-woven mats, are customarily given a sizing or coupling coating treatment. For example the treatment may include the application of one or more substances that beneficially modify the surface properties, such as wetting behavior of glass fiber with the gypsum matrix, for subsequent processing. Some sizing formulations are intended to function only during a part of the mat formation process, and may be removed thereafter. Other formulations are intended to remain, and are chosen for their beneficial effect on properties of finished products. For example, lubrication is generally required to minimize or eliminate breakage that results from bare fibers rubbing each other during processing and may be subsequently removed. Suitable sizing may also facilitate the dispersion of fibers in the initial slurry, thereby improving the uniformity of the wet-laid mat, and improving the coupling of a mat binder resin (e.g. an acrylic, melamine, or urea formaldehyde resin) used to secure the fibers in the mat, thereby strengthening the finished mat. Desirably, the mat has high tensile and tear strength in both the machine and cross-machine directions and high hot wet retention, i.e. a high percentage of retained strength after exposure to hot water. Ideally, a sizing formulation may improve other mat properties, such as by reducing fuzz and fly. Sizing is also known to influence fiber dispersion and processability. These effects are believed to result from changes in the ionic character of the fiber surface-water interface. Furthermore, an ideal sizing formulation would produce fiber with a long shelf life. Sizing processes that reduce the emission of volatile organic compounds (VOCs), and other substances that are of environmental concern, are also desired. Various theories have been advanced to associate finished mat properties with different constituents of known sizing treatments. However, actual mat properties are generally found to be unpredictable. As a

result, formulation of sizing has generally been carried out by trial and error. Moreover, the multiple constituents used in sizing, and their interacting roles, make it especially difficult to predict or achieve fully satisfactory properties in glass fibers dispersed into a gypsum matrix, either as fibers or as finished products like non-woven mats.

[0007] Gypsum wallboard and gypsum panels are traditionally manufactured by a continuous process. The conventional process for manufacturing gypsum wallboard includes premixing of dry ingredients of the core composition, which can include calcium sulphate hemihydrate ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$, also known as calcined gypsum, stucco, and plaster of Paris), accelerator, starch, glass fiber and others. The premix of dry ingredients is then mixed with "wet" portion of the core composition in a pin mixer. The "wet" portion can include water, foaming agent, paper pulp, fluidity-increasing agent, and other conventional additives. Various additives, e.g. cellulose and glass fibers, are often added to the slurry to strengthen the gypsum core. Starch is frequently added to the slurry in order to improve the adhesion between the gypsum core and the facing.

[0008] The resulting gypsum slurry is continuously deposited to form a gypsum wallboard core between two continuously supplied moving sheets of cover paper. The two cover sheets are typically a pre-folded face paper and a backing paper. As the gypsum slurry is deposited onto the face paper, the backing paper is laid over the gypsum slurry and bonded to the pre-folded edges of the face paper with a suitable adhesive. The enclosed gypsum core slurry is then sized for thickness through forming plates or roller bars and allowed to set between two cover sheets, thereby forming a board. The setting process is a rehydration reaction that transforms calcium sulfate hemihydrate to calcium sulfate dihydrate, shown as follows.



[0009] Once the gypsum core has set sufficiently, the continuously produced board is cut into desired lengths and vertically stacked. After the cutting and stacking step, the gypsum boards are fed into drying ovens or kilns to evaporate the excess water. Inside the drying ovens, the boards are blown with hot drying air. After the dried gypsum boards are removed from the ovens, the ends of the boards are trimmed off and the boards are cut to desired sizes. The boards are commonly sold to the building industry in the form of sheets. These sheets are usually 4 feet wide, 8 to 12 feet long and 0.5 to 1 inches thick, the width and length dimensions defining the two faces of the board.

[0010] Wallboard formed of a gypsum core sandwiched between facing layers is used in the construction of virtually every modern building. In its various forms, the gypsum board is used as an interior or exterior surface for walls, ceilings and the like. The gypsum board is relatively easy and inexpensive to install, finish, and maintain, and depending on the composition of the gypsum matrix, may be relatively fire resistant. A number of patents discuss various reinforcement fibers with sizing coatings within gypsum and other hydrated matrices.

[0011] U.S. Pat. No. 4,240,944 to Temple discloses a binder composition and a method for using it in sizing compositions for treating glass fibers. The binder composition is an aqueous emulsion containing isotactic carboxy-

lated polypropylene along with amorphous carboxylated polypropylene, base, and surfactant. The isotactic carboxylated polypropylene is incorporated in the emulsion by a method of co-emulsification of the isotactic and amorphous carboxylated polypropylene in a ratio ranging from 1:1 to 1:4 parts by weight along with the base and surfactant. Water is added to the co-emulsified blend to obtain the emulsion with the desired solids content. The coupling agent is disclosed to be any interfacial boundary area adhesive compound which acts to unite the surface of the fibers with the polyolefin polymer. Among typical coupling agents for uniting glass fiber and polymers are metal salts, such as basic chromium chloride, basic chromium sulfide having a trivalent metal ion selected from the group consisting of chromium, cobalt, nickel, copper, and lead having at least one hydroxyl group attached to the metal and at least one anion of a strong mineral acid attached to the metal. Werner complexes in which the trivalent nuclear atom, such as chromium, is coordinated with an organic acid such as methacrylic acid, for instance, methacrylic complex of chromic chloride, and other coupling agents, having vinyl alkyl, amino, epoxy, mercapto, thioalkyl, thioalkaryl and phenol groups. Coupling agents from the silane and siloxane groups are also disclosed as suitable. Such coupling agents are typically hydrolysable vinyl, allyl, beta-chloropropyl, phenyl, thio-alkyl, thio-alkaryl, amino-alkyl, methacrylate, epoxy, and mercapto silanes, their hydrolysis products, polymers of hydrolysis products, and mixtures of any of these agents. A preferred coupling agent is gamma-amino-propyltriethoxysilane. Such material is said to provide a very good coupling between the glass fiber strands and polyolefin polymers at low concentrations and with good stability. The '944 patent does not disclose a coupling agent or a sizing composition that bonds glass fibers to gypsum. In addition, the coupling agent disclosed by the '944 patent does not contain titanium or zirconium.

[0012] U.S. Pat. No. 4,241,136 to Dereser et al. (hereinafter, "the '136 patent") discloses a process and composition for treating glass fibers for use in reinforcement of cementitious materials. The fibers are first sized with a cationic fiber forming organic polymer and then with a second coating containing an anionic film-forming organic polymer. The resulting fibers are said to have good wetting and dispersibility characteristics. The '136 patent suggests that the high surface charge density of asbestos fibers, in combination with a high specific surface area, permits them to flocculate cement mixed therewith, thereby providing a substantial degree of reinforcement to structural articles. However, replacement of asbestos fibers with glass is said not to have the expected benefit, in that the glass fibers tend to adhere together and thereby inhibit the removal of water during mat or board production. The '136 patent does not disclose a sizing that contains titanium or zirconium.

