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GLASS FIBER SIZING

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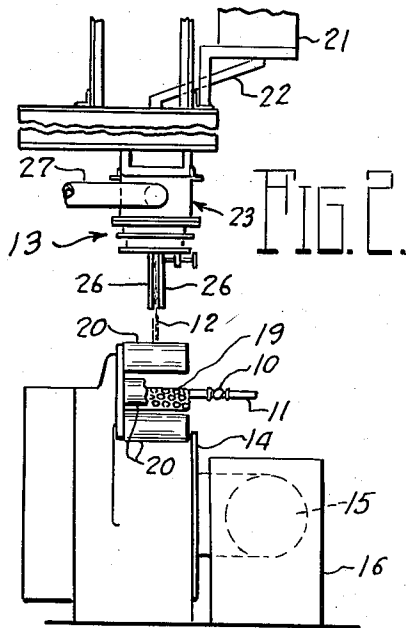


FIG. 1

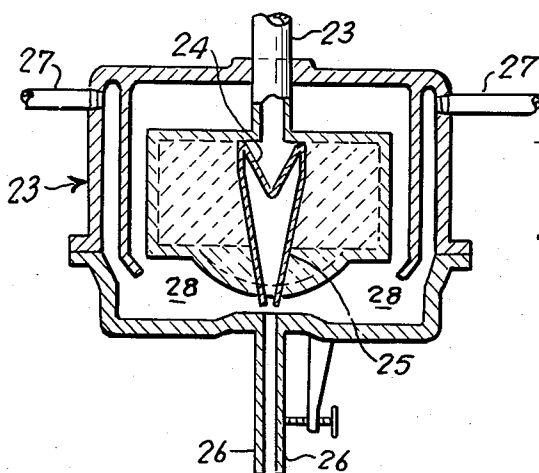
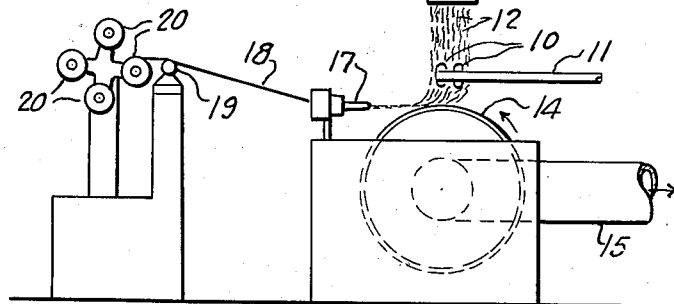
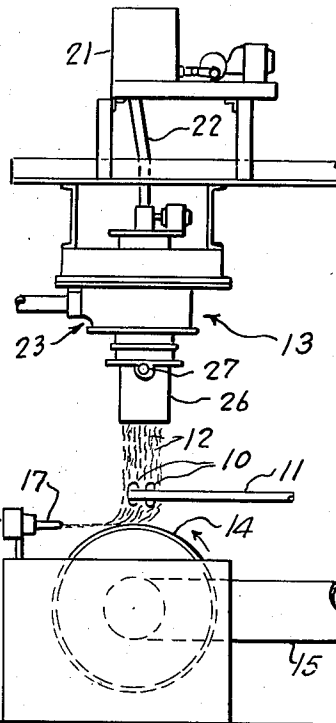


FIG. 3

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GLASS FIBER SIZING

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6 Claims. (Cl. 154—90)

This invention relates to the sizing of fibrous glass and to sized fibrous glass products, and, more particularly, to an improved sizing for glass fiber rovings, slivers or the like.

In the production of glass fiber slivers, rovings and the like a plurality of fine glass fibers are formed, deposited and accumulated in a confined zone, progressively removed therefrom, and laterally compacted during their removal from such zone into a continuous elongated mass with the fibers closely adjacent each other in sliver form, or twisted together in roving form. In order to prevent or minimize the fracture of individual fibers during the gathering step, and also during subsequent processing, and to provide some type of interfilament cohesion, it has been found to be advantageous to apply the size to the fibers in the enclosed zone. Various sizes have been employed for this purpose in the past, with greater or lesser degrees of success. At least in some instances, it is essential that the size be removed from the fibers at an intermediate point during their processing, for example prior to dyeing or printing on fabrics made therefrom.

Most satisfactory results have been achieved when size was removed by a burning operation which is described in more detail in co-pending application Serial No. 453,782, filed September 12, 1954, by Marzocchi, Caroselli and Rammel. However, serious problems have arisen during the removal by burning of most sizes that are satisfactory for use during the operation. A noteworthy problem that is almost universally encountered is that the burning step to remove size must be carried out at a temperature above the combustion point of the size or of decomposition products formed from the size. If such a size is removed by a burning process, combustion of the size or of its decomposition products may occur in contact with, or in close proximity to, the fibrous glass, with the result that the glass is badly overheated and loses its mechanical strength. In extreme instances, the fibrous glass may be completely useless because of such overheating.

