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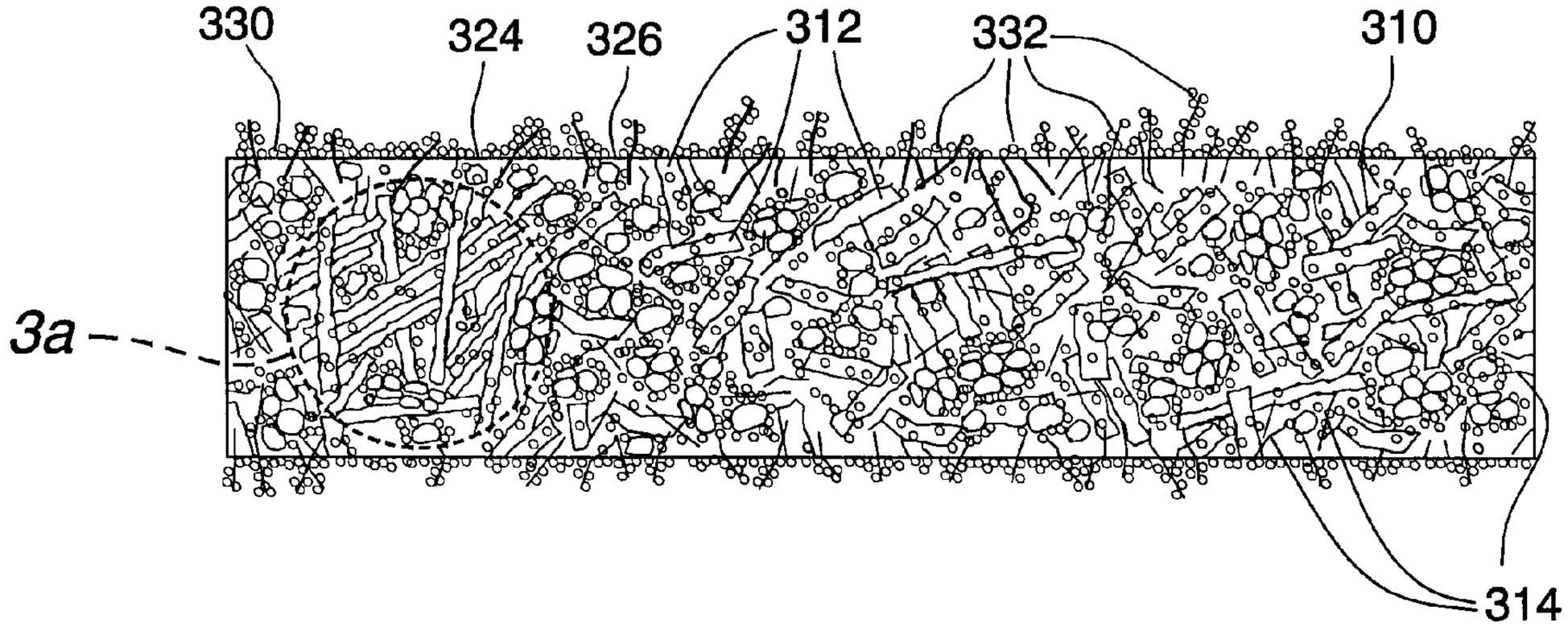
(54) Title: FIBER GLASS CARRIER HAVING INCREASED SURFACE AREA AND PHOTO-ACTIVE MATRICES FORMED THEREFROM



(57) Abrégé/Abstract:
A fiber glass carrier having a high surface area is disclosed for use as a carrier for photo-active materials, such as photocatalyst materials and photovoltaic materials. The fiber glass carrier can be formed by conventional fiber glass processing techniques, such as air-laid mat processes and wet-laid mat processes, and then further treated to provide increased surface area for β the deposition of the photo-active material thereon. Treatments to increase the surface area of the fiber glass carrier include etching with acid solution and coating of the fibers with a high surface area silica. Additionally, methods of distributing the photo-active material in carrier during the formation of the carrier are disclosed.

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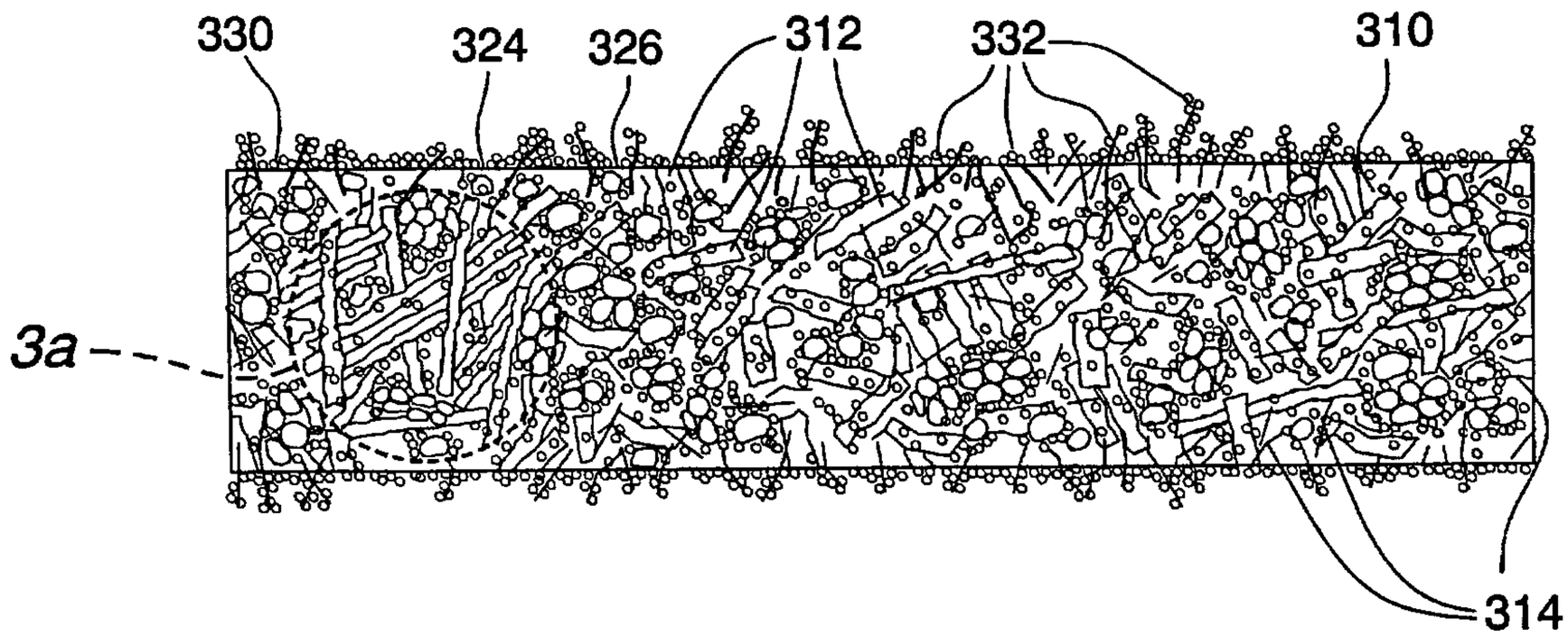

(57) Abstract: A fiber glass carrier having a high surface area is disclosed for use as a carrier for photo-active materials, such as photocatalyst materials and photovoltaic materials. The fiber glass carrier can be formed by conventional fiber glass processing techniques, such as air-laid mat processes and wet-laid mat processes, and then further treated to provide increased surface area for β the deposition of the photo-active material thereon. Treatments to increase the surface area of the fiber glass carrier include etching with acid solution and coating of the fibers with a high surface area silica. Additionally, methods of distributing the photo-active material in carrier during the formation of the carrier are disclosed.

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FIBER GLASS CARRIER HAVING INCREASED SURFACE AREA AND PHOTO-ACTIVE MATRICES FORMED THEREFROM

CROSS REFERENCE TO RELATED PATENT APPLICATION

This application claims the benefit if U.S. Provisional Application Serial No. 60/139,166, filed on June 15, 1999 and is related to U.S. Patent Application Serial No. 09/183,570 entitled "Photocatalytic Filter with Fiber Glass Mat Carrier" filed October 30, 1998.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention involves a structure for utilizing the known photo-active effect of certain materials, such a photocatalyst materials and photovoltaic materials, and more particularly involves a combination of photo-active material on a particular fiber glass carrier surface.

2. Technical Considerations

As used herein, the term "photo-active materials" means materials that actively interact with radiation of certain wavelengths, for example, photocatalyst materials and photovoltaic materials. The terms "photocatalyst" or "photocatalyst material", as used herein, mean a material wherein valence band electrons, upon exposure to photons of a given energy, are promoted into the conduction band with the simultaneous generation of corresponding holes in the valence band. These electrons and holes are consumed by reducing electron acceptors and oxidizing electron donors, respectively, that are adsorbed on the surface of the photocatalyst. See T. Sakata, "Heterogeneous Photocatalysis at Liquid-Solid Interfaces", Photocatalysis: Fundamentals and Applications, N. Serpone and E. Pelizzetti eds., (1989) at pages 311-313, which are hereby incorporated by reference. As used herein, the

term "photovoltaic material" means a material that is capable of converting radiation (typically solar radiation) into electricity when a photon collides with an atom in the material with enough energy to dislodge the electron from its fixed position in the material. See Van Nostrand's Scientific Encyclopedia, D. Considine and G. Considine eds., (7th Ed. 1989) at pages 2635-2636, which are hereby incorporated by reference.

The use of metal oxides such as titanium dioxide to photocatalytically decompose organic material has been extensively treated in the prior art. In addition to titanium dioxide, the photocatalytic effect has been reported to have been achieved with the oxides of zinc, tungsten, and tin. The present invention is expected to be useful with any photocatalyst that can be coated onto fiber glass. These can include some known photocatalytic non-oxide substances as well, but the ease of depositing the metallic oxides by presently known techniques makes them the preferred category for use with extended surface area substrates.

In U.S. Patent No. 5,045,288, a layer of catalyst particles is loosely supported on a filter or in a granular bed. A more practical approach to use the photocatalyst is to coat a solid support member with the catalyst. For example, use of porous ceramic substrates to support titanium dioxide coatings is disclosed in U.S. Patent No. 5,035,784. Because the photocatalytic effect requires exposure of the catalyst to ultraviolet radiation, the use of a transparent substrate such as glass has been suggested. In particular, it has been recognized in U.S. Patent Nos. 4,892,712; 4,966,759 and 5,032,241 (to Robinson et al.) that fiber glass combines both transparency and high surface area, whereby carriers made from matrices of fiber glass are ideally suited for this purpose. The Robinson et al. patents disclose both woven and non-woven fiber glass

substrates, but woven meshes are preferred, and no details regarding non-woven embodiments are provided.

In a similar manner, it has been observed that the efficiency of photovoltaic cells can be improved by applying the photovoltaic material to a roughened or high surface area carrier. For example, Japanese Patent Application No. 58120459 discloses a solar battery comprising an amorphous silicon thin film formed on a metallic foil which is laminated on a cloth. This configuration is believed to improve the conduction performance and conversion efficiency of the battery due to the uneveness of the surface of the cloth and foil.

It would be advantageous to provide high surface area carriers for use in forming photo-active matrices and, in particular, non-woven fiber glass carriers having high surface area, to permit an increase in both the amount and contact area of the photo-active material incorporated therein. Furthermore, it would be advantageous if the surface area of non-woven carriers could be further increased to provided for an additional level of performance enhancement in such applications. It has now been found that a uniquely processed fiber glass carriers can meet these objectives of providing high available surface area that permit it to be used directly to manufacture photo-active matrices for various applications.

SUMMARY OF THE INVENTION

One aspect of the present invention is a fiber glass carrier comprising a plurality of glass fibers wherein at least a portion of the plurality of glass fibers have a surface area of at least about 10 square meters per gram as measured by BET surface area analysis using nitrogen.

Another aspect of the present invention is a non-woven fiber glass carrier comprising a plurality of glass fibers at least a portion of the

plurality of glass fibers having a high surface area silica material positioned thereon.