[0013] U.S. Pat. No. 4,284,538 to Graham (hereinafter, "the '538 patent") discloses a sizing composition for glass fibers said to render the fibers more dispersible in aqueous solutions. The sizing composition has present an aqueous dispersion of cationic imidazoline; aliphatic, aromatic and/or polymeric ester; and polyethylene in an amount equivalent to an amount in the range of about 0.1 to about 1.5 weight percent of the aqueous sizing composition based on an approximately 30 percent active aqueous dispersion. Depending on the use, the sizing composition may contain other components such as starch, lubricant, emulsifying

agents, wetting agents, plasticizers, biocides and the like. Significantly, the '538 patent does not disclose or suggest any sizing composition that includes a titanium or zirconium composition.

[0014] U.S. Pat. No. 4,341,877 to Das et al. discloses a sizing composition for treating glass fibers in a process to produce treated glass fiber strands. These disclosed treated strands have improved properties of wettability and compatibility in polymer matrices to produce reinforced polymers with improved mechanical and fatigue properties. In particular, the disclosure is directed to a sizing composition for treating glass fibers in a process to produce treated glass fiber strands said to have improved wettability and compatibility when used in unsaturated polyester or vinyl ester or epoxy matrices for producing high glass content reinforced polyester materials. Also provided are the sized glass fiber strands, glass fiber reinforced polymers and processes for producing these materials. The sizing composition comprises one or more organo silane coupling agents. A major amount of the solids of the aqueous sizing composition is an epoxidized polar thermoplastic copolymer wherein there are three to about twelve parts of epoxy per 100 parts of the other comonomer and one or more nonionic, cationic or anionic lubricants. The sizing composition can also have one or more compatibilizing agents, such as a polyvinyl-acetate-ethylene copolymer unsaturated polyester resin, polyvinylacetate homopolymer, epoxy polymers and epoxy polyester copolymers. The co-monomers for the epoxidized polar thermoplastic copolymer are vinyl acetate, acrylates, polyurethane condensate monomer, polyester condensate monomer, and polyamide condensate monomer. The sizing composition bonds glass fibers in a polymeric matrix, not a gypsum matrix, and does not contain titanium or zirconium containing compounds.

[0015] U.S. Pat. No. 4,477,524 to Brown et al. (hereinafter, "the '524 patent") discloses an aqueous sizing composition having a cationic lubricant, amide compound, and cationic silicone polymer aqueous emulsion which is used to produce wet chopped sized glass fiber strands or which also has a film former to produce continuous glass fiber strands. Any suitable cationic lubricant can be used. These are typically amine salts of a fatty acid having 4 to 26 carbon atoms and, in most cases, an even number of carbon atoms per molecule. A particularly suitable fatty acid moiety of the salt is said to have between about 12 and 22 carbon atoms. The amines useful for forming the salt are tertiary amines of substantially low molecular weight, i.e., the alkyl groups attached to the nitrogen atom should have between 1 and 6 carbon atoms. Any suitable cationic lubricant can be used that imparts compatibility for the glass fibers and imparts slip to the exterior of the glass fibers. A particularly suitable cationic lubricant is said to be material available under the trade designation "Cation-X" which is an alkyl imidazoline reaction product of a tetraethylene pentamine and stearic acid. Acid solubilized water dispersible stearic amides and anhydrous acid solubilized water dispersible low molecular weight fatty acid amides as well as anhydrous acid solubilized polyunsaturated low molecular weight fatty acid amides can also be used. Further examples of cationic lubricants include certain alkyl imidazoline derivatives. The moisture content of the wet chopped glass fiber strands is controlled to within about 9 to about 20 weight percent. The sized wet chopped glass fiber strands have good flowability and can be used to produce a non-woven glass fiber strand

mat by any process similar to the "wet laid" process on any type of suitable machinery. The mat is said to have good flexibility and tensile strength. The production of a flexible mat of glass fiber strand is achieved by wet or dry chopped glass fiber strand produced by the present invention, but the flowability of the wet chopped glass fiber strand is achieved only when the chopped glass fibers have been produced by a wet chop glass fiber forming process. The '524 patent also discloses the use of treated glass fiber strands to reinforce materials such as calcium sulfate dihydrate (gypsum) and other calcium compound products such as cementitious products. The sizing composition disclosed in the '524 patent is a lubricant and does not bind glass fibers to a gypsum matrix. Further, it does not contain titanium or zirconium based compounds.

[0016] U.S. Pat. No. 4,536,447 to Hsu discloses treated glass fibers having adequate protection for gathering into strands, and when chopped being more dispersible in aqueous media. The treated glass fibers have a coating of an aqueous treating composition having nonionic surfactant and a cationic quaternary ammonium salt surfactant and one or more organo polar functional coupling agents. In addition, the aqueous treating composition can also have one or more water dispersible, emulsifiable or soluble polyols. Glass fibers treated with the aqueous treating compositions and produced into wet or dry chopped glass fiber strands have a length of $\frac{1}{16}$ of an inch to about 3 inches, and have good dispersibility in aqueous media with or without addition of dispersing agents. A nonwoven sheet-like mat is produced from aqueous dispersions having chopped treated glass fibers, wherein an amount of water is removed, usually by vacuum, suction or thermal means. In addition, polymeric binders, commonly referred to as wet strength binders, are applied to the mat and the mat is cured. The resulting nonwoven sheet-like mat product is said to have very good strength properties for use as a reinforcing element for roofing products, construction products and flooring products. The sizing composition does not comprise titanium or zirconium based compositions.

[0017] U.S. Pat. No. 4,935,301 to Rerup et al. relates to a cement composite containing glass fibers encapsulated with a polymeric coating which is formed from an organic solution of an interpolymer complex of an anionic polymer and a cationic polymer. The fiber reinforcement is said to impart to the composite improved high apparent toughness, ductility, and flexural and tensile strengths, along with improved resistance to embrittlement and strength loss with age. The fibers are disposed in bundles which are encapsulated with an elastomeric material, wherein the encapsulant wraps the bundles of fibers but does not coat the individual fibers, nor impregnate the bundle or fill the voids between the individual fibers. The fibers are disposed in any cementitious matrix, including Portland cement, concrete, mortar, gypsum, and hydrous calcium silicate. The elastomeric coating is applied in an organic solvent and is not applied in a water based system. The composite formed is primarily a cement composite even though gypsum composite is casually mentioned in the patent. The anionic and cationic polymers are related to bond creation with the fiber prior to incorporation in the matrix, and does not contain titanium or zirconium compounds.