The present invention is based upon the discovery of a particular class of sizes which can be removed by the burning process without overheating the fibrous glass and, consequently, without adversely affecting the mechanical strength thereof.

It is, therefore, an object of this invention to provide an improved size for fibrous glass.

It is a further object to provide an improved method for sizing fibrous glass.

It is still another object to provide an improved sized fibrous glass sliver, roving, strand or the like.

It is still a further object to provide an improved fibrous glass sliver roving strand or yarn carrying sizing components which can easily be removed by heat cleaning with minimum reduction in tensile strength of the fibrous glass.

Other objects and advantages will be apparent from

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the description which follows, reference being had to the accompanying drawings, in which:

Fig. 1 is a partially schematic view in side elevation of apparatus for forming and applying a size to fibrous glass;

Fig. 2 is a front elevational view of the apparatus of Fig. 1; and

Fig. 3 is a view in vertical section, on an enlarged scale, of a melting and attenuating portion of the apparatus of Figs. 1 and 2.

According to the invention a glass fiber sliver, roving or the like is produced. The individual fibers of such sliver or the like carry a thin coating of size which is an aqueous dispersion containing from about 5 percent to about 25 percent of a linear polymer, and from 0 to 25 percent of a plasticizer such as tricresyl phosphate which acts as a flame depressant, the ratio of tricresyl phosphate to linear polymer in said dispersion being at least as high as the minimum non-tacky, tricresyl phosphate to polymer ratio.

The terms "percent" and "parts" are used herein, and in the appended claims, to refer to percent and parts by weight, unless otherwise indicated.

The term "linear polymer" is used herein and in the appended claims in its usual sense, namely, to refer to chain compounds formed by reaction, usually a condensation polymerization, between different molecules of a single compound or between two or more compounds where there are two reactive groups in each molecule of the starting material or materials. Polyglycols, polyglycol ethers and polyglycol esters constitute a preferred class of linear polymers. Methods for producing linear polymers of this preferred class are given in the following U. S. patents: 2,425,755; 2,425,845; 2,448,664; 2,480,185; 2,520,611 and 2,520,612. Examples of other linear polymers that have been used satisfactorily in the sizing of glass fibers according to the invention include polyesters, preferably saturated polyesters such as those produced from phthalic acid or anhydride and ethylene glycol, propylene glycol, diethylene glycol, and the like, similar polyesters from fatty acids, and polyamine linear polymers.

The term "minimum non-tacky, tricresyl phosphate to polymer ratio" is used herein, and in the appended claims, to refer to the lowest ratio of these constituents at which a size, after the aqueous dispersing medium has been substantially evaporated, is not appreciably tacky or sticky, and still provides sufficient interfilament cohesion that a sliver or roving coated therewith is suitable for further processing. In the production of glass fiber rovings or slivers (see U. S. Patent 2,264,345) a web of the fibers is collected on a perforate drum or conveyor. Such web is formed by directing fibers, immediately after attenuation, through an enclosed zone and directly onto the drum or conveyor, the fibers being sprayed with the size in such enclosed zone. The temperatures involved in this operation are sufficiently high that the water from a size according to the invention is substantially evaporated prior to removal of the web from the drum or conveyor. It has been found that most linear polymers which can be formed into an aqueous dispersion are tacky, with the result that they cannot be used per se as a size because they stick to the drum or conveyor to an extent such that removal of the web therefrom for gathering is impractical, if not impossible. It has been found, however, that admixing tricresyl phosphate with linear polymers reduces the viscosity of the latter with the result that there is a minimum ratio of tricresyl phosphate to linear polymer at which tackiness, when the admixture is substantially dry, disappears, and a glass fiber sized with such admixture can be readily removed from

the drum or conveyor. It has also been found that the minimum non-tacky tricresyl phosphate to linear polymer ratio is a function of molecular weight of the latter, which is usually considered to be a direct function of viscosity, the higher the molecular weight as indicated by the viscosity of the linear polymer, the larger the amount of tricresyl phosphate required to produce a non-tacky material. In some instances it has been found that the minimum non-tacky tricresyl phosphate to linear polymer ratio is 0. For example, a linear polymer sold under the trade designation 75HB1400, which is a polyglycol produced from 75 parts of ethylene glycol and 25 parts of propylene glycol, condensed to a viscosity of 1400 Saybolt Universal seconds at 100° F. is non-tacky alone, and can be dispersed in water in the above-indicated proportions and used for sizing according to the invention without tricresyl phosphate. A linear polymer identical except that it is condensed to a viscosity of 90,000 Saybolt Universal seconds at 100° F., however, is tacky, and can be used only in a dispersion which contains at least about 2 percent of tricresyl phosphate.