Another aspect of the present invention is a method of forming a high surface area fiber glass carrier, the method comprising the steps of forming a fiber glass carrier comprising a plurality of glass fibers, and modifying at least a portion of the plurality of glass fibers such that the at least a portion of the plurality of glass fibers has a surface area that is at least about 10 square meters per gram as measured by BET surface analysis using nitrogen.

Yet another aspect of the present invention is a method of forming a high surface area fiber glass carrier, the method comprising the steps of forming a non-woven, fiber glass carrier, and applying a high surface area silica material to at least a portion of a surface of the non-woven, fiber glass carrier.

Still another aspect of the present invention is a method of forming a photocatalytic matrix, the method comprising the steps of forming an aqueous dispersion comprising a plurality of chopped glass fibers and a foaming agent, agitating the dispersion to form a foamed slurry, casting the foamed slurry to form a sheet, removing at least a portion of the foam from the sheet, at least partially drying the sheet to form a fiber glass carrier, and incorporating a photocatalyst material into the fiber glass carrier to form a photocatalytic matrix.

Another aspect of the present invention is a method of forming a photocatalytic matrix, the method comprising the steps of forming an aqueous dispersion comprising a plurality of chopped glass fibers and a high surface area silica material, casting the dispersion to form a sheet, at least partially drying the sheet to form a fiber glass carrier, and incorporating a photocatalyst material into the fiber glass carrier to form a photocatalytic matrix.

DESCRIPTION OF THE DRAWINGS

Figs. 1 and 1a are schematic, cross-sectional views of a fiber glass carrier incorporating features of the present invention;

Figs. 2 and 2a are schematic, cross-sectional views of another embodiment of a fiber glass carrier incorporating features of the present invention; and

Figs. 3 and 3a are schematic, cross-sectional views of a photo-active matrix incorporating features of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The fiber glass carriers of the present invention are advantageous in providing high surface area supports for photo-active materials and, in particular, photocatalyst and photovoltaic materials, that can provide for enhanced performance of photo-active matrices formed therefrom. As used herein, the terms "photo-active matrix" or "photo-active matrices" mean a fiber glass carrier having a photo-active material incorporated therein. Although not meant to be limiting in the present invention, preferably the photo-active material is incorporated into the carrier by applying a coating comprising the photo-active material to at least a portion of a surface of the carrier after formation of the carrier, incorporating into the carrier at least one fiber having a photo-active material applied to at least a portion of a surface thereof, or incorporating the photo-active material into carrier during formation of the carrier. Methods of incorporating photo-active materials into the carriers of the present invention are discussed in detail below.

Referring to Figs. 1 and 1a, in one, non-limiting embodiment according to the present invention, preferably the fiber glass carrier 10 is formed from a plurality of fiber glass strands 12, comprising a plurality of individual fibers or filaments 14. As used herein, the term "strand" means

a plurality of individual fibers and the term “fiber” means an individual filament.

The fiber glass strands 12 can be comprised of fibers 14 formed from known glass compositions based upon silicon oxide selectively modified with other oxide and non-oxide compounds. Useful glass fibers can be formed from any type of fiberizable glass composition known to those skilled in the art, and include those prepared from fiberizable glass compositions commonly known as "E-glass," "A-glass," "C-glass," “D-glass,” “R-glass,” "S-glass,” and E-glass derivatives. As used herein, “E-glass derivatives” means glass compositions which include minor amounts of fluorine and/or boron and are preferably fluorine and/or boron-free. Furthermore, as used herein, minor means less than about 1 weight percent fluorine and less than about 5 weight percent boron. Preferred glass fibers are formed from E-glass or E-glass derivatives. Such compositions and method of making glass filaments therefrom are well known to those skilled in the art and further discussion thereof is not believed to be necessary in view of the present disclosure. If additional information is needed, such glass compositions and fiberization methods are disclosed in K. Loewenstein, The Manufacturing Technology of Continuous Glass Fibres, (3rd Ed. 1993) at pages 30-44, 47-60,115-122 and 126-135; and U.S. Patent Nos. 4,542,106 and 5,789,329, which are hereby incorporated by reference.

Glass fibers have been made with nominal filament diameters ranging from about 3.5 micrometers to about 35.0 micrometers (microns), and any filament diameter could theoretically be used in the present invention. Even smaller filament diameters are possible, particularly with spun fiber glass. Although not required, it is preferred to use fibers having a nominal filament diameter above 3.5 microns to avoid the presence of respirable fibers when, for example, the photo-active matrix is

a photocatalytic matrix for use in air filtration applications. Furthermore, filament diameters less than 7 microns are not readily available commercially. Thus, in one, non-limiting embodiment of the present invention, a majority of the glass fibers of the fiber glass carrier have a nominal filament diameter of at least about 1.0 micron and preferably at least about 3.5 microns. In other specific, non-limiting embodiments of the present invention, the majority of fibers have a nominal filament diameter of about 10 microns. Higher diameters, on the order of 17 microns or greater, can also be considered for use in the present invention and can have advantages in ease of processing. The filament diameter, however, is not critical to the present invention. For further information regarding nominal filament diameters and designations of glass fibers, see Loewenstein (*supra*) at page 25, which is hereby incorporated by reference.

Individual filaments are usually gathered together to form strands. The number of filaments per strand can range from about 100 to about 15,000, and is typically about 200 to about 7000. For more information regarding glass fiber strand designations, see Loewenstein (*supra*) at page 27, which is hereby incorporated by reference.

To prevent destructive abrasion between filaments during processing, glass fibers are conventionally coated on at least a portion of their surfaces with a sizing composition which serves to lubricate the fibers and to bind the filaments into the strands. Conventionally, most sizing compositions contain as their largest organic component a polymeric film-forming material. Most conventional sizing compositions also contain a coupling agent, a lubricant, and a surfactant. Other minor additives can also be present, such as anti-static agents. In order to minimize the organic content of the fiber glass, the present invention uses sizing compositions that include little or none of the materials that would

normally be considered primarily film-forming. This is not to imply that no film forming occurs with the remaining components. Coupling agents in particular, when present, are believed to produce some degree of film forming, although not of the elastomeric type for which the conventional film formers are chosen. In one non-limiting embodiment of the present invention, a relatively friable film is not considered disadvantageous because such a film aids in the filamentizing of strands which takes place in the subsequent mat forming steps. As used herein the term "filamentizing" means the opening and at least partial separation of the strand bundle into individual filaments or fibers. Filamentizing is advantageous because the surface area of the carrier is increased and greater opportunity for mechanical intertwining of the filaments is presented. Although not limiting, in one embodiment of the present invention the sizing components are chosen primarily for their lubricating function, and therefore preferably include a conventional lubricant. Coupling agents can also serve a lubricating function, so sizing compositions of the present invention can include coupling agents in place of or in addition to a conventional lubricant.

The glass fiber lubricants, at least one of which is included in the sizing according to one, non-limiting embodiment of the present invention, are different from what are conventionally considered polymeric film-forming materials. The glass fiber lubricants can have some film-forming capability, but would not otherwise be chosen for that purpose. Useful glass fiber lubricants include, but are not limited to, cationic, non-ionic or anionic lubricants and mixtures thereof. The fiber lubricant can comprise 0 to 100 weight percent of the sizing composition based on total solids. Preferably, although not required, a combination of lubricant and coupling agent can be used, in which case the lubricant can be present in amounts of 1 to 20 weight percent based on total solids of the sizing composition.

Non-limiting examples of the many known fiber lubricants include amine salts of fatty acids (including, for example, a fatty acid moiety having 12 to 22 carbon atoms and/or tertiary amines having alkyl groups of 1 to 22 atoms attached to the nitrogen atom), alkyl imidazoline derivatives (such as can be formed by the reaction of fatty acids with polyalkylene polyamines), acid solubilized fatty acid amides (for example, saturated or unsaturated fatty acid amides having acid groups of 4 to 24 carbon atoms such as stearic amide), condensates of a fatty acid and polyethylene imine and amide substituted polyethylene imines, such as EMERY® 6717, a partially amidated polyethylene imine commercially available from Henkel Corporation of Cincinnati, Ohio.

Although not limiting in the present invention, useful alkyl imidazoline derivatives include CATION X from Rhone Poulenc of Princeton, New Jersey, and LUBRIL CAT-X/VC from Rhodia of Cranbury, New Jersey. Other useful, non-limiting lubricants include RD-1135B epoxidized polyester which is commercially available from Borden Chemical of Louisville, Kentucky, CIRRASOL 185A fatty acid amide, KETJENLUBE 522 partially carboxylated polyester which is commercially available from Akzo Chemicals, Inc. Of Chicago, Illinois and PROTOLUBE HD high density polyethylene emulsion which is commercially available from Sybron Chemicals of Birmingham, New Jersey.

Non-limiting examples of coupling agents that can be included in the sizing compositions of the present invention can be selected from the group consisting of organo silane coupling agents, transition metal coupling agents (such as titanium, zirconium and chromium coupling agents), amino-containing Werner coupling agents and mixtures thereof. These coupling agents typically have dual functionality. Each metal or silicon atom has attached to it one or more groups which can react with the glass fiber surface or otherwise be chemically attracted, but not

necessarily bonded, to the glass fiber surface. Conventionally, the other functionality included in coupling agents provides reactivity or compatibilization with film forming polymers. Since the usual film forming polymers are not relied upon in the present invention, this functionality is less important. However, some self cross-linking capability with some coupling agents can be provided by the additional functionality.

Although not required, organo silane compounds are the preferred coupling agents in the present invention. Non-limiting examples of suitable organo silane coupling agents include Z-6040 gamma-glycidoxypropyltrimethoxysilane commercially available from Dow Corning of Midland, Michigan; A-187 gamma-glycidoxypropyltrimethoxysilane, A-174 gamma-methacryloxypropyltrimethoxysilane and A-1100 gamma-aminopropyltriethoxysilane, each of which are commercially available from CK Witco Corporation of Tarrytown, New York. Although not limiting in the present invention, the amount of coupling agent can be 0 to 80 weight percent of the sizing composition on a total solids basis. In preferred, non-limiting embodiments, the coupling agent content is at least 10 weight percent and more preferably at least 30 weight percent of the sizing composition on a total solids basis. Although not required, the organo silane coupling agent can be at least partially hydrolyzed with water prior to application to the glass fibers.

One non-limiting embodiment of the sizing composition can include one or more surfactants for stabilizing the other components of the sizing composition in an aqueous medium. Non-limiting examples of suitable surfactants include polyoxyalkylene block copolymers (such as PLURONIC™ F-108 polyoxypropylene-polyoxyethylene copolymer which is commercially available from BASF Corporation of Parsippany, New Jersey), ethoxylated alkyl phenols (such as IGEPAL CA-630 ethoxylated octylphenoxyethanol which is commercially available from GAF

Corporation of Wayne, New Jersey), polyoxyethylene octylphenyl glycol ethers, ethylene oxide derivatives of sorbitol esters and polyoxyethylated vegetable oils (such as EMULPHOR EL-719, which is also commercially available from GAF Corp.). Generally, the amount of surfactant can be 0 to 40 weight percent of the sizing composition on a total solids basis.

Although not required, minor amounts of various additives can also be present in the sizing such as anti-static agents, fungicides, bactericides, and anti-foaming materials. Also, organic and/or inorganic acids or bases in an amount sufficient to provide the aqueous sizing composition with appropriate pH (typically 2 to 10) can be included in the sizing composition.

When it is applied to the glass fibers, the sizing composition is preferably diluted with water by several times its weight. The amount of water (preferably deionized) included in the sizing composition can be any amount sufficient to facilitate application of a generally uniform coating on the fiber glass. Although not limiting in the present invention, the weight percentage of solids of the sizing composition can generally range from about 5 weight percent to about 20 weight percent, but the dilution of the sizing can vary considerably depending upon such factors as the type of applicator used.