[0018] U.S. Pat. No. 5,034,276 to Zwiersch et al. discloses a sizing for the treatment of glass fibers, which are incor-

porated into thermoplastic materials as reinforcement. The sizing contains a Schiff's base, preferably in concentrations ranging from 0.05 to 2% by weight, based on the dry matter. Through the use of a sizing with this component, the tensile and impact strength properties of the glass fiber-reinforced thermoplastic materials are said to be improved significantly. The Schiff's base is prepared from a conventional aminosilane and a simple ketone using a catalyst. An exemplary sizing composition further comprises a polyolefin dispersion, a polyurethane dispersion, a vinylsilane and a lubricant. The polyolefin dispersion is prepared from a 30 wt % partially saponified, oxidized, polyethylene with a molecular weight of between 1500 and 2000. The lubricant may be a fatty acid ester of a polyglycol. The sizing bonds glass fibers to a thermoplastic matrix not to a gypsum matrix and does not contain titanium or zirconium based compositions.

[0019] U.S. Pat. No. 5,605,757 to Klett discloses aqueous sizing compositions for application to glass fibers used in reinforcing thermosetting polymeric composites, such as filament wound composites or pultrusions. The composition comprises: (a) a non-ionic thermosetting urethane-modified epoxy polymer; (b) a water soluble, dispersible or emulsifiable epoxy film-forming polymer different from the urethane-modified epoxy polymer and adapted to emulsify the urethane-modified epoxy polymer of (a); (c) an organo functional silane coupling agent; and (d) a fiber lubricant. The sizing composition bonds glass fibers with thermosetting resins and does not bond to a gypsum matrix. Moreover, the sizing does not comprise titanium or zirconium based compositions.

[0020] U.S. Pat. No. 5,786,080 to Andersen et al. discloses compositions and methods for the deposition of ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{Ca}(\text{SO}_4) \cdot 30\text{--}32\text{H}_2\text{O}$) onto the surfaces of fibers, aggregates, or other fillers. The ettringite is produced in situ within an aqueous suspension while in proximity of the fibers, aggregates, or fillers, to form a mineralized composite material comprising ettringite coated fibers, aggregates or other fillers. The ettringite-coated materials can be added to hydraulically settable materials to improve the chemical and mechanical bond between the fibers or other substrate within the resulting hardened hydraulically settable materials, particularly cementitious or concrete materials. The presence of the coated fiber materials is said generally to increase the toughness, flexibility, tensile strength, and flexural strength of the composite and articles made therefrom. It is indicated that the ability of fibers to modify the mechanical properties of a composite is dependent on the strength of the bonding between the fibers and the matrix material. The ettringite process is said to increase the roughness of the coated fibers, thereby enhancing the mechanical interlocking with the matrix over that achieved with relatively smooth glass fibers. The ettringite composition does not contain titanium or zirconium based compositions and does not chemically bond to glass fiber and the gypsum matrix, but instead relies on mechanical roughening of glass fiber surfaces.

[0021] U.S. Pat. No. 5,879,825 to Burke, et al. discloses a gypsum wallboard and method of making same. The board is made with a core of calcium sulfate hemihydrate (stucco), water, and a strengthening agent from a slurry. The slurry contains paper pulp fiber reinforcement. The strengthening agent is an acrylic polymer composition having a glass

transition temperature of about 15° C. or greater, and preferably has good divalent ion stability so that it is suitable in a medium of calcium ions. The method provides a wallboard having increased core strength, paper-to-core bonding, and strength-to-weight ratio. The gypsum board is not reinforced with glass fibers and the acrylic polymer does not contain a titanium or zirconium composition forming a chemical bond between the glass fiber and the gypsum matrix.

[0022] U.S. Pat. No. 6,294,253 to Smith, Jr., discloses a sized, staple fiber product useful in the manufacture of gypsum board. The fiber surface is coated with an aqueous chemical size composition containing a high level of surfactant. Particularly, such as a poly (Oxy-1,2-ethanediyl), alpha(2-(bis(2-Aminoethyl)Methyl-ammonio)Ethyl)-omega-Hydroxy-, N,N'-Di(C14-18 and C16-18 unsaturated) Acyl Derivs., Me Sulfate (Salts) and optionally, a polymer film former such as polyvinyl alcohol and a biocide. The sized fibers may ultimately be incorporated as reinforcements in the gypsum core of a construction board. Preferred fibers are 5-23 μ m in diameter and chopped to less than 1.5 inches long. The sizing provides a thin polymeric coating that does not contain titanium or zirconium based compositions.

[0023] U.S. Pat. No. 6,171,388 to Jobbins discloses a lightweight gypsum composition. The composition comprises (a) gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$); (b) one or more naturally occurring or synthetic latex polymers including ethylenically unsaturated monomers selected from (meth)acrylic based acids and esters, acrylonitrile, styrene, divinylbenzene, vinyl esters, acrylamide, methacrylamide, vinylidene chloride, butadiene and vinyl chloride and mixtures thereof; and (c) one or more nonionic surfactants; wherein the gypsum composition has a density less than 0.64 g/cm³. The gypsum board is made from a slurry that has a low density due to foaming, and does not contain glass fibers incorporated within the gypsum matrix. The bond is therefore between gypsum hydrated crystals via a latex binder and not between a glass fiber and gypsum matrix. Furthermore, the bonding agent does not comprise titanium or zirconium based compositions.

[0024] U.S. Pat. Nos. 6,342,284, 6,632,550 to Yu et al. disclose gypsum-containing products having increased resistance to permanent deformation and methods and compositions for producing the same. The gypsum-containing products comprise a mixture of a calcium sulfate material, water, and an appropriate amount of one or more enhancing materials. The enhancing materials are chosen from condensed phosphoric acids, each of which comprises 2 or more phosphoric acid units, and salts or ions of condensed phosphates, each of which comprises 2 or more phosphate units. The mixture is then maintained under conditions sufficient for the calcium sulfate material to form a set gypsum material. The enhancing materials include sodium trimetaphosphate, potassium trimetaphosphate, ammonium trimetaphosphate, lithium trimetaphosphate and aluminum trimetaphosphate. The sodium hexametaphosphate may have 6-27 repeating phosphate units, and ammonium polyphosphate may have 1000-3000 repeating phosphate units. The overall strength of the board is higher because of the increased strength provided by the inclusion of the trimetaphosphate ion in the mixture used to form the board. The exact mechanism of this strength improvement is unclear and may be due to phosphate repeating units bonding to the

hydrated gypsum crystal. There are no glass fibers in this system and the binder does not bond to the glass fiber and to the gypsum matrix.

