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METHOD OF FORMING GLASS-ASBESTOS WATER-LAID SHEET

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ABSTRACT OF THE DISCLOSURE

A water-laid web of asbestos fibers, reinforcing fibers, and synthetic resinous binder. The web is made by mixing an aqueous dispersion of asbestos fibers at pH 2.0 to 5.0 with an aqueous dispersion of binder having an anionic charge on the binder particles to form a first furnish, mixing the first furnish with a second aqueous furnish containing reinforcing fibers, forming a web from the mixture of furnishes, and drying it.

This invention relates to a paper comprising chopped glass strands and pertains more specifically to such a paper suitable for use in making a laminate or a base sheet for printed circuits, and to a method for making the same.

There has long been a need for paper having high dielectric strength which is stable to changes in temperature as well as to varying humidity during use, which is resistant to deterioration at high temperatures, and which retains sufficient strength when saturated with solvent to enable it to be impregnated with resin solutions. While woven glass cloth has such characteristics, its surface is uneven and pebbly because of the weave; in addition, base sheets made from impregnated glass cloth tend to fray at the edges when subjecting to such operations as punching or the like. While attempts have been made to produce paper from glass fibers, there has been great difficulty in forming a continuous and uniform water-laid web of such fibers on conventional paper-making machinery and in providing adequate strength in the finished web.

One object of the present invention is to provide a water-laid web of fibrous material having high dielectric strength suitable for impregnation with resin to form a base sheet for printed circuits or to form laminated products.

Another object is to provide a water-laid web containing chopped glass strands or mixtures of chopped glass strands with individual glass filaments or with non-hydratable synthetic textile fibers, and also containing fibers of chrysotile asbestos together with a synthetic resinous binder.

Still another object is to provide a method for making a web of the type described on conventional paper-making machinery.

Other and further objects will be apparent from the description which follows.

It has been found that by mixing with an aqueous furnish containing reinforcing fibers including chopped glass strands a second aqueous furnish containing chrysotile asbestos fibers together with a dispersion of synthetic

resinous binder in the proper proportion, a uniform coherent web of good strength may be laid down on a conventional paper-making machine such as a Fourdrinier. The asbestos fibers not only make it possible to form a uniform web on conventional machinery but because these fibers exhibit substantivity toward the particles of an anionic resinous binder dispersion they serve also as carriers for the binder and eliminate excessive loss of binder with the white water. In addition, the asbestos fibers together with the resinous binder serve to hold together and stabilize the reinforcing fibers of the finished web, which reinforcing fibers by themselves exhibit very little affinity for each other and form a very weak web.

The chopped glass strands which form an essential element of the web of the present invention may be made by chopping to the desired length conventional glass strands composed of bundles containing from 100 to 400 individual glass monofilaments bonded together with a resin such as an epoxy, each monofilament having a diameter from 5 to 15 microns. Excellent results have been obtained using strands which are chopped to lengths from one-eighth to three-fourths inch, best results being obtained with mixtures of relatively short strands, from one-eighth to three-eighth inch in length, with relatively long strands from one-half to three-fourths inch in length. It has been found that the longer strands provide improved impact strength in the finished sheet, while the short strands facilitate the formation of the web on the Fourdrinier wire. Satisfactory results have been obtained with strands composed of bundles having approximately 200 ends, the individual monofilaments in the bundle having a diameter of approximately 9 microns.

While chopped glass strands are an essential element of the web of the present invention a portion of these chopped strands may be replaced by individual glass monofilaments having a diameter from 2 to 9 microns. The monofilaments are dispersed in the aqueous furnish by passing the mix through a pulper; after dispersion in this fashion the average length of the individual monofilaments is from 2 to 10 millimeters.

It is preferable that both the chopped glass strand and the monofilaments, when present, be composed of borosilicate glass, and that the glass be coated with a coupling agent such as gamma-aminopropyl triethoxysilane, or other conventional coupling agent to improve the bonding of the glass to the resinous binding agent. It is also preferred that the aqueous furnish containing the chopped glass strands, or other fibrous glass material, have a low pH from 2.0 to 5.0, this being achieved by the addition of an acid such as sulfuric acid if necessary. Best results are obtained when the pH is from 2.5 to 3.0.

It has also been found that the tear strength of the finished web may be improved by substituting a synthetic textile fiber for a portion of the glass. Such textile fibers as polyesters, super polyamides and polyacrylonitrile have been found useful in the form of staple fiber, i.e. in lengths ranging from one-eighth to three-fourths inch. The synthetic textile fibers are preferably present as individual monofilaments having diameters from 10 to 40 microns.