In one non-limiting embodiment of the present invention, a sizing was made as follows:

TABLE 1

	Component	Amount (parts by weight)
1	Water	3632.00
2	Acetic acid	45.40
3	Silane [1]	169.50
4	Cationic softener[2]	18.16
5	Warm water	484.20
6	Surfactant[3]	84.80
7	Warm water	484.20

Components 4 and 5 were pre-mixed by stirring for 20 minutes before being added to the other components. Components 6 and 7 were pre-mixed by stirring for 20 minutes before being added to the other components.

In one non-limiting, preferred embodiment of the present invention, the sum total of all of the organic constituents of the sizing composition described above are minimized so as to avoid the need for a heat cleaning the fiber glass carrier. In general, although not limiting, the loss on ignition (LOI) of the fiber glass carrier is less than 1.0 weight percent, preferably less than 0.5 weight percent, most preferably less than 0.4 weight percent. Some sizing is preferably present, but, as described above, its constituents are selected so as to minimize the LOI. In those preferred, non-limiting embodiments where some sizing is present, the LOI of the carrier is at least 0.1 weight percent.

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[1] A-1100 gamma aminopropyltriethoxysilane from CK Witco of Tarrytown, New York.

[2] LUBRIL CAT-X/VC, an imidazoline from Rhodia, Inc., Cranbury, New Jersey.

[3] IGEPAL CA-630 from GAF Corporation, Wayne, New Jersey.

As used herein, the term "loss on ignition" or "LOI" means the weight percent of dried coating composition present on the carrier as determined by Equation 1:

$$LOI = 100 \times [(W_{dry}-W_{bare})/W_{dry}] \qquad \text{(Eq. 1)}$$

wherein W_{dry} is the weight of the fiber glass carrier plus the weight of the coating composition after drying in an oven at 220°F (about 104°C) for 60 minutes, and W_{bare} is the weight of the bare fiber glass carrier after heating the carrier in an oven at 1150°F (about 621°C) for 20 minutes and cooling to room temperature in a dessicator.

Sizing can be applied to the filaments of the present invention by any of the various ways known in the art, for example, although not limiting herein, by contacting the filaments with a static or dynamic applicator, such as a roller or belt applicator, or by spraying or by other means. For a discussion of suitable applicators, see Loewenstein (*supra*) at pages 165-172, which are hereby incorporated by reference. Sized filaments can be gathered together into strands as previously discussed.

Although not required, the sized strands can be dried at room temperature or at elevated temperatures to remove water content and to cure any curable sizing or secondary coating composition that may be present. Drying of glass fiber strands is conventional in the art and further details can be seen in Loewenstein (*supra*) at pages 219-222, which are hereby incorporated by reference.

Although not a preferred practice for the present invention, a secondary coating can be applied to the strands. If employed, preferably the secondary coating composition is aqueous-based and can include components similar to the sizing compositions discussed above. The secondary coating composition can be applied to at least a portion of the surface of the strands in an amount effective to at least partially coat or impregnate the portion of the strands. The secondary coating can be

conventionally applied by dipping the strand in a bath containing the composition, by spraying the composition upon the strand or by contacting the strand with a static or dynamic applicator such as a roller or belt applicator, for example. The coated strand can be passed through a die to remove excess coating from the strand and/or dried as discussed above for a time sufficient to at least partially dry and cure the secondary coating. Although not required, if used, preferably a secondary coating would have a composition similar to that of the sizing compositions disclosed above.

The processes of manufacturing fiber glass and forming it into a substrate or carrier are well known in the art and are not themselves part of the present invention. Accordingly, any conventional means for performing these steps can be used and need not be described in detail. The description herein of the fiber forming and substrate forming steps are not intended to limit the types of processes that can be used, but rather are merely examples that are included for the sake of disclosing the best mode of carrying out the invention. If needed, further details of these conventional aspects of the invention can be found in Loewenstein, at pages 13-14, 18-19, 115-235, 293-312, and 322-324, which are hereby incorporated by reference.

Referring again to Fig. 1, the fiber glass carriers 10 of the present invention can be formed by any conventional process for forming fiber glass substrates that are well known in the art, including weaving processes that are well known in the art. However preferably, although not limiting in the present invention, the fiber glass carriers are non-woven carriers. As used herein, the term "non-woven" carrier means a carrier formed by processes other than weaving processes. Examples of suitable non-woven carriers include, but are not limited, to air-laid mats and wet-laid mats which are discussed below in detail. Other non-woven carrier

suitable for use in the present invention included, but are not limited to, chopped strand mats and continuous strand mats.

Although not required, the use of non-woven fiber glass carriers is preferred in one non-limiting embodiment of the present invention. The use of non-woven carriers is believed to be advantageous over the use of woven carriers, in that non-woven carriers tend to have a higher surface area available for the deposition of the photo-active material thereon. Nevertheless, in another non-limiting embodiment of the present invention, the use of a woven glass carrier having enhanced surface area is contemplated. Although not limiting in the present invention, enhanced a surface area can be achieved in a woven carrier by, for example, needling, etching, and/or applying a high surface area silica material to the carrier as discussed below in detail.

Referring again to Fig. 1, in one non-limiting embodiment according to the present invention, preferably the fiber glass carrier 10 is formed from a plurality of strands 12 and fibers 14 that have been chopped by a chopper into discontinuous lengths.

Although not limiting in the present invention, in order to facilitate fabricating carrier 10 and interlocking filaments 14, the chopped strands 12 and fibers 14 have an average length of at least about 2 centimeters and generally no greater than about 10 centimeters. Smaller lengths are generally difficult to convert into a structurally integrated mat, and longer lengths are difficult to handle in the mat forming process. Chopped lengths of about 5 centimeters have been used successfully, and some strength advantage can be achieved with slightly larger lengths on the order of about 7 to about 8 centimeters. Commercially available choppers are suitable, such as Model 90 chopper from Finn and Fram, Inc. of San Fernando, California. Useful apparatus and processes for forming a layer

of chopped strands is disclosed in Loewenstein (*supra*) at pages 293-303, which are hereby incorporated by reference.

For the sake of providing high surface area in the photo-active matrices of the present invention, the fiber glass strands 12 are at least partially filamentized, as shown in Figs1 and 1a. In one non-limiting embodiment of the present invention, the glass strands 12 are preferably at least 70 weight percent filamentized, more preferably at least 80 percent filamentized, and most preferably at least 90 percent filamentized. Although 100 percent filamentizing would be optimum, it is seldom fully achieved. Filamentizing *per se* is known in the art, and can be accomplished by mechanical or pneumatic means that are typically associated with the mat forming apparatus. A non-limiting example of such an apparatus which advantageously imparts a high degree of filamentizing to the strands is the RANDO-OPENER BLENDER, which is a part of the MODEL B RANDO-WEB® processor commercially available from Rando Machine Corporation of Macedon, New York. Alternatively, the strand opener can be a carding machine, such as those commercially available from Hollingsworth on Wheels, Inc. of Greenville, South Carolina or N. Schlumberger (USA) Inc. of Charlotte, North Carolina. The opening action of the Rando model is the agitation produced by passing the strands between a series of rolls rotating in opposite directions. The percentage of strand filamentized can be adjusted by adjusting the spacing between the opposing rolls of the strand opener and the rotational speed of the rolls.

Following the opening process, the fibers 14 and strands 12 can be conveyed to an air-laid mat forming apparatus. A non-limiting mat former is a RANDO-WEBBER®, part of the MODEL B RANDO-WEB® processor discussed above. In the Rando process the glass fibers and strands are conveyed by an air stream and the fibers and strands are deposited upon

the surface of a rotating cylindrical feed mat condenser screen maintained at a pressure below atmospheric pressure to form a feed mat. The feed mat is doffed from the feed mat condenser and fed to a lickerin which combs individual strands and monofilaments from the feed mat which are then carried by another air stream and deposited as a mat on the surface of another rotating cylindrical condenser screen which is maintained at a pressure below atmospheric pressure. The mat thus formed is conveyed from the mat former to a needling station.

Conventional mats are sometimes combined with minor amounts of unidirectional glass fibers, thermoplastic fiber and/or fabrics. The purpose for these additional fibers is to provide temporary strength to the mat during further processing steps. These supplemental strands and/or fabric can be positioned between layers of the mat or on one side of the mat and then subjected to the needling operation. Although not precluded by the present invention, these supplemental layers have not been found necessary with preferred embodiments of the present invention. It is noteworthy that the mechanical strength of the mats of the present invention can be attained without such reinforcing strands or fabric.

In one non-limiting embodiment of the present invention, the glass fibers 14 and strands 12 of carrier 10 (as well as any supplemental fibers) are intermeshed by subjecting carrier 10 to a needling process. The needling can be accomplished using a conventional needling apparatus as used in the fiber glass reinforcement industry, wherein the carrier is passed between spaced needling boards. An example of such an apparatus is disclosed in U.S. Patent No. 4,277,531, which is hereby incorporated by reference. An example of one suitable needling machine is Model NL 9 which is commercially available from Textilmaschinenfabrik Dr. Ernest Fehrer AG of Germany. In the needling operation, an array of barbed needles is used to entangle or intertwine the monofilaments and

strands of the mat to impart mechanical strength and integrity to the mat. As indicated in Fig. 1, the effect of needling is to displace a portion 16 of the filaments 14 and/or strands 12 out of the generally planar array of the carrier 10 and into a direction substantially normal to the plane of the carrier 10. The extent to which this displacement occurs depends upon such factors as the type of needles used, the depth of needle penetration through the mat, and the density of needle punches.

In one non-limiting embodiment of the present invention, the needling operation can use needles that are constructed with barbs that angle toward the needle tips, whereby fibers and strands in the mat are entangled as the needles pass into the mat. On the withdrawal stroke, this needle type generally releases fibers. Although needles with downwardly pointed barbs are preferred, the use of reverse barb needles (i.e., angled away from the needle tip) is not precluded in the present invention. Because of the low density of the mats of certain non-limiting embodiments of the present invention, it has been found advantageous to use needles that are relatively thin. As used herein, the term "low density" with respect to the mats means mats having an area density of not greater than about 1.0 ounces per square foot (about 305.1 grams per square meter) and more preferably not greater than about 0.5 ounces per square foot (about 152.6 grams per square meter). Needles of heavier gauge than 25 gauge (i.e., with smaller gauge numbers) tend to break undue numbers of filaments, thereby failing to improve strength as intended. Although not required, needles of 30 gauge and lighter, and preferably 32 gauge and lighter, are recommended with the low density mats of the present invention. A particularly useful commercially available needle type is the "star" type of needle which has six barbs spaced in a triangular arrangement around the shaft of the needle, with pairs barbs in vertical alignment above each other. Because it has also

been found desirable to limit needle punch depth, it is advantageous that the "star" type of needle locates the barbs close to the tip of the needle. Suppliers of these types of needles include the Foster Needle Company, Manitowoc, Wisconsin, and Groz-Beckert USA, Charlotte, North Carolina.

As used in the description of the needling operation herein, the terms "horizontal" or "horizontally" refer to a plane generally parallel to the major plane of the mat, which is typically parallel to the ground. As used herein, the terms "vertical" or "vertically," "downwardly," and "upwardly" refer to a direction generally normal to "horizontal." It should be understood that these specific directional terms are used to describe the needling operation for convenience, reflecting the usual orientation of the needling apparatus, and for defining the directions relative to each other, but that these orientations are not limitations on the process.

In one non-limiting embodiment, on the entering needling stroke, the needles carried on the needle board pass through the mat and into generally cylindrical orifices in a backer board supporting the mat. Depending upon the needling depth, one or more of the tiers of barbs pass entirely through the mat and into the backer board orifices. For the purposes of one non-limiting embodiment of the present invention, when a two-tier needle design is used, it is preferred that both tiers of barbs pass through and beyond the mat. The distance that the needles pass beyond the mat and into the orifices in the backer board is termed the "needling depth." Needling depth in preferred, non-limiting embodiments range from 0.45 to 0.65 inches (1 centimeter to 1.7 centimeter).