Other plasticizers than tricresyl phosphate can also be used. In general, any plasticizer which acts as a flame depressant in the sense that it raises the combustion temperature of the linear polymer is operable if compatible with the polymer. Examples of other plasticizers that can be used include dibutyl phthalate, dioctyl phthalate, glycol phosphates and glycol titanates.

The term "dispersion" is used herein, and in the appended claims in its usual meaning, as a generic term including stable suspensions and solutions. In the case, for example, where polyethylene glycol is the linear polymer, the dispersion may be a solution in the true sense of the word, while in the case of polypropylene glycol, for example, the dispersion is a suspension. When the linear polymer is not water soluble, it is usually necessary to employ a dispersing agent in addition to the linear polymer and tricresyl phosphate, if required. Particularly satisfactory results have been achieved with dispersing agents of the polyglycol ether type, an example of such dispersing agent being an isooctyl phenyl ether of polyethylene glycol sold under the trade designation "Triton X100." Although it is theoretically possible to use dispersing mediums other than water in sizing glass fibers according to the invention, practical considerations almost invariably militate against their use. The necessity for a glass melting furnace in close proximity to the enclosed zone where the size is applied to the fibers discourages the use of inflammable organic solvents as dispersing mediums, while hazardous to personnel or cost, or both, usually make the use of non-inflammable organic solvents as dispersing mediums unfeasible.

Although, as has been indicated above, it is possible in some instances to use an aqueous dispersion of a linear polymer as a size, it is usually preferred that the dispersion contain from 2 percent to 20 percent of tricresyl phosphate in addition, as it has been found in practice that slivers, rovings, fabric and the like are more easily heat cleaned when tricresyl phosphate is used. Optimum results from the standpoint of strength of the sliver, roving or the like, after removal of the size, and also from the standpoint of ease of removal from the drum or conveyor, have been achieved from dispersions containing from about 2 percent to about 8 percent of tricresyl phosphate, from about 7 percent to about 13 percent of a polyglycol or a polyglycol ether, and from about 0.2 percent to about 1 percent of a dispersing agent. Most desirably the dispersing agent is chemically similar to the linear polymer, a polyglycol ether having been used for this purpose when the linear polymer was a polyglycol ether. Most preferably, the polyglycol or polyglycol ether linear polymer is produced from a mixture of ethylene glycol and propylene glycol, and in proportions ranging from about 45 percent to about 75 per-

cent of ethylene glycol, and 55 percent to about 25 percent of propylene glycol.

The following examples are presented solely for the purpose of further illustrating and disclosing the invention, and are in no way to be considered as limitations thereon.

Example 1

An aqueous dispersion containing a linear polymer, tricresyl phosphate, and a dispersing agent was used as a size for fine glass fibers according to the following procedure:

An aqueous dispersion was formed from 5 parts of tricresyl phosphate, 5 parts of a polyglycol produced from 75 parts of ethylene glycol and 25 parts of propylene glycol condensed to a viscosity measured at 100° F., of 1400 Saybolt Universal seconds, 2 parts of a polyglycol identical except that it had been condensed to a viscosity, measured at 100° F., of 90,000 Saybolt Universal seconds, and 88 parts of water. This dispersion was introduced into a receptacle (not illustrated) and forced therefrom into a spray nozzle 10 through a pipe 11 as shown in Figs. 1 and 2 of the attached drawings. The spray nozzle 10 was disposed adjacent a plurality of glass filaments 12 which were formed in a melting and attenuating apparatus indicated generally at 13. The dispersion was sprayed onto the fibers 12 to provide a coating, and coated fibers were accumulated on a perforated drum 14. A vacuum was applied to the interior of the drum 14 through a conduit 15 by a blower 16. The fibers 12 were collected on the drum 14 in the form of a web, which web was progressively removed from the drum and laterally compacted in an eye 17 into a sliver 18. The size was substantially dry, or water-free at the time of removal from the drum.

The sliver 18 was passed over a guide 19 and collected on one of four spools 20. The sliver was subsequently converted into yarn by standard twist and ply operations. The yarn was then woven into a fabric which was subsequently subjected to a heat cleaning operation. The heat cleaning involved passing the fabric over a preheat roll at a temperature of 600° F. to drive off the volatile gases and then through a muffle oven at an average temperature of 1190° F. for approximately two to three minutes under strongly oxidizing conditions to remove the remainder of the size.