[0025] U.S. Pat. No. 6,409,824 to Veeramasuneni et al. discloses gypsum compositions with enhanced resistance to permanent deformation. The set gypsum-containing composition includes an interlocking matrix of gypsum crystals and an enhancing material. The enhancing material can be selected from (i) an organic polyphosphonic compound, or a mixture thereof; (ii) a borate selected from ulexite colemanite, or a mixture thereof, (iii) a carboxylic compound or a mixture thereof; or a mixture of (i), (ii) and/or (iii). The polyphosphoric compound is polyphosphate compound selected from the group consisting of a trimetaphosphate compound, sodium hexametaphosphate having 6-27 repeating phosphate units, ammonium polyphosphate, tetrapotassium pyrophosphate, sodium tripolyphosphate, tetrasodium pyrophosphate, sodium acid pyrophosphate, and polyphosphoric acid having 2 or more repeating phosphoric acid units. Organic phosphonic compounds include, for example, aminotri (methylene-phosphonic acid), aminotri (methylene-phosphonic acid) pentasodium salt, 1-hydroxyethylidene-1,1-diphosphonic acid, 1-hydroxyethylidene-1,1-diphosphonic acid tetrasodium salt, diethylenetriamine penta(methylene phosphonic acid) pentasodium salt, diethylenetriamine penta(methylene phosphonic acid) trisodium salt, hexamethylene diamine tetra(methylene phosphonic acid), hexamethylene diamine tetra(methylene phosphonic acid) potassium salt, or the like. The polycarboxylic compound can be in the form of a polyacrylate, a polymethacrylate, a polyethacrylate, and the like with a molecular weight of from about 100,000 daltons to about 1 million daltons. Borates, and in particular, naturally occurring ulexite ($\text{NaCaB}_5\text{O}_{10} \cdot 8\text{H}_2\text{O}$) and colemanite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$), or mixtures of ulexite and colemanite, also can be included as the enhancing material. The gypsum matrix does not include glass fibers and therefore there is no bond between glass fibers and a gypsum matrix. The enhancers presumably only bond to gypsum crystals due to phosphate, borate or carboxyl bonds. The enhancers do not contain titanium or zirconium based compounds.

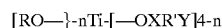
[0026] U.S. Pat. No. 6,525,116 to Sethuraman et al. discloses a gypsum composition with ionic styrene butadiene latex additive. The gypsum composition comprises functionalized styrene butadiene latex polymers crosslinked by a dimethacrylate having from 2 to 30 ethoxy units between methacrylate functionalities. The composition is prepared by aqueous emulsion polymerization of a monomeric mixture comprising styrene and butadiene in the presence of a seed polymer. The functionalized styrene butadiene latex is added to gypsum slurry. There is no glass fiber incorporated in the gypsum slurry and the latex bond is provided between the gypsum crystals in the form of uniform dispersion. The functionalized latex formed is crosslinked and does not contain titanium or zirconium based compositions forming a chemical bond between glass fiber and gypsum matrix.

[0027] U.S. Patent Application 2003/0134079 to Bush et al. discloses a method and composition for coating mats and articles produced therewith. The coated glass mat comprises a glass mat substrate having non-woven glass fibers and a coating, which essentially uniformly penetrates the glass mat substrate to desired fractional thickness of the coated glass mat. The coating is preferably a coating blend com-

prised of water, latex binder, inorganic pigment, and inorganic binder. This coating imparts a tensile strength to the coated glass mat, which on average is at least 1.33 times greater than the tensile strength of the glass mat substrate without the coating. Moreover, a non-coated thickness of the coated glass mat is sufficiently thick for bonding purposes with a gypsum slurry or other core materials, such as thermoplastics or thermosetting plastics. The coating has porosity, which provides the coated glass mat with a porosity sufficient to allow water vapor to escape from a gypsum slurry when heated. A glass mat with non-woven glass fibers is coated with water, latex binder, inorganic pigment, and inorganic binder using a larger wrap kiss coater. The binder penetrates 25% to 75% of the thickness of the mat leaving a rough uncoated free surface. The mat may be placed on gypsum slurry, thereby reinforcing the gypsum board. The non-woven glass mat is bonded with water, latex binder, inorganic pigment, and inorganic binder and the binder is not water soluble or reversible. The glass fiber mat is placed on top of gypsum slurry forming the gypsum board and is not incorporated within the gypsum board. U.S. Patent Application 2004/0082240 to Rodrigues (hereinafter, "the '240 patent application") is directed to a fiberglass non-woven binder. It employs an aqueous solution of a copolymer binder having a monomer of acid functionality and a monomer of hydroxyl or amine functionality. The copolymer binder is applied to hot nonwoven fiberglass fibers and heat cured to form a fiberglass mat that is strongly bound, yet flexible. The '240 patent application discloses a number of acid functionality monomers and hydroxyl or amine functionality monomers. Specifically, it discloses acrylic acid [para 0011] a carboxylic acid monomer and triethanol amine, an amine functionality monomer that crosslinks without the need for external crosslinking agents [para 0020]. The monomer mixture polymerizes or crosslinks when it comes into contact with the hot fiber surface, creating a bond at the contact points. This is strictly a creation of a bond between two fiberglass fibers, not between a glass fiber and gypsum matrix. Moreover, the polymer is created during cure by crosslinking and does not pre-exist in the solution.

[0028] U.S. Patent Application 2004/0082241 to Rodrigues (hereinafter, "the '241 patent application") is directed to a fiberglass nonwoven binder. It is a continuation in part of U.S. Patent Application 2004/0082240 (discussed herein above). The '241 patent application relates to the use of polyamines as crosslinkers for a polymer binder. It employs an aqueous solution of a copolymer binder having a monomer of acid functionality and a monomer of hydroxyl or amine functionality. The aqueous solution is applied to hot nonwoven fiberglass fibers and heat cured to form a fiberglass mat that is strongly bound, yet flexible. The '241 patent application discloses a number of acid functionality monomers and hydroxyl or amine functionality monomers and polyamine crosslinking agents. Specifically, it discloses acrylic acid [para 0013] a carboxylic acid monomer and triethanol amine, an amine functionality monomer that crosslinks without the need for external crosslinking agents [para 0023]. The monomer mixture polymerizes or crosslinks when it contacts the hot fiber surface creating a bond at the contact points. This is strictly creation of bond between two fiberglass fibers, not between a glass fiber and gypsum matrix. The polymer is created during cure by crosslinking and does not pre-exist in the solution.