During the withdrawal stroke, after the needles exit the mat, they are passed through a plurality of generally cylindrical orifices in a metal stripper plate spaced from the mat during the needling process. The filaments and strands are pulled from the barb by the stripper plate, and the mat is then advanced after the complete stroke of inserting and

withdrawing the needles. Although not required, the needle board can be reciprocated with a frequency of about 80 to about 3000 strokes per minute. A needler is typically provided with rolls to propel the mat in the horizontal direction during needling. At slower frequencies the advancement occurs intermittently in the interval between punches of the needles. At faster frequencies, the advancement approaches a continuous motion.

The punch density also can be varied to affect the reinforcement of the mat. Needle punch density will depend upon the particular type of needles used, the mat thickness, and other factors. Although not limiting in the present invention, in the context of the other preferred needling parameters disclosed herein, needle punch density preferably ranges from 100 to abut 160 punches per square inch (15 to 25 punches per square centimeter). Smaller punch densities are possible, but may not attain the desired mat strength without binders (discussed below). Larger punch densities at some point tend to produce diminishing returns, actually decreasing the mat strength. Preferred, non-limiting embodiments employed approximately 140 punches per square inch (23 punches per centimeter). The needling process is described in further detail in U.S. Patent No. 4,335,176, which is hereby incorporated by reference.

In a typical needling process, the mat entering the needler can have an overall average thickness of about 5 to about 30 millimeters. After passage through the needler, the mat can have a compressed average thickness of about 2.5 to about 7 millimeters. The thickness, or "loft" of the mat is influenced by the extent to which spikes of fiber extend from the face of the mat due to the needling process. In certain, non-limiting embodiments of the present invention, the loft of the mat is relatively high for its low density. Loft in preferred, non-limiting embodiments of the mat of the invention exceeds 0.25 inch (6.3 millimeters), and preferably

exceeds 0.35 inch (8.9 millimeters). Although not required, maximizing loft is generally desirable in present invention, but to achieve loft greater than about 0.5 inch (about 12.7 millimeters) with mats of the type involved here can require excessive needling, which can have a detrimental effect on tensile strength. Loft can be measured by placing a weight of one ounce on a one foot square area and measuring the thickness of the compressed mat.

Tensile strength of carriers made from the air-laid process discussed above was measured with a 3 inch (7.6 centimeters) by 9 inch (22.9 centimeters) specimen of the mat drawn in its long dimension with an Instron Series IX Materials Testing System. Although not required in the present invention, preferably the mat carriers exhibit a tensile strength greater than 8.0 pounds per linear foot width of mat (about 11.9 kilograms per linear meter), and more preferably greater than 10.0 pounds per linear foot width of mat (about 14.9 kilograms per linear meter).

After the fiber glass carrier 10 is formed, it can be treated to further enhance the surface area of the fibers and strands and/or the carrier and a coating comprising a photo-active material can be applied thereto to form a photo-active matrix, as discussed below in detail.

In another non-limiting embodiment according to the present invention, the fiber glass carrier is formed using a wet-laid, paper-making process. Wet-laid processes are well known to those skilled in the art and the following examples are illustrative of typical wet-laid processes and are not meant to be limiting in the present invention.

In one non-limiting example of a method of forming a fiber glass carrier via a conventional wet-laid process, chopped glass fiber strands are dispersed into a white water solution. As used herein, the term "white water solution" means a solution, preferably an aqueous solution, which can comprise dispersants, thickeners, softening and hardening

chemicals, and dispersed or emulsified polymers. Such white water solutions are well known to those skilled in the art. If additional information is required, see U.S. Patent No. 5,393,379, which is hereby incorporated by reference. After the chopped glass fiber strands are dispersed into the white water solution, the dispersion or slurry is deposited into a head box and then cast onto a moving wire screen to form a fiber glass sheet. As used herein, the term "cast" means deposited. The sheet is then at least partially dried by a suction or vacuum device to form a fiber glass carrier. After the fiber glass carrier is formed, it can be treated to further enhance the surface area of the fibers and/or the carrier and a coating comprising a photo-active material can be applied thereto to form a photo-active matrix, as discussed below in detail.

In another non-limiting embodiment of a method of forming a fiber glass mat carrier according to the present invention, which is a preferred method of forming a fiber glass mat carrier using a wet-laid process, the carrier is formed by dispersing chopped glass fibers into an aqueous slurry along with one or more foaming agents and agitating the slurry to form a foam. A non-limiting example of a foaming agent suitable for use in the present invention is TRITON X100, which is a ethoxylated octylphenol that is commercially available Union Carbide Corporation of Danbury, Connecticut. Although not required, if desired, a polymeric material can be dispersed in the aqueous slurry along with the chopped fiber strands and the foaming agent to bind the carrier together after drying.

After forming the foamed slurry, the slurry is cast onto a web and the foam is vacuumed away to leave a fiber glass sheet. The fiber glass sheet can then be at least partially dried to form a fiber glass carrier in the form of a non-woven mat. After the fiber glass carrier is formed, it can be treated to further enhance the surface area of the fibers and/or the

carrier and a coating comprising a photo-active material can be applied thereto to form a photo-active matrix, as discussed below in detail.

Although not meant to be limiting in the present invention, it is believed that foamed slurry process of forming a fiber glass carrier (also known as the Radlite™ process) is advantageous in that at least a portion of the chopped glass fiber strands are opened and at least partially filamentized during the agitation step. As previously discussed, by opening the fiber glass strand bundles, the individual filaments are exposed thereby providing additional surface area onto which the photo-active material can be adhered. Furthermore, if the photo-active material is incorporated into the dispersion prior to casting, an essentially homogenous distribution of the photo-active material in the carrier can be achieved. Methods of incorporating photo-active materials into the carriers of the present invention to form a photo-active matrices in accordance with the present invention are discussed in more detail below.

If desired, a binding material (or binder) can be applied to carrier 10 after formation to improve the integrity of the carrier prior to treating with the photo-active material. Non-limiting examples of organic binders that are believed to be useful in the present invention include polyvinyl alcohol, polyvinyl acetate, carboxymethyl cellulose, and starch. However, in one, non-limiting embodiment of the present invention, wherein the fiber glass carrier of the present invention is used to form a photocatalytic matrix, the carrier preferably has a low organic content. Carriers having a low organic content are generally desirable for use in photocatalytic matrix applications, since during the photocatalytic process, organic materials are decomposed. Thus, if the photocatalyst material is applied over an organic coating layer, the organic layer can be degraded and the adhesion of the photocatalyst reduced. Furthermore, if the structural integrity of the carrier is dependent upon the organic material, the carrier itself can be

degraded during the photocatalytic process. Accordingly, if an organic binder is applied to the carrier, the minimum amount of organic binder that is required to achieve the desired handling and processing characteristics will preferably be used. If a binder is employed preferably, although not limiting in the present invention, the binder comprises one or more organic materials that can be converted into essentially inorganic materials in lieu of or in addition to the conventional organic binder materials previously discussed. For example, although not limiting in the present invention, the mat binder can comprise one or more organo-metal oxide chelates and/or one or more metal alkoxides. Specific, non-limiting examples of preferred organo-metal chelates are disclosed in U.S. Patent No. 5,908,497, which is hereby incorporated by reference.

Although not meant to be bound by any particular theory, it is believed that by employing organic materials that can be converted into essentially inorganic materials in lieu of or in addition to more conventional organic mat binders, a fiber glass carrier having good integrity and a low organic content can be obtained, for example, by removing the organic components from the carrier by thermal treatment. During the thermal treatment, such organic materials can be decomposed and converted into inorganic compounds, such as oxides, nitrides, and carbides, to produce a carrier having good integrity and a low organic content.

Methods of modifying at least a portion of the glass fibers of the fiber glass carrier to enhance the surface area of the glass fibers and carriers of the present invention will now be discussed generally. Referring again to Fig. 1, in one, non-limiting embodiment according to the present invention, fiber glass carrier 10 is subjected to an etching process to modify the surface area of at least a portion 20 of the plurality of glass fibers 14 and strands 12 of carrier 10 prior to coating the carrier

with the photo-active material. Although not limiting in the present invention, as previously discussed, the carrier 10 can be formed by any method known in the art for forming carriers and is preferably formed by the air-laid or wet-laid processes described above.

The etching processes of the present invention are believed to include removing ions from the surface of the glass so as to roughen the surface 18 of glass fibers 14 and strands 12, and thereby increase the surface area of the fibers 14 and strands 12 and, in turn, the carriers 10 made therefrom. In the case of E-glass fibers, ions such as calcium ions, magnesium ions, iron ions, aluminum ions, and sodium ions are believed to be removed from the glass surface during acid etching. The remaining material is predominately silicon dioxide. See B. Ramachandran et al., "Effect of Organic Acids on E-Glass Fabric," Communications of the American Ceramic Society, (September 1981) at pages C122-C124, which are hereby incorporated by reference.

Although not meant to be bound by any particular theory, by increasing the surface area of the glass fibers available for deposition of the photo-active material, it is believed an overall higher loading of the photo-active material can be achieved for carriers incorporating such high surface area fibers. In one particular, non-limiting embodiment of the present invention, where the photo-active material is selected from a group of photocatalytic materials which includes titanium dioxide, a further advantage of the etched fibers of the present invention is the reduced alkali content of the glass. Such alkali materials can react with (or poison) the photocatalyst to form compounds with reduced photocatalytic activity. For example, calcium cations can react with the titanium dioxide photocatalyst materials to form a calcium titanate compounds having reduced photocatalytic activity.

Etchants useful in the present invention include, but are not limited to, mineral acids such as hydrochloric acid, nitric acid, sulfuric acid and organic acids such as acetic acid and oxalic acid. In a preferred embodiment of the present invention the etchant is hydrochloric acid.

The carrier can be etched in any manner known in the art. For example, and without limiting the present invention, the carrier can be etched by submersion into an acid bath or the acid can be applied to the surface of the carrier and later removed by rinsing. Preferably, although not limiting herein, the carrier is submerged in the acid for a period of time sufficient to effect the desired level of etching. In one embodiment according to the present invention, where the etchant used is 2 Normal hydrochloric acid at about 70°C, preferably the etching time is less than about 90 minutes, more preferably less than about 30 minutes and most preferably less than about 10 minutes.

It will be appreciated by one skilled in the art that both the temperature and concentration of the etchant can be adjusted to give the desired etching. By increasing the temperature and/or the concentration of the etchant, the time necessary to effect the desired etching can be reduced. Preferably, although not required, the concentration and temperature of the etchant is adjusted to give etching times of less than about 10 minutes.

Referring again to Figs. 1 and 1a, although not limiting in the present invention, at least a portion 20 of the plurality of glass fibers 14 and strands 12 of carrier 10 of the present invention are etched to have a surface area of at least about 10 square meters per gram, preferably at least about 50 square meters per gram, more preferably at least about 100 square meters per gram, and most preferably at least about 250 square meters per gram as measured by BET surface area analysis using nitrogen. BET surface area analysis is well known in the art and further

discussion is not believed to be necessary in view of the present disclosure; however, if more information is required see P. Hiemenz, Principles of Colloid and Surface Chemistry (2nd Ed.1986) at pages 513-529, which are hereby incorporated by reference.

Referring now to Figs. 2 and 2a, in another non-limiting embodiment of a method of modifying the surface area of the fiber glass carriers according to the present invention, the surface area of fiber glass carrier 210 can be enhanced by applying a coating 220 comprising a high surface area silica material 222 to at least a portion 224 of an outer surface 226 of the carrier 210 prior to applying the photo-active material 232 to the carrier 210. For example, although not limiting, carrier 210 can be treated by applying a coating 220 of precipitated silica 222 (or other high surface area silica material) to a portion 224 of surface 226 of carrier 210 by spraying or dip coating the carrier 210 in an aqueous dispersion of the silica. Thereafter, the photo-active material 232 can be applied as described in detail below. As used herein, the term "high surface area silica material" means a silica material having a surface area of at least about 5 square meters per gram, preferably at least about 50 square meters per gram, more preferably at least about 100 square meters per gram, and most preferably at least about 250 square meters per gram as measured by BET surface area analysis using nitrogen.

Similarly, a coating 220 comprising a high surface area silica material 222 can be applied to portions 229 of surfaces 218 of the fibers 214 and strands 212 of carrier 210 by deposition processes that are well known in the art. For example, although not limiting, the high surface area silica material 222 can be added to a sizing composition and applied to the fibers 214 and strands 212 during formation by contacting the fibers 214 and strands 212 with a stationary or rotating applicator (as discussed above).