The second essential ingredient of the web is opened chrysotile asbestos. Particularly preferred is the high quality grade of such asbestos obtained from California which contains less than 0.5% iron, such as Union Car-

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bide High-Purity California chrysotile asbestos. The asbestos fibers are dispersed with agitation in a separate aqueous furnish, the pH of which is also preferably adjusted to 2.0 to 5.0 by the addition of acid, if necessary. Excellent results are obtained when the pH is maintained within the range 2.5 to 3.0 and when it approximates the pH of the aqueous furnish containing the glass fibers.

A synthetic resinous binder in the form of an aqueous dispersion in which the individual resinous particles have an anionic charge is also stirred into the aqueous furnish containing the asbestos fibers. Any one of a variety of synthetic resinous binders may be employed in the form of aqueous dispersions, the preferred resin being heat advancing so that it can be cured or cross-linked simply by heating after formation of the web. Among suitable binders are urea-formaldehyde resins, melamine-formaldehyde resins, phenol-formaldehyde resins and heat-advancing or cross-linkable acrylic resins. Aqueous dispersions of such resinous binders are readily available commercially. When the resin binder emulsion or dispersion is mixed with the dispersion of asbestos fibers in water, it is found that the originally milky appearance of the mixture rapidly becomes clarified, indicating that the particles of resin binder solution are attracted to and held by the asbestos fibers, presumably because of the anionic nature of the charge on the individual particles of resin binder and the inherent nature of the asbestos. This is an important feature of the present invention since it facilitates the introducing of the resinous binder particles into the web and insures their retention in the web during the formation of the latter.

In the finished web, the reinforcing fibers amount to approximately 50 to 90% by weight of the total web, the chrysotile asbestos amounts to approximately 7 to 35% by weight, and the resinous binder amounts to 3 to 15% by weight. In order to permit the asbestos fibers to act effectively as a carrier for the resinous binder particles the weight of asbestos should be at least about one and one-half the weight of the binder. Up to 75% by weight of the chopped glass strands may be replaced with glass monofilaments if desired, and of the remaining chopped glass strands up to 30% by weight may be replaced by non-hydratable synthetic textile fibers. In a preferred embodiment the reinforcing fiber consists of a mixture of 20 to 60% by weight of glass monofilaments having a diameter from 2 to 9 microns, and correspondingly from 80 to 40% by weight of chopped glass strands which are bundles containing 100 to 400 glass monofilaments, each monofilament having a diameter from 5 to 15 microns.

The concentration of fibers present in the aqueous furnish is not critical but may vary from about 0.1% to about 5% by weight in the case of both furnishes. The furnish containing the glass fibers and the furnish containing the mixture of asbestos fibers and resinous binder dispersion are preferably kept separate until shortly before formation of the web. They may be mixed in a chest or in any convenient location shortly before the mixture reaches the headbox of the paper-making machine. After formation of the web it may be dried on steam heated cans in the usual manner, the time and temperature of heating being sufficient in some cases to cause at least partial curing or cross-linking of the resinous binder to occur. In other cases it may be desirable to heat the web in an oven after drying in order to bring about partial or complete curing or cross-linking of the binder. In those cases where it is desired to impregnate the web, after formation, with a relatively large quantity of a suitable impregnating resin such as an epoxy as is commonly used in preparing base sheets for use in printed circuits, completion of the cure or cross-linking of the resinous binder may be carried out simultaneously with the cure or cross-linking of the impregnating resin.

The following specific examples are intended to illustrate more fully the nature of the invention without restricting it.

Example 1

There were stirred into about 2200 gallons of water in a pulper approximately 280 pounds of chopped glass strand and 120 pounds of C-glass monofilaments. The pH was adjusted to 2.5 to 3.0 by the addition of sulfuric acid. The chopped glass strand consisted of a mixture of approximately equal parts by weight of strands having a length of one-fourth inch and strands having a length of one-half inch. The strands consisted of bundles containing 204 individual monofilaments each monofilament being a borosilicate glass filament having a diameter of approximately 9 microns. The C-glass monofilament was broken up in the pulper to provide individual monofilaments having an average length from 2 to 10 millimeters and having an average filament diameter of about 6 microns, while the chopped strands remained essentially unchanged. There were added to the mixture while passing to the headbox approximately 1750 gallons of water to provide the desired consistency.