[0029] "Neoalkyl Titanate and Zirconate Coupling Agent Additives in Thermoplastics" by Salvatore J. Monte discloses a number of titanium and zirconium based organic coupling agents that couple to a glass surface, calcium carbonate fillers and thermoplastics (hereinafter, "the Monte paper"). Monte, Salvatore, J., *Polymer and Polymer Composites*, Vol. 10, No. 1, 2002, "Neoalkyl Titanate and Zirconate Coupling Agent Additives in Thermoplastics", p 1-53. The coupling reagents react with glass fiber, silica, and other silane reactive surfaces, and provide resistance to delamination. The Monte paper discloses titanium based compositions including KR TTS, KR 9S, KR 26S, KR 34S, KR 38S, KR 41B, KR 101, KR 112, KR 134SP, KR 138S, KR 138T, KR 201, KR 238S, KR 238M, LICA 01, LICA 09, LICA 12, LICA 12WE33, LICA 38, LICA 38ENP, LICA 38J, LICA 44, LICA 97, KS N100, and KS N60WE. The Monte paper also discloses zirconium based coupling compositions including KZ 55, NZ 12, NZ 37, NZ 38, NZ 38J, NZ 44, NZ 97, KS MZ100 and KS MZ60WE; the compositions are also provided. The titanate or zirconate coupling is of the following generic composition:



where RO is a hydrolyzable group or substrate reactive group with surface hydroxyl or protons that bond to the fiber; Ti is a tetravalent titanium or zirconium with Ti—O or Zr—O bond capable of dissociation allowing transesterification, transalkylation and other catalyst mechanisms; X is a binder functional group, such as phosphato, pyrophosphato, sulfonyl, carboxyl etc., imparting intumescence, burn rate control, anticorrosion, quaternization sites, dissociation rate/electron transfer control etc.; R' is a thermoplastic functional group, such as aliphatic and non-polar isopropyl, butyl, octyl, isostearyl groups, naphthenic and mildly polar dodecylbenzyl groups or aromatic benzyl cumyl phenyl groups; and Y is a thermoset functional group such as acryl, methacryl, mercapto, amino etc and 4-n is mono, di or tri organofunctionality. Hybrid titanate or zirconate coupling agents such as those containing 1 mole of function X carboxyl function R' aliphatic isostearyl ligand and 2 moles of function X carboxyl and function Y acryl ligands are possible. Thus the coupling agent provides bonding to silica containing glass fibers and a thermoplastic or thermosetting polymer. There is no indication that a bonding is possible with gypsum. However, bond with calcium carbonate is indicated. These compositions are manufactured by Kenrich Petrochemicals Inc, 140 East 22nd street/P.O. Box 32, Bayonne, N.J. 07002-0032.

[0030] Notwithstanding the advances in the field of gypsum boards and related articles, there remains a need in the art for a readily and inexpensively produced gypsum board having improved strength and flexure resistance with superior nail pull out resistance.

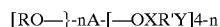
SUMMARY OF THE INVENTION

[0031] The present invention provides a high strength, improved flexure resistant and improved nail pull out resistant gypsum board with a titanium or zirconium based coupling agent that enhances bonding between gypsum crystals and provides improved bonding between the gypsum matrix and glass fibers. The coupling agent chemically bonds the glass fibers to the gypsum matrix and bonds gypsum crystals together. The coupling agent provides a thin layer of coating on the glass fibers, with the hydroxyl group

present on glass fibers replaced by a Ti—O or Zr—O group; while phosphate or pyrophosphate functionality potentially creates a chemical bond with calcium ions of hydrated gypsum crystal when the gypsum board is dried. The gypsum crystals are bonded to each other by the phosphate or pyrophosphate functionality of the coupling agent. The composition is suitable for use in aqueous mediums wherein different functionality of the coupling agent disassociates forming these chemical bonds.

[0032] The titanium based coupling agents have a composition selected from the group consisting of LICA 12 (Titanium IV 2,2 [bis 2-propenolatomethyl] butanolato, tris [dioctyl] phosphato-O), LICA 38 (Titanium IV 2,2 [bis 2-propenolatomethyl]butanolato, tris [dioctyl]pyrophosphato-O), LICA 38J (Titanium IV [bis-2-propenolato-methyl]-1-butanolato, bis(dioctyl) pyrophosphato-O, {adduct} 3 moles N,N-dimethylamino-alkyl propenoamide), and LICA 38ENP (Titanium IV [bis-2-propenolatomethyl]-1-butanolato, tris(dioctyl) pyrophosphato-O:Ethoxylated Nonyl Phenol-1:1)).

[0033] The zirconium based coupling agents have a composition selected from the group consisting of NZ 38 (Zirconium IV 2,2[bis-2-propenolato methyl] butanolato, tris-(dioctyl)pyrophosphato-O, and NZ 38J (Zirconium IV 2,2-dimethyl 1,3 propanediolato, bis [dioctyl] pyrophosphato-O [adduct] 2 moles N,N-dimethylamino-alkyl propenoamide). The titanate or zirconate coupling agents have the following generic composition:



where RO is a hydrolyzable group or substrate reactive group with surface hydroxyl or protons that bond to the fiber; A is a tetravalent titanium or zirconium with Ti—O or Zr—O bond capable of dissociation allowing transesterification, transalkylation and other catalysis mechanisms; X is a binder functional group such as phosphato, pyrophosphato, etc. imparting quaternization sites and bond to Ca ions of hydrated gypsum crystal; R' is a thermoplastic functional group such as aliphatic and non-polar isopropyl, butyl, octyl, isostearoyl groups; naphthenic and mildly polar dodecylbenzyl groups or aromatic benzyl cumyl phenyl groups; Y is a thermoset functional groups such as acryl, methacryl, mercapto, amino etc.; and 4-n is mono, di or tri organo functionality. Hybrid titanate or zirconate coupling agents, such as those containing 1 mole of function X carboxyl and function R' aliphatic isostearyl ligand and 2 moles of function X carboxyl and function Y acryl ligands, are possible.

[0034] The RO group can dissociate and allow Ti bond to the glass fiber while the X functionality bonds to gypsum crystals (if the compositions are selected correctly). The functional groups that bond to thermoplastic or thermoset resins do not have any functionality in bonding glass fibers to a gypsum matrix. Not all compositions manufactured by Kenrich, outlined in the last reference (the Monte paper discussed hereinabove), provide the functionality of bonding glass fibers to gypsum or bonding gypsum crystals together. The compositions that provide this bonding are LICA 12, LICA 38, LICA 38J, LICA 38ENP, NZ 38, and NZ 38J, and these compositions have the X functionality as phosphato or pyrophosphato.

[0035] The glass fibers may be treated with the titanium or zirconium based coupling composition. The coupling com-

position is dissolved in an aqueous solution and is agitated. The solution may be coated uniformly on glass fibers by roller coating. The glass fibers may then be inserted into a dry premix of gypsum slurry such as calcium sulfate hemihydrate, starch, and accelerator. The coated glass fibers may also be laid in an organized form, such as a mat, over which the gypsum slurry is cast between a first bottom facer sheet and a second top facer sheet defining the gypsum matrix to form a gypsum board.