Although not required, if desired, the silica material 222 can first be coated with a photo-active material prior to applying the silica material 222 to the carrier 210 and/or the fibers 214 and strands 212 thereof. Methods of coating particles are well known to those skilled in the art and further discussion is believed unnecessary in view of the present disclosure.

In another, non-limiting embodiment of the present invention, a silicon based organo-metallic material or alkoxide can be applied to portions 224 of surface 226 of carrier 210 and/or portions 229 of surface 218 of the fibers 214 and strands 212, such as by spraying or dip coating the carrier 210 with an aqueous or non-aqueous solution of the silicon based organo-metallic material or alkoxide. The carrier 210 can then be thermally or chemically treated to condensed the precursor material and form a high surface area silica coating 223 on the portions 224 of carrier 210 and portions 229 of fibers 214 and strands 212 of carrier 210. Thereafter, the carrier 210 having an increased surface area coating can be treated with a photo-active material 232, as discussed below in detail, to form a photo-active matrix 230.

In still another, non-limiting method of incorporating a high surface area silica material 222 into the carriers 210 and/or onto fibers 214 and strands 212 of the present invention, a high surface area silica material 222 or a precursor to a high surface area silica material 222 can be applied thereto during the formation of carrier 210. For example, although not limiting, an aqueous dispersion comprising a plurality of chopped glass fibers 214 and strands 212, and high surface area silica material 222 (or a precursor to a high surface area silica material) can be formed and then cast to form a sheet. Thereafter, the sheet can be at least partially dried to form a fiber glass carrier 210 and, if required, the carrier can be treated, such as by heating, to convert any precursor

material into a high surface area silica material 222. A photo-active material 232 (and preferably a photocatalyst material) can then be applied to at least a portion of a surface 226 of the carrier 210 to form a photo-active, and preferably a photocatalytic matrix 230. Alternatively, a photo-active material 232 or a precursor to a photo-active material 232 can be incorporated into the carrier 210 during carrier formation in addition to the high surface area silica material 222 or precursor to a high surface area silica material 222 as discussed herein.

The amount of high surface area silica employed can be any amount to achieve the desired surface area enhancement. It will be recognized by one skilled in the art, that the higher the surface area of the high surface area silica material 222 used in the present invention, the lower the amount of high surface area silica 222 needed to achieve the desired surface area enhancement will be. Although not limiting, in one embodiment of the present invention, the amount of high surface area silica employed can range from about 1 weight percent of the weight of the glass fibers of the carrier to greater than about 100 weight percent of the weight of the glass fibers of the carrier.

Although not meant to be limiting in the present disclosure, it is believed that by applying or forming a coating comprising a high surface area silica material 222 on the fibers 214 and strands 212 and/or outer surface 226 of the fiber glass carrier 210 prior to treatment with the photo-active material 232, more of the photo-active material 232 can be adhered to the carrier 210 as compared to a carrier not having such a high surface area coating. As previously discussed, it is believed that by providing more available surface area to which the photo-active material can adhere, a larger amount of the photo-active material can be incorporated into the carrier and the performance of photo-active matrices formed therefrom can be improved.

The application of a photo-active materials to the high surface area fiber glass carriers of the present invention to form photo-active matrices according to the present invention will now be discussed generally. Although not limiting in the present invention, preferred photo-active materials include photocatalyst materials and photovoltaic materials.

Photocatalyst materials suitable for use in forming a photocatalytic matrix in accordance with the present invention include, but are not limited to photosensitive organic molecules, semiconductors and combinations thereof. Preferably, although not limiting in the present invention, the photocatalyst material is a semiconductor photocatalyst. As used herein, the term "semiconductor photocatalyst" means a photocatalyst material that is formed from a semiconductor, and the term "semiconductor" means an element or compound that has a filled valence band at 0 K, has a relatively narrow band-gap energy and has an electrical conductivity intermediate between that of a conductor and an insulator. Generally, the conductivities of semiconductors range from about 10^{-6} (Ohms-meters)$^{-1}$ to about 10^{4} (Ohms-meters)$^{-1}$, whereas the conductivities of insulators ranges between about 10^{-10} (Ohms-meters)$^{-1}$ to about 10^{-20} (Ohms-meters)$^{-1}$ and conductors have conductivities on the order of about 10^{7} (Ohms-meters)$^{-1}$. See W. Callister, Jr., Materials Science and Engineering An Introduction (2nd Ed., 1991) at page 608 and 756; and G. Hawley, The Condensed Chemical Dictionary, (10th Ed., 1981) at page 914-915, which are hereby incorporated by reference.

Although not limiting in the present invention, suitable semiconductor photocatalysts can have a crystal structure selected from the group consisting of diamond cubic, zincblende, rock salt, wurtzite, and anatase. Examples of suitable semiconductor photocatalysts having a diamond cubic crystal structure include, but are not limited to, silicon and germanium. Examples of suitable semiconductor photocatalysts having a

zincblende structure include, but are not limited to, zinc sulfide, gallium arsenide, indium phosphide and gallium phosphide. Examples of suitable semiconductor photocatalysts having a rock salt structure include, but are not limited to, lead sulfide, lead selenide, and tin telluride. Examples of suitable semiconductor photocatalysts having a wurtzite structure include, but are not limited to, zinc selenide, cadmium selenide and zinc oxide. A non-limiting example of a suitable semiconductor photocatalyst having an anatase structure is titanium dioxide. For more information on suitable semiconductor crystal structures see N. Lewis et al., "Theory of Semiconductor Materials", Photocatalysis: Fundamentals and Applications (*supra*) at pages 46-48, which are hereby incorporated by reference.

Other non-limiting suitable photocatalysts include metal dichalcongenides and metal oxides. As used herein the term "dichalcogenide" means a material generally having a AB_2 stoichiometry wherein a metal layer (A) is positioned between two chalcogenide layers (B), and where the intermolecular bonding between the layers A and B is due solely to van der Waals forces. Examples of suitable metal dichalcogenides include, but are not limited to, molybdenum disulfide, tungsten diselenide, and tungsten disulfide. Examples of suitable metal oxides include, but are not limited to, titanium dioxide, tungsten trioxide, iron oxide, and zinc oxide.

Non-limiting examples of a photovoltaic material suitable for use in forming a photovoltaic matrix in accordance with the present invention are silicon, gallium-arsenide, and selenium. It will be recognized by those skilled in the art that in order to take advantage of the photovoltaic properties of materials such as silicon, other materials, such as a electrical conductors, can also be applied to the carriers of the present invention in any combination with the photovoltaic materials. For example, although

not limiting in the present invention, a transparent conducting layer, such as tin oxide or indium-tin oxide, can be applied to the glass fibers of the carriers of the present invention prior to the application of the photovoltaic material. Similarly, a non-transparent conductor layer, such as aluminum or copper can be first applied to the glass fibers of the carriers of the present invention and the photovoltaic material can be applied thereon by any method well known in the art. Alternatively, the photovoltaic material can be positioned between two conductor layers, at least one of which is applied directly to the fiber glass carrier, to form a photovoltaic cell. Accordingly, the application of one or more other materials to the fiber glass carrier, in addition to the photo-active material, is contemplated in the present invention.

Referring now to Figs. 3 and 3a, extensive literature exists describing the application of photo-active materials onto glass substrates and the present invention is not limited to any particular technique of producing a photo-active matrix 330 by incorporating a photo-active material 332 onto at least a portion 328 of a surface 318 of the fibers 314 and strands 312 and/or at least a portion 324 of an surface 326 of the carrier 310. However, for the sake of impregnating a high surface area fiber glass carrier 310, it is advantageous to use those photo-active materials 332 that can be applied from a liquid medium. For example, although not limiting in the present invention, the carrier 310 can be dipped into a liquid coating composition to coat a large surface area with the photo-active material 332. Although not limiting in the present invention, metal oxide photocatalysts lend themselves to a dip coating process because metallic alkoxides can be dissolved in a liquid solvent (usually alcohol) in which the carrier can be immersed. Subsequently, although not required, the deposited alkoxides can be hydrolyzed and condensed to form a metallic oxide film that bonds well to the glass

substrate. A preferred, non-limiting process of this type is disclosed in U.S. Patent No. 4,966,759, which is hereby incorporated by reference. More specifically, the process of that patent entails using a metal alkoxide as the starting material, which in the preferred case of titanium dioxide photocatalysts, can be, for example titanium ethoxide. The titanium ethoxide is dissolved in an organic solvents such as anhydrous ethanol and reacted with a controlled amount of an acid, such as nitric acid, and water to form a coating solution. The fiber glass carrier can be dipped into that coating solution under dry conditions for a period of time on the order of one minute. Subsequently drying the coated carrier in room temperature air causes the alkoxide to hydrolyze, thereby producing an amorphous, polymeric titanate layer on the carrier. After drying the coating for one to two hours, the coated mat is heated to a temperature sufficient to converting the amorphous layer to a photocatalytically active crystalline form (anatase in the case of titanium dioxide). The heating cycle to produce anatase titanium dioxide can include a slow heat-up period on the order of 2 to 5 hours, a one hour hold at about 400°C, and a cool-down period on the order of 5 hours or more. It should be understood that the coating and heat treating conditions will vary, depending upon the particular materials used, as would be known to those of skill in the art.

It is also known to apply photocatalytic metal oxide onto substrates using aqueous media. For example, although not limiting herein, aqueous solutions or slurries of titanate products available under the name TYZOR from E.I. duPont de Nemours and Company of Wilmington, Delaware, particularly the chelated versions, or similar products from Degussa Corporation of Germany, can be used to coat the carriers of the present invention.

An additional advantage thought to be attributable to the presence of the coupling agents in the preferred, non-limiting embodiments of the present invention is that improved coating of the wet photo-active material onto the fiber glass carrier is attained. In the conventional practice of heat cleaning the carrier, this advantage is lost due to thermal decomposition of any coupling agent present.

It also is known to dope photo-active materials, and in particular photocatalyst materials, with other metals such as platinum to enhance the photocatalytic activity of the catalyst, and the photocatalytic matrix of the present invention can include such dopants. However, in one, non-limiting embodiment of the present invention, the photocatalytic matrix formed from the fiber glass mat carrier according to the present invention is essentially free of secondary catalytically active agents selected from the group consisting of oxides of copper, iron, molybdenum, vanadium, and tungsten.

While the photo-active material can be incorporated into the carrier by applying the photo-active material to the surface of the fiber glass carrier, such as by treating the carrier with the photo-active material after the carrier is formed (as discussed above), in one, preferred non-limiting embodiment of the present invention, the photo-active material is incorporated into the carrier during formation thereof. For example, although not limiting, a powdered form of the photo-active material can be dispersed along with the glass fibers and a foaming agent in an aqueous solution prior to agitating the dispersion to form a foamed slurry. The foamed slurry can then be cast to form a sheet. Thereafter, at least a portion of the foam can be removed and the sheet can be least partially dried to form a photo-active matrix in the form of a fiber glass carrier having a photo-active material distributed therein. If desired, an additional coating comprising a photo-active material can be applied to the carrier

after formation in accordance with the present invention. Although not meant to be limiting in the present invention, it is believed that by adding a powdered form of the photo-active material to foamed slurry of the Radlite™ process (described above in detail) a relatively large amount of photo-active material can be more uniformly distributed throughout the carrier formed therefrom as compared to adding the powdered photocatalyst to a conventional wet-laid paper-making process. The used of a foamed slurry can aid in reducing or eliminating settling of the photo-active material and can permit enhanced mixing among the powdered photo-active material, the glass fibers, and glass strands. Furthermore, as previously discussed, the Radlite™ process can produce high surface area carriers due to the large amount of filamentization that occurs during agitation and foaming.