In a separate vessel, 3000 gallons of water were adjusted to a pH of 2.5 to 3.0 with sulfuric acid and 240 pounds of California chrysotile asbestos (containing less than 0.5% iron) were stirred in. To this asbestos slurry were added 120 gallons of aqueous resin binder emulsion containing a mixture of 7 gallons of an aqueous emulsion of an intermediate to high molecular weight copolymer of esters of acrylates or methacrylates (Rhoplex E303), capable of cross-linking with subsequently employed impregnating resins, 18 gallons of a heat advancing modified polyacrylic ester (Hycar 2679), and three-fourths pound of an anionic polymer-type dispersing agent (Tamol SN). The initially milky appearance of the mixture changed during continued agitation as the resin particles were deposited upon the asbestos fibers until the aqueous portion of the dispersion was quite clear.

The furnish thus prepared was metered into the paper machine system through its own secondary system of tanks and pipes to a convenient point just ahead of the headbox and was there continuously blended with the other furnish containing the glass fibers, the rate of feed of the latter being approximately twice the rate of feed of the former. From the headbox the mixed furnish passed to the wire of the Fourdrinier where a web was formed. While still on the wire the web was sprayed with a conventional solution of gamma-aminopropyl triethoxysilane.

After forming, the sheet was dried on can dryers in the usual manner and subjected to infrared heat to cause the resin binder to cure or cross-link. The finished web or sheet weighed about 104 pounds per 3000 square feet when dry and possessed a length tensile strength in excess of 5 pounds per inch width. It contained approximately 17% by weight of asbestos and approximately 8.5% by weight of resinous binder, the remainder consisting of chopped glass strand and glass monofilament in approximately the proportion supplied in the furnish.

The web displayed a uniform distribution of fibers throughout its extent and a relatively smooth, paper-like surface. It was readily saturated with a solution of an epoxy impregnating resin to provide a base sheet for a printed circuit. The web retained its strength well during impregnation with the resin solution, as evidenced by the fact that when saturated with a mixture of two parts by weight of toluene and one part of ethanol it displayed a length tensile strength of about 1 pound per inch width. The web also retained its strength well when saturated with other conventional resin solvents such as a mixture of butyl alcohol with water, acetone, a mixture of acetone with 2-methoxy ethanol, dimethyl formamide, and the like.

When the web is intended to be impregnated with a polyester resin instead of an epoxy resin it is desirable to replace the gamma-aminopropyl triethoxysilane with a different silane such as a methacrylate functional silane

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or other surface treating composition conventionally used to enhance the bonding of polyester resins to glass.

Example 2

There were agitated in about 2200 gallons of water in a suitable vessel 200 pounds of chopped glass strand, as described in Example 1, 100 pounds of C-glass monofilaments, as described in Example 1, and 100 pounds of polyester filaments (Dacron staple fiber) having a diameter of 12–13 microns and an average length of one-fourth inch. In addition 1750 gallons of water together with sulfuric acid to produce a pH of 2.5 to 3.0 were added, as described in Example 1. The aqueous furnish so produced was used in place of the furnish containing the glass fibers of Example 1 to make a web as described in that example.

The finished web, after drying, weighed about 105 pounds per 3000 square feet and contained approximately 17% by weight of asbestos and 8.5% by weight of resinous binder. The remainder consisted of a mixture of glass fibers and polyester fibers in approximately the proportions given in the furnish. The web displayed a length tensile strength in excess of 5 pounds per inch width when dry and was adapted for impregnation with a resin solution, as evidenced by the fact that is possessed a length tensile of about 1 pound per inch width when saturated with a mixture of two parts by weight toluene and one part by weight of ethanol.

Example 3

A hand sheet was prepared from a mixture of a glass fiber furnish and an asbestos-binder furnish. The glass fiber furnish was prepared by dispersing in approximately 1 liter of water, adjusted to pH 2.5 to 3.0 with sulfuric acid, approximately 2.8 grams of C-glass fibers and 1.4 grams of chopped strands of the type described in Example 1. The dispersion was accomplished by agitating the mixture in a Waring Blendor at medium speed for a few seconds.

The asbestos-binder dispersion was prepared by mixing together 11 grams of the copolymer emulsion described in Example 1 (Rhoplex E303) and 30 grams of the heat-advancing polyacrylic ester emulsion described in Example 1 (Hycar 2679), then diluting with 159 grams of water. The resulting blend was added slowly with mild agitation to a dispersion of 45 grams of California chrysotile asbestos in 2 liters of water. Agitation was continued until the milky emulsion was broken and the resin solids deposited upon the asbestos fibers to leave a clear aqueous medium.

One liter of the glass fiber dispersion was blended with 90 ml. of the asbestos-binder dispersion and used to make a hand sheet in conventional equipment.