[0036] The quantity of coupling agent is selected to be in the range of 0.01 to 3 weight percent of the glass fiber weight, providing a thin layer of coating on the glass fiber's external surface, sufficient to provide a bond. Excessive amounts of coupling agents do not provide the gypsum board strength improvement since multiple layers interfere with each other. During the gypsum cure cycle, the excess water is evaporated and the coupling layer coated glass fiber comes into intimate contact with acicular gypsum crystals, forming a localized and intermittent chemical bond. When the board is flexed or subjected to stress during nail pullout, the glass fiber—gypsum matrix interface is stressed. Instead of the glass fiber separating from the gypsum matrix the structure is retained by the chemical nature of the bond between the gypsum matrix and the glass fiber's external surface. The bond also provides energy absorption due to crack deflection and the board absorbs significant energy prior to breakage, thereby providing increased flexure strength.

[0037] In a second embodiment, the wet alkaline gypsum slurry has a water-soluble coupling agent dissolved in it. The coupling agent composition has hydroxy functional groups attached on one end to a titanium or zirconium group of the coupling composition and is available to bond to the siloxy group present on the glass fiber. The phosphate or pyrophosphate functional group is attached to the titanium or zirconium group of the coupling and is available for forming chemical bonds with gypsum crystals when the cast gypsum slurry is dried via the process step and the water in the gypsum slurry is evaporated. In this mode, the coupling agent is brought into contact with the gypsum crystals and glass fiber through the wet gypsum slurry. Since the gypsum slurry now contains the coupling agent, a larger quantity of coupling agent must be added in order to provide sufficient reactivity to promote adherence to glass fibers, replacing the —OH bond with Ti—O or Zr—O bonds. A typical quantity required for this purpose is 0.001 wt % to 0.8 wt % of the gypsum weight.

[0038] In a third embodiment, it has been surprisingly found that addition of the titanium or zirconium based composition to the wet gypsum slurry has the ability to bond to gypsum crystals in the absence of the glass fibers. The titanium or zirconium based coupling composition chosen has three phosphate or pyrophosphate attachments sites suitable for interacting with calcium ions of the gypsum crystal and one attachment site to join with the hydroxyl group of glass fiber. Since three attachment sites are available in the coupling composition to attach to calcium ions of the gypsum crystal, a cross-linking bond between gypsum crystals is achieved. This attachment results in strength and nail pullout resistance of the gypsum wallboard. Addition of the titanium or zirconium based coupling composition to the

gypsum slurry in an amount ranging from 0.001 wt % to 0.8 wt % of the gypsum weight provides effective bonding between gypsum crystals.

BRIEF DESCRIPTION OF THE DRAWING

[0039] The invention will be more fully understood and further advantages will become apparent when reference is had to the following detailed description of the preferred embodiments of the invention and the accompanying drawings, in which:

[0040] **FIG. 1a** is a schematic diagram of a manufacturing process for gypsum boards involving an embodiment of the invention wherein a titanate or zirconate coupling is coated on external surfaces of glass fibers;

[0041] **FIG. 1b** is a schematic diagram of a manufacturing process for gypsum boards involving a second embodiment of the invention, wherein a titanate or zirconate coupling composition in the gypsum slurry creates a bond between glass fibers and the gypsum matrix;

[0042] **FIG. 1c** is a schematic diagram of a manufacturing process for gypsum boards involving a third embodiment of the invention, wherein a titanate or zirconate coupling composition in the gypsum slurry creates a bond between gypsum crystals in the gypsum matrix;

[0043] **FIG. 2** is a highly magnified cross-sectional view of a glass fiber illustrating attachment of a titanium coupling agent of composition $[\text{RO—}]_n\text{Ti}[\text{—OXR}'\text{Y}]_4\text{—n}$ according to the disclosure in the Monte paper (Monte, Salvatore, J., "Neoalkyl Titanate and Zirconate Coupling Agent Additives in Thermoplastics", *Polymer and Polymer Composites*, Vol 10, No. 1, 2002, p 1-53; discussed herein above in the "Background of The Invention" section).

[0044] **FIG. 3** is a highly magnified cross-sectional view of a glass fiber illustrating attachment thereof to a gypsum matrix in accordance with the first or second embodiment of the invention, when a titanium or zirconium coupling agent having a composition comprising LICA 12, LICA 38, LICA 38J, LICA 38ENP, NZ 38, and/or NZ 38J is utilized; and

[0045] **FIG. 4** is a highly magnified cross-sectional view of a gypsum matrix illustrating attachment of gypsum crystals through a titanium or zirconium based coupling agent in accordance with the third embodiment of the invention, when a composition comprising LICA 12, LICA 38, LICA 38J, LICA 38ENP, NZ 38, and/or NZ 38J is utilized.

DETAILED DESCRIPTION OF THE INVENTION

[0046] The present invention provides a gypsum board having added thereto a titanium or zirconium based coupling composition that (i) bonds reinforcing glass fibers to the gypsum matrix; and (ii) bonds gypsum crystals to each other.

[0047] In a first embodiment, the glass fibers are coated with a thin layer of titanium or zirconium coupling agent or sizing composition that chemically adheres to the glass fiber surface due to OH groups bonded to the Titanium IV or Zirconium IV ion. The titanium based coupling composition is selected from the group consisting of LICA 12, LICA 38, LICA 38J, and LICA 38ENP. The zirconium based coupling composition is a member selected from the group consisting of NZ 38 and NZ 38J. The amount of coupling agent needed

is generally small. Specifically, the quantity of coupling agent is selected to be in the range of 0.01 to 3 weight percent of the glass fiber weight, providing a thin coating on the glass fibers external surface sufficient to provide a bond. A rotating roller covered with coupling agent solution may be used to deliver the titanium, or zirconium based, coupling composition to the glass fibers and produce a uniform coating. The coated glass fibers, which may be inserted into a gypsum slurry mix comprising calcium sulfate hemihydrate, together with usual additives such as surfactants, foam formers, biocides and the like. In this case, the titanium or zirconium based coupling coating is applied as a sizing for the glass fibers, promoting the bond between the glass fibers and the gypsum matrix.

[0048] In a second embodiment, the titanium or zirconium based coupling agent is added to the gypsum matrix instead of being provided as a thin coating on the glass fibers. The coupling agent functions as a bond-enhancing agent between glass fibers and gypsum crystals in the gypsum matrix. It also functions as a bond-enhancing agent between the gypsum crystals. In this mode, a larger quantity of coupling agent is needed. Typically, the titanium (or zirconium) based coupling agent is added in the range of about 0.001 wt % to 0.8 wt % based on the gypsum weight. The coupling agent has one Ti—O or Zr—O active bond site to bond with glass fibers by the replacement of the —OH group and three active phosphate or pyrophosphate groups to bond with calcium ions of the gypsum crystal. As a result, the titanium or zirconium based coupling agent added to the gypsum slurry is bonded to the calcium ion sites of the gypsum crystal through phosphate or pyrophosphate active site bonding. As the gypsum crystal grows, the Ti—O or Zr—O active site creates bonds with the glass fibers. The titanium or zirconium based coupling composition provides bonds between (i) the gypsum crystals, themselves, and (ii) between the gypsum crystals and the glass fibers. Due to improved glass fiber to gypsum matrix bonding and improved bonding between gypsum crystals in the gypsum matrix, strength properties of the gypsum board are significantly enhanced.