In a specific, non-limiting example of a method of forming a photo-catalytic matrix according to the present invention, wherein the photocatalyst material is titanium dioxide, one or more water soluble titanium complexes, such as are disclosed in U.S. Patent No. 5,908,497 for example, is solubilized in an aqueous solution comprising one or more foaming agents or a white water solution prior to dispersing glass fibers therein. A sheet is then cast from the dispersion and dried to form a carrier. After drying, the carrier is exposed to elevated temperatures for a period of time sufficient to condense and crystallized the titanium complex to form a photocatalytically active form of titanium dioxide. Although not limiting in the present invention, preferably the titanium complex is converted into the anatase form of titanium dioxide. One skilled in the art will recognize that the exact temperature and time required to form the anatase phase of titanium dioxide will depend, in part, upon the type of titanium complex used. Although not meant to be limiting in the present disclosure, for example, a temperature ranging from

about 300°C to about 500°C can be used to convert the water soluble titanium complexes described in detail in U.S. Patent No. 5,908,497. It will be further recognized by one skilled in the art that the aforementioned methods of adding the photocatalyst can be used in either conventional wet-laid processes or the Radlite™ process discussed above.

In another specific, non-limiting example of applying the photocatalytic material to a fiber glass carrier formed via the wet-laid processes discussed above, a water soluble titanium complex is solublized in an acidic white water solution. Chopped fiber glass strands are then dispersed in the solution to form a dispersion which is subsequently cast and dried to form a carrier. The carrier is then treated with an alkaline solution, such as by dipping the sheet into an alkaline bath having a pH of at least about 3.5, to condense the titanium complex. Since titanium dioxide has an isoelectric point at a pH of 3.5, the titanium complex can be condensed by such an alkaline treatment to form titanium dioxide. It will be recognized by one skilled in the art that the isoelectric point of other photocatalysts can vary from that of titanium dioxide and the pH of the alkaline solution should be selected according to the isoelectric point of the particular photocatalyst material employed. Although not meant to be bound by any particular theory, it is believed that by condensing the photocatalyst using an alkaline treatment, as opposed to a heat treatment, the integrity of the fiber glass carrier can be improved since high temperature treatments can embrittle and damage the glass fibers causing the carrier to be more friable.

In another non-limiting embodiment of the present invention wherein the fiber glass carrier is formed using an air-laid process, as discussed above, the photo-active material can be sprayed or deposited (such as by chemical vapor deposition or plasma spraying) onto the carrier prior to, during or after needling the carrier.

It will be further appreciated by those skilled in the art that the photo-active material can be applied directly to the fiber glass strands during fiber formation in lieu of or in addition to applying the photo-active material during or after carrier formation. For example, although not limiting in the present invention, a photocatalyst material, or a pre-cursor to the photocatalyst material, can be added directly to the sizing composition applied to the glass fibers immediately after forming. The fibers can then be gathered together to form strands and the strands further processed into fiber glass carriers as discussed above. Additional photocatalyst material can be added to the carrier during the formation of the thereof, for example by adding the photocatalyst to the foamed slurry used in the Radlite™ process (as discussed above), and/or applied to the carrier after formation as previously discussed.

Similarly, the surface of the fibers can be treated by etching or by the application of a high surface area silica coating during the fiber forming process and thereafter processed into a carrier and/or photo-active matrix as previously discussed.

An embodiment of the present invention will now be illustrated in the following specific, non-limiting example.

EXAMPLE

Fiber glass carriers having high surface area were formed using an air-laid mat process according to the following procedure. A plurality of E-glass fiber strands comprising filaments having an average diameter of about 9 micrometers (designated "G" fibers) were treated during forming with the sizing composition given in Table 2. The fiber strands were then wound to form packages and the packages were subsequently dried at about 245°F (about 118°C) for about 12 hours.

Table 2

COMPONENT	AMOUNT (PARTS BY WEIGHT)
Water	3632.00
Acetic acid (glacial)	45.40
Silane [4]	169.50
Cationic softener[5]	18.16
Warm water	968.4
Surfactant[6]	84.80

After drying, the packages were unwound from the inside and the fiber strands were fed continuously into a chopping apparatus where they were chopped into approximately 2 inch (approximately 5 centimeter) lengths. After chopping the strands were immediately passed into a RANDO-OPENER BLENDER (which is a part of the MODEL B RANDO-WEB® processor commercially available from Rando Machine Corporation of Macedon, New York) where they were opened or filamentized (as discussed in detail above). The opened strands were then feed into a RANDO-WEBBER® (which is also part of the MODEL B RANDO-WEB® processor) and formed into a continuous web. The web was then passed into a needling apparatus and needled at a punch density of about 150 punches per square inch (about 23 punches per square centimeter) using a needle board reciprocating rate of about 359 strokes per minute and a punch depth of about 0.55 inches (about 1.4 centimeters) to form a mat. The needles used in the needling apparatus were 32-gauge, star needles (described in detail above) which are commercially available from Groz-Beckert USA of Charlotte, North Carolina. The average surface weight (or

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[4] A-1100 gamma aminopropyltriethoxysilane from CK Witco, of Tarrytown, New York.

[5] LUBRIL CAT-X/VC, an imidazoline from Rhodia, Inc., Cranbury, New Jersey.

[6] IGEPAL CA-630 from GAF Corporation, Wayne, New Jersey.

mat density) of the mat was about 0.7 ounces per square foot (about 214 grams per square meter).

After forming, three square samples weighing from about 20 to about 24 grams were cut from the mat. Each of the samples was then independently submerged in about 3 to 4 liters of 2 Normal hydrochloric acid (commercially available from Fisher Scientific of Pittsburgh, Pennsylvania) and the acid was heated to a temperature of about 90°C to about 95°C. Upon reaching the desired temperature, the sample was soaked in the acid for the time indicated below in Table 2 to etch the glass fibers. After the etching, the heat was turned off and the acid was allowed to cool to room temperature before removing the sample. After removal of the sample from the acid, the sample was rinsed with deionized water and dried.

BET surface area analysis was then conducted on each of the 3 samples and an unetched control using a Micromeritics ASAP2400 nitrogen porosimeter at liquid nitrogen temperatures. Prior to taking the measurements, the samples were dried in the porosimeter at about 165°C under vacuum for about one hour or until the vacuum level dropped below about 200 milliTorr. The results are shown in Table 3.

Table 3

Sample	Etch Time (Hours)	BET Surface Area (square meters per gram)
Control Sample	0	0.8
Sample 1	1	440
Sample 2	2	441
Sample 3	3	454

The surface area of the unetched control is significantly lower than the etched samples indicating that the etching procedure was successful in increasing the surface area of the glass fibers.

The invention has been described in connection with particular embodiments for the sake of providing the best mode of the invention. It should be understood that other variations and modifications as would be known to those of skill in the art may be employed within the scope of the invention as defined by the claims.

WE CLAIM:

1. A fiber glass carrier comprising a plurality of glass fibers wherein at least a portion of the plurality of glass fibers have a surface area of at least about 10 square meters per gram as measured by BET surface area analysis using nitrogen.

2. The fiber glass carrier according to claim 1 wherein the surface area is at least about 100 square meters per gram as measured by BET surface area analysis using nitrogen.

3. The fiber glass carrier according to claim 2, wherein the surface area is at least about 250 square meters per gram as measured by BET surface area analysis using nitrogen.

4. The fiber glass carrier according to claim 1, wherein the fiber glass carrier has a loss on ignition of no greater than about 1.0 percent by weight of the fiber glass mat.

5. The fiber glass carrier according to claim 4, wherein a majority of the glass fibers of the plurality of glass fibers have a nominal filament diameter of at least about 1.0 micron.

6. The fiber glass carrier according to claim 5, wherein the nominal filament diameter is at least about 3.5 microns.

7. The fiber glass carrier according to claim 6, wherein the fiber glass carrier is a non-woven carrier.

8. The fiber glass carrier according to claim 7, further comprising a coating comprising a photo-active material applied to the at least a portion of the plurality of glass fibers.

9. The fiber glass carrier according to claim 8, wherein the photo-active material is a photocatalyst material selected from the group consisting of titanium dioxide, zinc oxide, and molybdenum disulfide.

10. The fiber glass carrier according to claim 8, wherein the photo-active material is a photovoltaic material.

11. The fiber glass carrier according to claim 10, further comprising a conductive layer interposed between the at least a portion of the plurality of glass fibers and the coating comprising the photovoltaic material.

12. The fiber glass carrier according to claim 11, further comprising a second conductive layer positioned upon at least a portion of the coating comprising the photovoltaic material to form a photovoltaic cell.

13. The fiber glass carrier according to claim 1, further comprising a high surface area silica material applied to the at least a portion of the plurality of glass fibers.

14. A non-woven fiber glass carrier comprising a plurality of glass fibers at least a portion of the plurality of glass fibers having a high surface area silica material positioned thereon.

15. The non-woven fiber glass carrier according to claim 14, wherein at least one of the at least a portion of the plurality of glass fibers has a surface area of at least about 10 square meters per gram as measured by BET surface analysis using nitrogen.

16. The non-woven fiber glass carrier according to claim 14, further comprising a photo-active material positioned upon at least a portion of the high surface area silica material.

17. The non-woven fiber glass carrier according to claim 16, wherein the photo-active material is a photocatalyst material selected form the group consisting of titanium dioxide, zinc oxide, and molybdenum disulfide.

18. The non-woven fiber glass carrier according to claim 16, wherein the photo-active material is a photovoltaic material.

19. A method of forming a high surface area fiber glass carrier, the method comprising the steps of:

A. forming a fiber glass carrier comprising a plurality of glass fibers, and

B. modifying at least a portion of the plurality of glass fibers such that the at least a portion of the plurality of glass fibers has a surface area that is at least about 10 square meters per gram as measured by BET surface analysis using nitrogen.

20. The method according to claim 19, wherein the modifying step includes applying a high surface area silica material to the at least a portion of the plurality of glass fibers.

21. The method according to claim 19, wherein the modifying step includes etching the at least a portion of the plurality of glass fibers.

22. The method according to claim 21, wherein a high surface area silica material is applied to the at least a portion of the plurality of glass fibers.

23. The method according to claim 21, wherein the surface area is at least about 100 square meters per gram as measured by BET surface analysis using nitrogen.

24. The method according to claim 23, wherein the surface area is at least about 250 square meters per gram as measured by BET surface analysis using nitrogen.

25. The method according to claim 19, further comprising applying a photocatalyst material to the at least a portion of the glass fibers.

26. The method according to claim 25, wherein the photocatalyst material is selected from the group consisting of titanium dioxide, zinc oxide, and molybdenum disulfide.

27. A method of forming a high surface area fiber glass carrier, the method comprising the steps of:

A. forming a non-woven, fiber glass carrier; and

B. applying a high surface area silica material to at least a portion of a surface of the non-woven, fiber glass carrier.

28. The method according to claim 27, wherein the high surface area silica material comprises a plurality of high surface area silica particles, and wherein at least one of the high surface area silica particles comprises at least a partial coating of a photo-active material.

29. The method according to claim 28, wherein the photo-active material is a photocatalyst material selected from the group consisting of titanium dioxide, zinc oxide, and molybdenum disulfide.

30. The method according to claim 28, wherein the photo-active material is a photovoltaic material.

31. A method of forming a photocatalytic matrix, the method comprising the steps of:

A. forming an aqueous dispersion comprising a plurality of chopped glass fibers and a foaming agent;

B. agitating the dispersion to form a foamed slurry;

C. casting the foamed slurry to form a sheet;

D. removing at least a portion of the foam from the sheet;

E. at least partially drying the sheet to form a fiber glass carrier; and

F. incorporating a photocatalyst material into the fiber glass carrier to form a photocatalytic matrix.

32. The method according to claim 31, wherein the incorporating step includes applying the photocatalyst material to the fiber glass carrier after at least partially drying the sheet.

33. The method according to claim 31, wherein the incorporating step includes adding the photocatalyst material to the aqueous dispersion.

34. The method according to claim 31, wherein the photocatalyst material is selected from the group consisting of titanium dioxide, zinc oxide, and molybdenum disulfide.

35. The method according to claim 31, wherein the photocatalytic matrix is essentially free of materials selected from the group consisting of oxides of copper, iron, molybdenum, vanadium, and tungsten.