After drying for approximately 3 minutes on a steam-heated can dryer and curing for about 5 minutes at 400° F. in a circulating air oven, the resultant hand sheet weighed approximately 4.8 grams and had a tensile strength in excess of 4 pounds per inch of width. When saturated with a mixture of two parts by weight of toluene and one part by weight of ethanol, a typical solvent mixture employed in resin impregnation, the sheet displayed a tensile strength of about three-fourths pound per inch width. The sheet contained approximately 17% by weight of asbestos, and about 8.5% by weight of resinous binder; the balance was glass, the ratio of chopped strands to monofilament glass being approximately the same as in the furnish.

Although specific embodiments of the invention have been described herein, it is not intended to limit the invention solely thereto but to include all of the obvious variations and modifications within the spirit and scope of the appended claims.

What is claimed is:

1. The method of making a web consisting essentially of fibrous material and synthetic resinous binder which comprises providing an aqueous dispersion containing opened chysotile asbestos fibers at a pH from 2.0 to 5.0, mixing with said dispersion an aqueous dispersion of synthetic resinous binder in which the dispersed particles have an anionic charge to form a first furnish in which the dispersed binder particles are deposited on the dispersed asbestos fibers providing a second separate aqueous furnish containing reinforcing fiber dispersed therein at a pH from 2.0 to 5.0, said reinforcing fiber consisting of 0 to 75% by weight of glass monofilaments and 25 to 100% by weight of chopped glass strands having a length from one-eighth to three-fourths inch, mixing said first and second furnishes to provide a mixed furnish in which said dispersed material consists essentially of a mixture of 50 to 90% by weight of said reinforcing fibers, from 7 to 35% by weight of said asbestos, and from 3 to 15% by weight of binder, the weight of asbestos being at least one and one-half times the weight of the binder, forming a web from said mixed furnish, and then drying said web.

2. The method of making a web consisting essentially of fibrous material and synthetic resinous binder which comprises providing an aqueous dispersion containing opened chrysotile asbestos fibers at a pH from 2.0 to 5.0, mixing with said dispersion an aqueous dispersion of synthetic resinous binder in which the dispersed particles have an anionic charge to form a first furnish in which the dispersed binder particles are deposited on the dispersed asbestos fibers, providing a second separate aqueous furnish containing reinforcing fiber dispersed therein at a pH from 2.0 to 5.0, said reinforcing fiber consisting of 0 to 75% by weight of glass monofilaments and 25 to 100% by weight of a mixture of chopped glass strands having a length from ⅛ to ¾ inch with up to 30% by weight of non-hydratable synthetic textile fibers, mixing said first and second furnishes to provide a mixed furnish in which said dispersed material consists essentially of a mixture of 50 to 90% by weight of said reinforcing fibers, from 7 to 35% by weight of said asbestos, and from 3 to 15% by weight of binder, the weight of asbestos being at least 1 and ½ times the weight of the binder, forming a web from said mixed furnish, and then drying said web.

3. The method of making a web consisting essentially of fibrous material and synthetic resinous binder in which said fibrous material consists essentially of a mixture of 50 to 90% by weight of reinforcing fibers and from 7 to 35% by weight of opened chrysotile asbestos, based on the total weight of the web, and said binder amounts to 3 to 15% of the total weight of the web, the weight of said asbestos being at least 1 and ½ times the weight of said binder, said asbestos containing less than 0.5% iron, said reinforcing fiber consisting of 0 to 75% by weight of glass monofilaments and 25 to 100% by weight of chopped glass strands having a length from ⅛ to ¾ inch, which method comprises providing an aqueous furnish containing said asbestos and said binder in which the binder is deposited on the asbestos, providing a separate aqueous furnish containing said reinforcing fibers, mixing said furnishes and forming a web therefrom, and then drying said web.

4. The method of making a web consisting essentially of fibrous material and synthetic resinous binder in which said fibrous material consists essentially of a mixture of 50 to 90% by weight of reinforcing fibers and from 7 to 35% by weight of opened chrysotile asbestos, based on the total weight of the web, and said binder amounts to 3 to 15% of the total weight of the web, the weight of said asbestos being at least 1 and ½ times the weight of said binder, said asbestos containing less than 0.5% iron, said reinforcing fiber consisting of 0 to 75% by weight of glass monofilaments and 25 to 100% by weight of a mixture of chopped glass strands having a length from ⅛ to ¾ inch with up to 30% by weight of non-hydratable synthetic textile fibers, which method comprises providing an aqueous furnish containing said asbestos and said

binder in which the binder is deposited on the asbestos, providing a separate aqueous furnish containing said reinforcing fibers, mixing said furnishes and forming a web therefrom, and then drying said web.

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