[0049] Referring now to **FIG. 1a**, there is shown at **10** a first embodiment of the subject invention. The vessel **11** contains water with titanium or zirconium based coupling composition solution, which dissolves readily in the water. Chopped fiber **12** is added to the aqueous coupling solution. The aqueous coupling solution is stirred by agitator **13** to promote a uniform coating of the coupling solution, or sizing, on the external surfaces of the glass fiber. Now calcium sulfate hemihydrate and other additives are added to the vessel at **14**. Agitator **13** stirs the mixture to form a gypsum slurry of desired consistency and the slurry is cast through a closure valve **16** onto a moving belt **17** that carries a Kraft paper facer **18** which rests on the bottom surface of the gypsum board. A second layer of Kraft paper facer **19** is placed on the top surface of the cast gypsum board and the continuous gypsum board is scored to size and dried and cured in oven.

[0050] Referring now to **FIG. 1b**, there is shown at **10** a second embodiment of the subject invention. Vessel **11** is filled with a solution containing water and titanium or zirconium based coupling composition, which dissolves readily in the water. Calcium sulfate hemihydrate and other additives are added to the vessel at **14**. Chopped fiber **12** is added to the aqueous gypsum mixture-containing coupling

solution. Agitator **13** stirs the coupling solution containing gypsum mixture to form a gypsum slurry of desired consistency. The slurry is cast through a closure valve **16** onto a moving belt **17** that carries a Kraft paper facer **18**, which rests on the bottom surface of the gypsum board. A second layer of Kraft paper facer **19** is placed on the top surface of the cast gypsum board. The continuous gypsum board is scored to size and dried and cured in an oven.

[0051] Referring now to FIG. 1c, there is shown at **10** a third embodiment of the present invention. Vessel **11** is filled with a solution containing water and a titanium or zirconium based coupling composition, which dissolves readily in the water. Calcium sulfate hemihydrate and other additives are added to the vessel at **14**. Agitator **13** stirs the coupling solution-containing gypsum mixture to form a gypsum slurry of desired consistency. The slurry is cast through a closure valve **16** onto a moving belt **17** that carries a Kraft paper facer **18**, which rests on the bottom surface of the gypsum board. A second layer of Kraft paper facer **19** is placed on the top surface of the cast gypsum board. The continuous gypsum board is scored to size and dried and cured in oven.

[0052] Referring to FIG. 2, there is shown at **20** a schematic bonding according to the prior art, as disclosed by the Monte paper (Monte, Salvatore, J., "Neoalkyl Titanate and Zirconate Coupling Agent Additives in Thermoplastics", *Polymer and Polymer Composites*, Vol. 10, No. 1, 2002 p 1-53). The Monte paper discusses the bonding process of the glass reinforcement coated with titanium or zirconium based coupling agent having a generic composition of the type $[\text{RO}-]_n\text{Ti}[-\text{OXR}'\text{Y}]_{4-n}$ and a thermoplastic or thermosetting polymeric composition. The glass fiber **21** contains silica and, in an aqueous medium, carries OH ions adhered as indicated. When the coupling composition of the form

several attachment points with the coupling providing a bond. The specific compositions of the coupling include titanium compositions of LICA 12, LICA 38, LICA 38J and LICA 38ENP; and zirconium composition of NZ 38, and NZ 38J. The terminations of these coupling compositions include phosphates and pyrophosphates, resulting in a bond to calcium ions.

[0054] In FIG. 4 there is shown generally at **40** a gypsum crystal **42**. One phosphato or pyrophosphate group active attachment site of the titanium (or zirconium) based coupling composition is attached to the calcium site of the gypsum crystal. The second phosphato or pyrophosphate group active attachment site of the titanium (or zirconium) based coupling composition attached to the calcium site of a second gypsum crystal **43** creating a cross-linked chemical bond between gypsum crystals **42** and **43**. The third phosphato or pyrophosphate group active attachment site of the titanium (or zirconium) based coupling composition **44** and the Ti—O (or Zr—O) active attachment site of the titanium (or zirconium) based coupling composition **45** is free and unattached. The specific compositions of the coupling include titanium compositions comprising LICA 12, LICA 38, LICA 38J and LICA 38ENP; and zirconium compositions comprising NZ 38, and NZ 38J. The terminations of these coupling compositions include phosphates and pyrophosphates, resulting in a bond to calcium ions.

[0055] The mechanical properties of gypsum boards manufactured with and without coupling bond coatings were measured. The flexure test and nail pullout results are obtained from unfaced normalized to density gypsum hand-board instead of faced gypsum board as described in the ASTM method.) The test results are set forth below in Table I.

TABLE I

| Process | Stucco Only | Standard Deviation | Product* | Standard Deviation | Product** | Standard Deviation |
|-----------------------|-------------|--------------------|----------|--------------------|-----------|--------------------|
| Flexure Strength KN | 0.096 | 0.009 | 0.097 | 0.005 | 0.102 | 0.002 |
| Nail Pull Strength KN | 0.180 | 0.022 | 0.275 | 0.015 | 0.288 | 0.030 |

*Without coupling coating

**With LICA 38J coupling bond coating

$[\text{RO}-]_n\text{Ti}[-\text{OXR}'\text{Y}]_{4-n}$ is added to the water, the Ti—O group displaces the OH groups, bonding the Ti to the silicon locations on the glass fiber, thereby creating an adhesive bond. The Ti ion is attached to other functional groups, which bond to the thermoplastic or thermosetting polymer creating a bond.

[0053] Referring now to FIG. 3 there is shown at **30** a glass fiber **31** with specific coupling composition that attaches on one end to glass fibers and on the other end to calcium ions of gypsum depicted at **32**. The attachment to glass fibers by replacement of OH group with Ti—O (or Zr—O) group of the coupling is essentially the same as that disclosed in the prior art as shown in FIG. 2. Since the gypsum crystals grow as a hydrated acicular species it may not surround the fiber completely and the contact between the glass fiber and the hydrated gypsum crystal occurs at

[0056] The test results clearly show that flexure strength of stucco without glass fibers is not improved when glass fibers are incorporated. This is due to the weak bond between the glass fibers and the gypsum matrix. When the gypsum board is stressed the fibers separate from the gypsum matrix providing practically no load transfer. On the other hand, when titanium based coupling bond coating is applied on the glass fibers the flexure strength is improved.