36. The method according to claim 31, further comprising modifying at least a portion of the plurality of chopped glass fibers of the fiber glass carrier prior to applying the photocatalyst material to the carrier.

37. The method according to claim 36, wherein modifying includes etching the at least a portion of the plurality of chopped glass fibers.

38. The method according to claim 36, wherein modifying includes applying a high surface area silica material to the at least a portion of the plurality of chopped glass fibers.

39. A method of forming a photocatalytic matrix, the method comprising the steps of:

A. forming an aqueous dispersion comprising a plurality of chopped glass fibers and a high surface area silica material;

B. casting the dispersion to form a sheet;

C. at least partially drying the sheet to form a fiber glass carrier; and

D. incorporating a photocatalyst material into the fiber glass carrier to form a photocatalytic matrix.

40. The method according to claim 39, wherein the incorporating step includes applying the photocatalyst material to at least a portion of the fiber glass carrier after at least partially drying the sheet.

41. The method according to claim 39, wherein the incorporating step includes coating at least a portion of the high surface area silica material with the photocatalyst material prior to casting.

42. The method according to claim 39, wherein the incorporating step includes adding the photocatalyst material to the aqueous dispersion.

43. The method according to claim 39, wherein the photocatalyst material is selected from the group consisting of titanium dioxide, zinc oxide, and molybdenum disulfide.

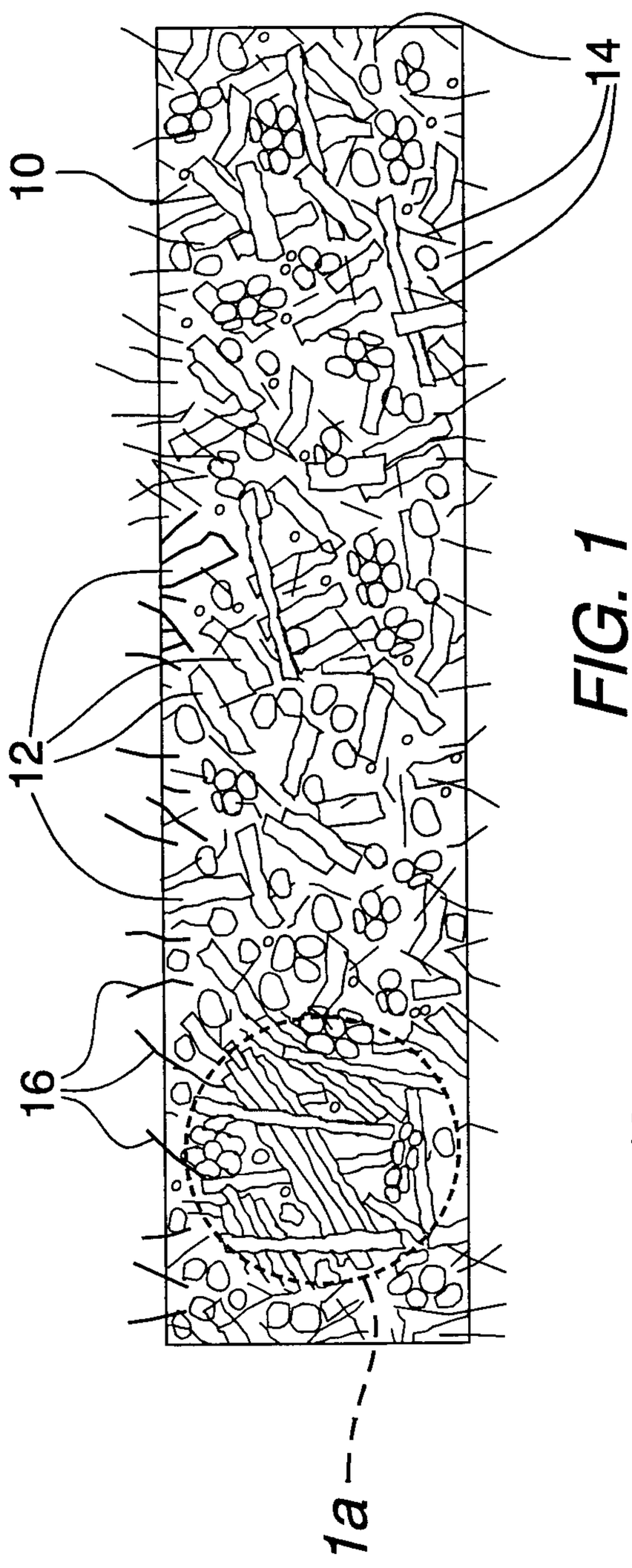

FIG. 1

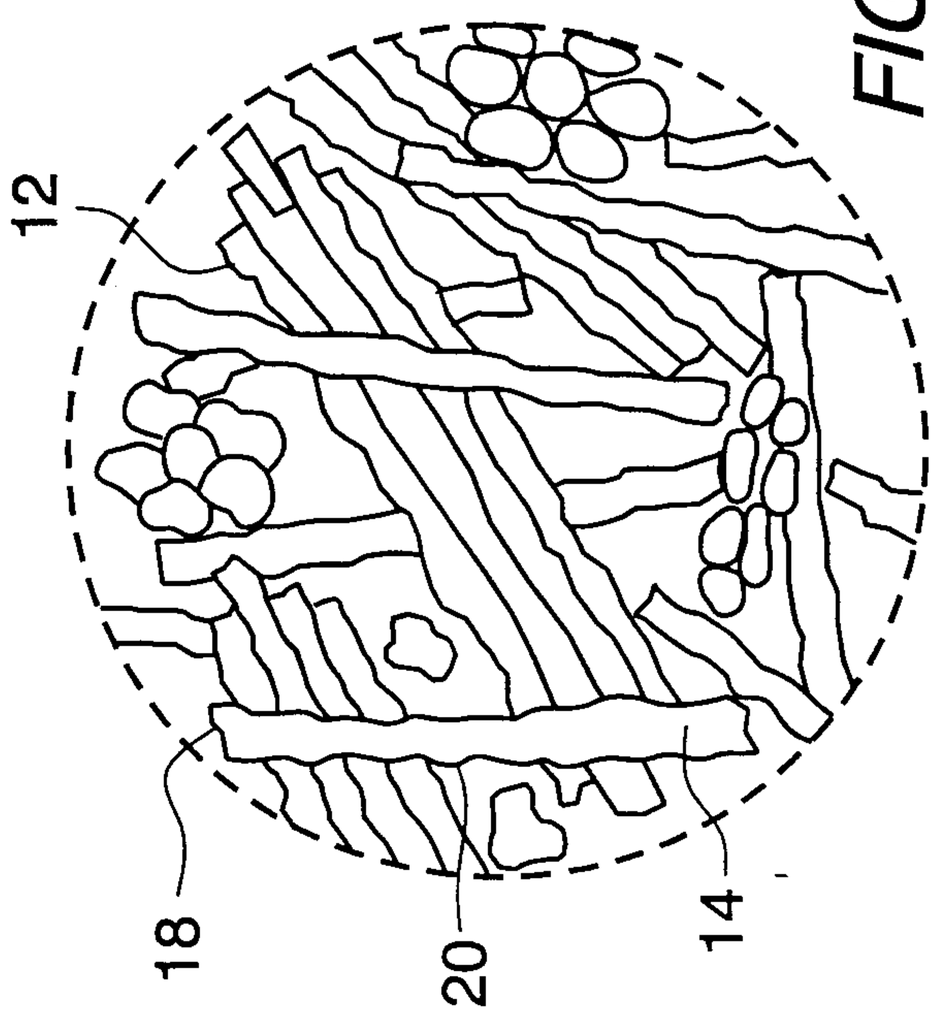

FIG. 1a

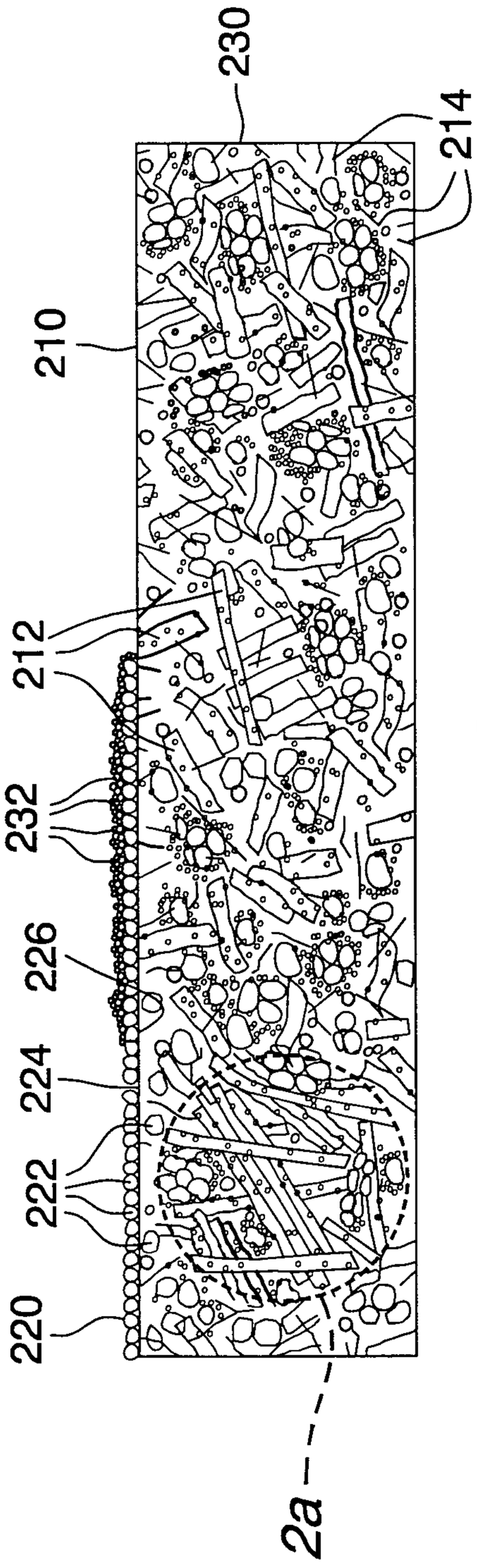
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FIG. 2

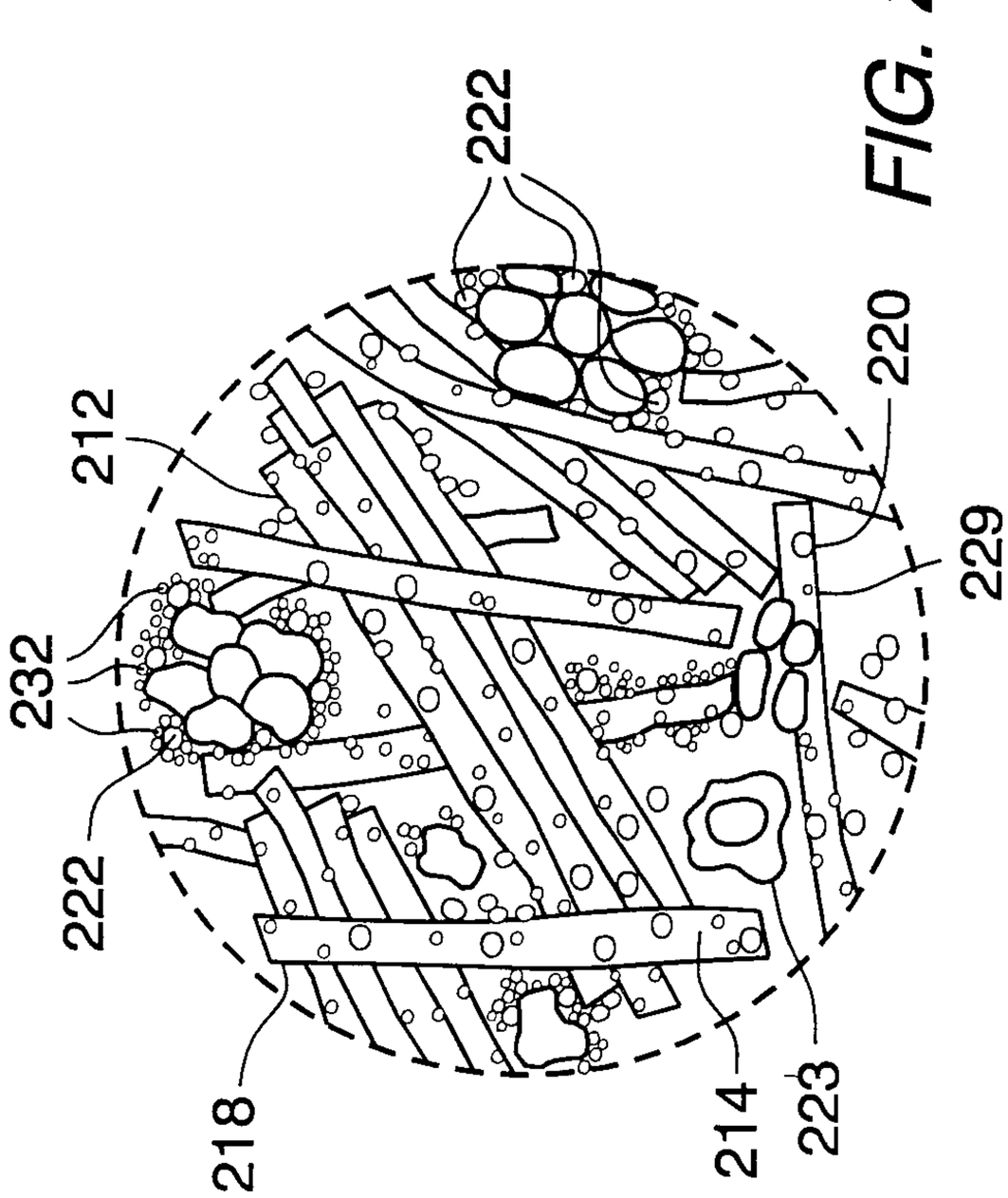
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FIG. 2a

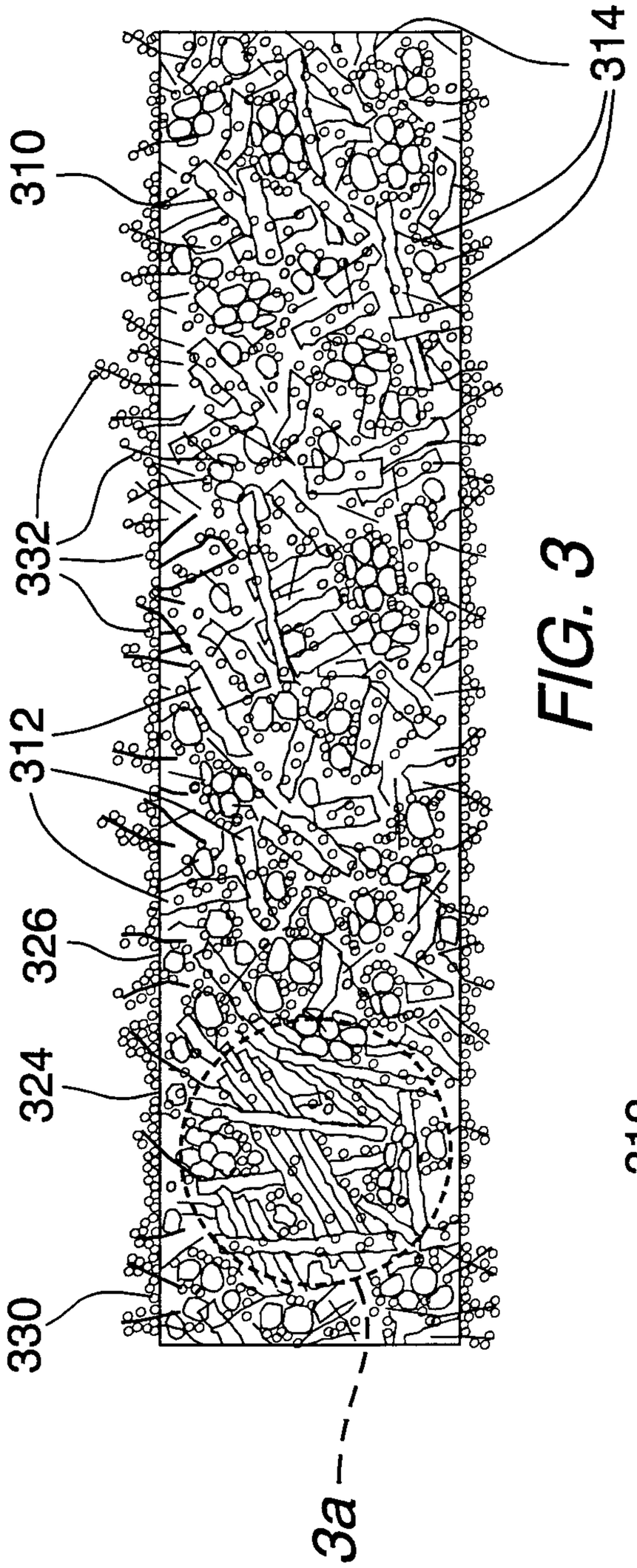


FIG. 3

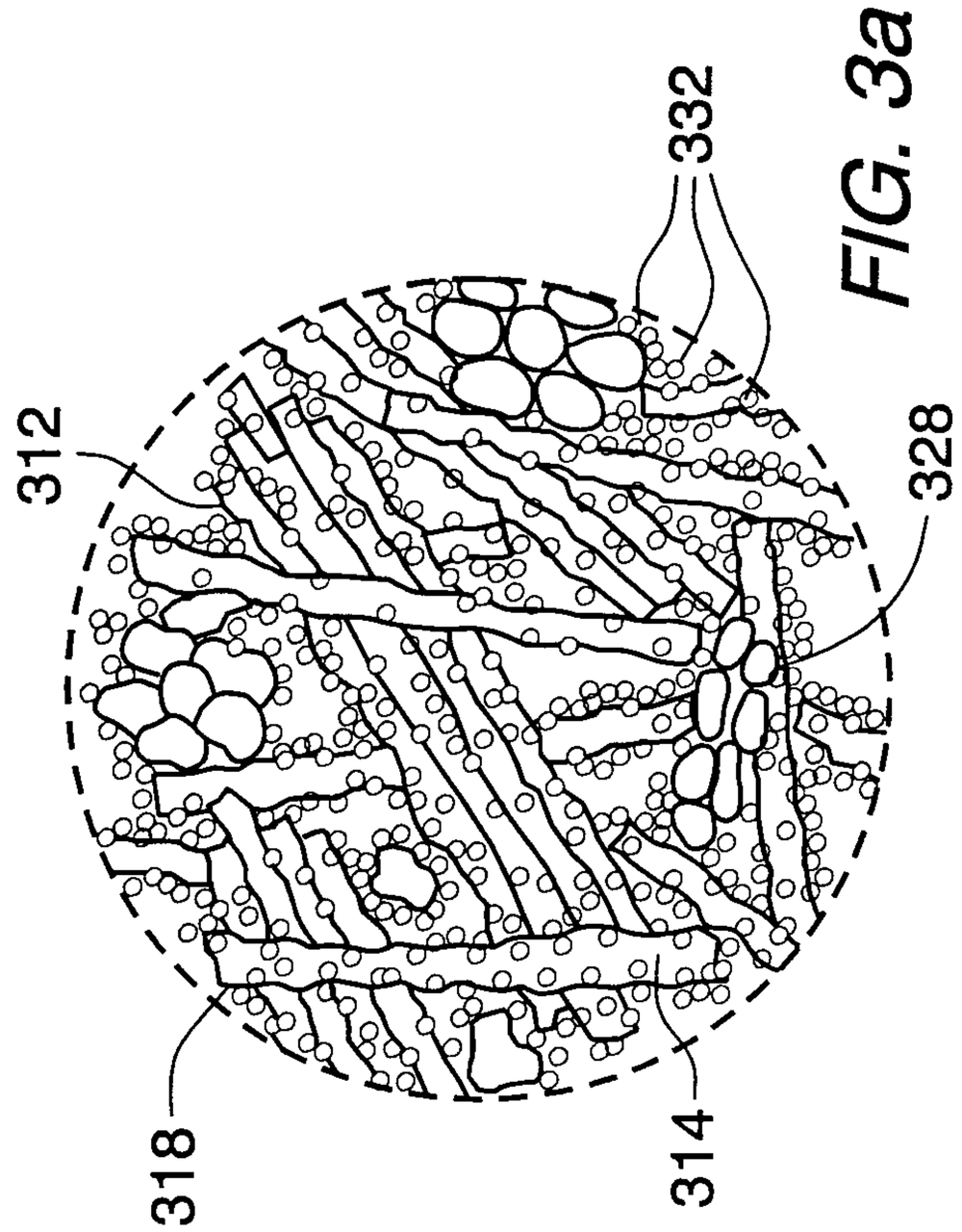
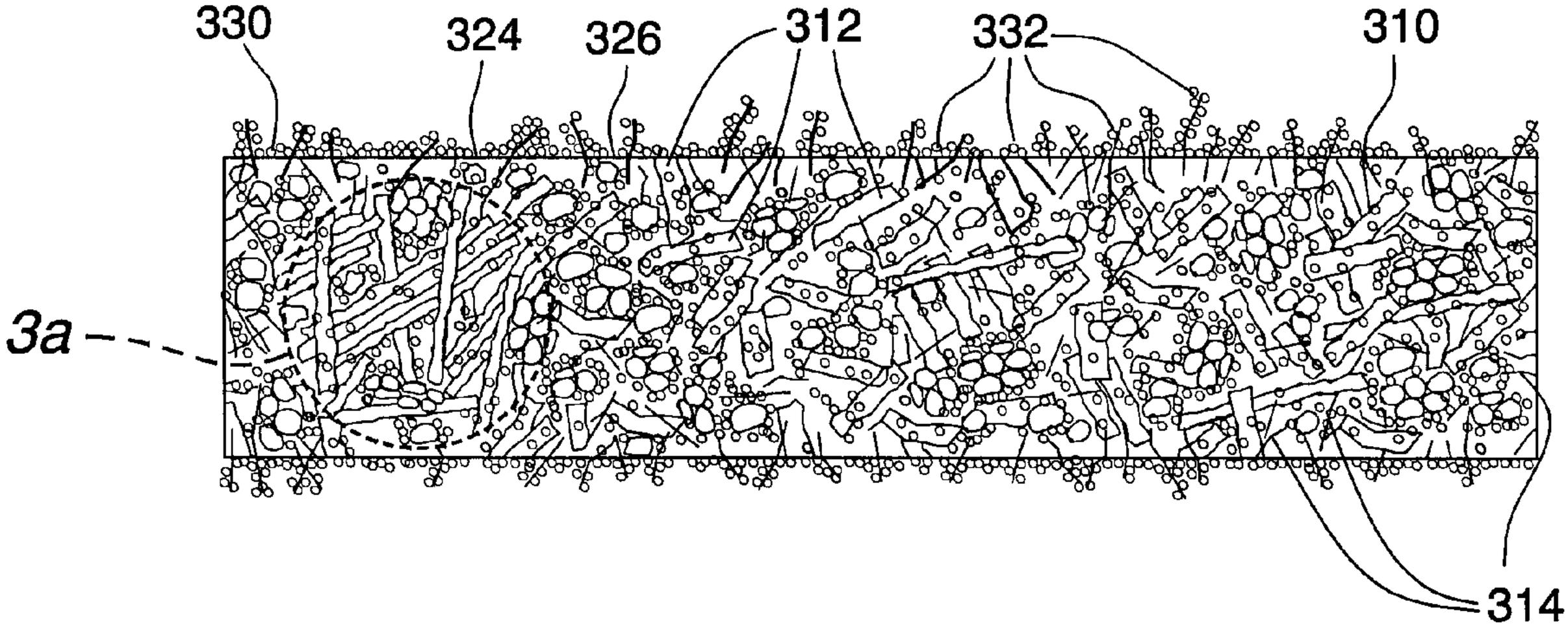


FIG. 3a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