[0057] The nail pullout resistance of stucco alone, i.e. without glass fibers is very low. Adding glass fibers improves nail pullout due to the snagging effect of the glass fibers. This does not mean that the gypsum does not break in the form of chunks, since the gypsum matrix does not transfer the load to the glass fibers. When glass fibers are coated with titanium based bond coating according to the subject invention, the nail pullout resistance is markedly

improved. In addition, the gypsum matrix does not break in the form of chunks when the nail is pulled out due to the load transferring capability of the coupling bond layer

[0058] The gypsum board without any glass fiber reinforcement also shows remarkable improvement in the flexure strength and nail pullout resistance when the titanium or zirconium based coupling composition is added to the gypsum slurry as shown by Table II below.

TABLE II

| Process | Stucco Only | Standard Deviation | Product*** | Standard Deviation |
|-----------------------|-------------|--------------------|------------|--------------------|
| Flexure Strength KN | 0.096 | 0.009 | 0.109 | 0.008 |
| Nail Pull Strength KN | 0.180 | 0.022 | 0.214 | 0.002 |

***With LICA 38J coupling bond added to gypsum

[0059] The test results clearly show that flexure strength of stucco without addition of glass fibers is improved when titanium based coupling composition is added. The nail pullout is significantly improved due to the bond created between the gypsum crystals by the titanium based coupling agent.

[0060] Having thus described the invention in rather full detail, it will be understood that such detail need not be strictly adhered to, but that additional changes and modifications may suggest themselves to one skilled in the art, all falling within the scope of the invention as defined by the subjoined claims.

What is claimed is:

1. A gypsum board, comprising:

- a gypsum matrix formed from an aqueous gypsum slurry containing titanium or zirconium based coupling composition and having a bottom and a top, said gypsum matrix being operable to form gypsum crystals having calcium ions when said gypsum board is cured;
- a first facer sheet placed on said bottom of said gypsum matrix;
- a second facer sheet placed on said top of said gypsum matrix;
- said gypsum slurry containing a coupling composition of the type $[\text{RO—}]_n\text{Ti}[\text{—OXR'Y}]_4\text{—n}$ or $[\text{RO—}]_n\text{Zr}[\text{—OXR'Y}]_4\text{—n}$, said coupling composition type being operable to form Ti—O or Zr—O bonds when bonding chemically to glass fibers and having X functionality, said X functionality being a phosphate or pyrophosphate group operable to bond to calcium ions of gypsum crystal;
- said coupling composition bonding chemically to said glass fibers by replacing said OH ions with said Ti—O or Zr—O bonds, and forming a coupling composition coating on said external surfaces of said glass fibers,
- said coupling composition bonding chemically to said calcium ions of said gypsum crystals during said gypsum board cure by forming a bond with said X functionality of said coupling composition, and said cou-

pling composition coating providing increased strength, flexure resistance and nail pull out resistance to said gypsum board.

2. A gypsum board as recited by claim 1, wherein said gypsum matrix contains one or more glass fibers, and said glass fibers having external surfaces with OH ions thereon.

3. A gypsum board as recited by claim 1, wherein each of said first and said second facer sheets comprises Kraft paper.

4. A gypsum board as recited by claim 1, wherein said gypsum matrix comprises calcium sulphate hemihydrate ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$), calcium sulphate anhydrite (CaSO_4), hydraulic setting cement and water.

5. A gypsum board as recited by claim 3, wherein said hydraulic setting cement is selected from the group consisting of Portland cements, sulphate resisting cements, blast furnace cements, pozzolanic cements, and high alumina cements

6. A gypsum board as recited by claim 1, wherein said coupling composition is added to said gypsum slurry in amounts ranging from 0.001 wt % to 0.8 wt % based on gypsum weight.

7. A gypsum board as recited by claim 1, wherein said coupling composition is added to the gypsum slurry in amounts ranging from 0.1 wt % to 0.8 wt % based on gypsum weight.

8. A gypsum board as recited by claim 1, wherein said coupling composition comprises LICA 12 Titanium IV 2,2 [bis 2-propenolatomethyl] butanolato, tris [dioctyl] phosphate-O.

9. A gypsum board as recited by claim 1, wherein said coupling composition comprises LICA 38 Titanium IV 2,2 [bis 2-propenolatomethyl] butanolato, tris [dioctyl] pyrophosphato-O.

10. A gypsum board as recited by claim 1, wherein said coupling composition comprises LICA 38 ENP Titanium IV 2,2 [bis 2-propenolatomethyl] butanolato, tris [dioctyl] pyrophosphato-O:Ethoxylated nonyl phenol-1:1.

11. A gypsum board as recited by claim 1, wherein said coupling composition comprises LICA 38J Titanium IV [bis-2-propenolato-methyl]-1-butanolato, bis(dioctyl) pyrophosphato-O, {adduct} 3 moles N,N-dimethylamino-alkyl propenoamide.

12. A gypsum board as recited by claim 1, wherein said coupling composition comprises NZ 38 Zirconium IV 2,2 [bis-2-propenolato methyl]butanolato, tris(dioctyl)pyrophosphato-O.

13. A gypsum board as recited by claim 1, wherein said coupling composition comprises NZ 38J Zirconium IV 2,2-dimethyl 1,3 propanediolato, bis [dioctyl]pyrophosphato-O [adduct]2 moles N,N-dimethylamino-alkyl propenoamide.

14. A gypsum board as recited by claim 2, wherein said glass fibers are randomly arranged.

15. A gypsum board as recited by claim 2, wherein said glass fibers are arranged in the form of organized structures such as mats.

16. A process for manufacture of gypsum board, comprising the steps of:

- dissolving a titanium or zirconium based coupling composition in an aqueous solution;
- adding calcium sulphate hemihydrate with additives including starch, binder, accelerator, retarder, super-

plasticizer, water resistant agent, foaming agents, biocides etc to said aqueous solution form a aqueous gypsum slurry;

c. adding glass fibers to said aqueous gypsum slurry;

d. casting said aqueous gypsum slurry having said titanium or zirconium based coupling composition with said glass fibers on a first facer sheet, said gypsum casting having a top and a bottom;

e. applying a second facer sheet placed on said top of said gypsum casting and forming a gypsum board; and

f. drying and curing said gypsum board, said gypsum board being operative to increase strength, flexure resistance and nail pull out resistance.

17. A process for manufacture of gypsum board, comprising the steps of:

a. dissolving a titanium or zirconium based coupling composition in an aqueous solution;

b. adding calcium sulphate hemihydrate with additives including starch, binder, accelerator, retarder, superplasticizer, water resistant agent, foaming agents, biocides etc to said aqueous solution form a aqueous gypsum slurry;

c. casting said aqueous gypsum slurry having said titanium or zirconium based coupling composition on a first facer sheet, said gypsum casting having a top and a bottom;

d. applying a second facer sheet placed on said top of said gypsum casting and forming a gypsum board; and

e. drying and curing said gypsum board, said gypsum board being operative to increase strength, flexure resistance and nail pull out resistance.

* * * * *