The Mullen burst strength of the heat cleaned fabric, as measured by a standard test conducted on apparatus called a "Mullen pop tester" by the paper trade, was found to be 148 pounds. The fabric was white in appearance and suitable for further finishing. The Mullen burst strength of the cleaned fabric was 403 pounds, or 70 percent of its original strength after finishing thereof with a piece-dyeing formula described in the above-identified copending application, Serial Number 453,782.

The specific melting and attenuating apparatus 13 shown comprises a hopper 21 for storage of glass marbles and a tube 22 for feeding marbles from the hopper to a melting and attenuating unit 23. Referring now to Fig. 3, marbles delivered to the unit 23 rest on platinum screens 24 disposed in platinum tips 25. The screens 24 and the tips 25 are electrically heated to melt the marbles, so that droplets of molten glass flow downwardly through the screens 24 and collect in the tips 25 and molten glass filaments flow downwardly therefrom between skirts 26. The fine glass filaments are attenuated by low pressure air supplied to the interior of the unit 23 through inlet pipes 27. The air supplied through the pipes 27 flows through a passage 28 and downwardly between the skirts 26 parallel to the streams of molten glass, thus causing the desired attenuation.

Fabrics prepared from conventionally sized glass fiber yarn using, as a size, an emulsified petroleum oil, applied under standard conditions, and heat cleaned as

described in the preceding paragraph, without previous washing or other cleaning, were found to be too weak to process through the equipment and had a gray-black appearance, thus being completely unsuitable for further finishing.

Fabrics produced as described above from slivers sized according to the invention have also been processed at 650° F. by a batch heat cleaning method. A white fabric resulted after forty-eight hours of such batch treatment. The Mullen burst strength of the white fabric, without finishing, was found to be 210 pounds, ignition loss 0.3 percent. Comparable results cannot be achieved using an emulsified petroleum oil size. Fabric with such a size, even if previously washed does not become white even after a seventy-two hour batch heat cleaning operation.

Example 2

Various other aqueous dispersions have also been used for sizing glass fibers in slivers, rovings or the like according to the invention. The procedures used for preparing the dispersions, applying the dispersions to the fibers, collecting the fibers into slivers, removing the size and testing were identical with those described in Example 1. The identity of various typical dispersions that have been used are presented in the table, below, together with tensile strength data on the slivers after removal of the size.

Composition of Dispersion in Parts by Weight				Type	Identity of Polymer			Mullen burst strength in pounds of fabric after removal of size
Tricresyl Phosphate	Linear Polymer	Isooctyl phenyl ether of polyethylene glycol or a dispersing agent	Water		Parts of Ethylene Glycol	Parts of Propylene Glycol	Viscosity in Saybolt Seconds	
5	5	1½	89½	Polyglycol	75	25	90,000	108.5
5	5	¾	89¾	do	58	42	660	162.5
5	10	¾	84½	do	58	42	660	135.8
5	5	¾	89½	Polyglycol monoether	58	42	625	168.4
5	10	¾	84½	do	58	42	625	122.2
2	5	¾	92¾	Polyglycol	75	25	90,000	90.0
5	0.5	-----	94.5	Isooctyl phenyl ether of polyethylene glycol	100	-----	-----	134.2
5	5	½	89½	Polyglycol monoether	60	40	1,750	141.8

It has been found that the minimum strength required of a glass fiber fabric, as measured by the "Mullen pop tester," depends upon the friability of the glass, the use to be made of the fabric, and other considerations. However, a fabric is usually sufficiently strong, if its Mullen burst strength is at least about 40 to 50 pounds.

Various modifications can be made within the spirit and scope of the following claims.

We claim:

1. In a method for producing a fibrous glass of the class described which includes the steps of forming a plurality of fine glass fibers, depositing and accumulating the fibers, and progressively removing and laterally compacting the accumulated fibers, the improvement which comprises spraying onto the fibers, prior to accumulation, an aqueous dispersion containing from about 8 percent to about 13 percent of a linear polyglycol polymer wherein the polyglycol is a mixed ethylene-propylene polyglycol produced from 45 percent to 75 percent of ethylene glycol and 55 percent to 25 percent of propylene glycol, from 2 to 8 percent of tricresyl phosphate, and from about 0.2 percent to about 1.0 percent of a dispersing agent which is chemically similar to the linear polymer.

2. A fibrous glass of the class described, the individual fibers of which carry a thin coating of a substantially dry size which is produced by evaporating water in situ on the fibers from an aqueous dispersion containing from about 8 percent to about 13 percent of a linear polyglycol polymer wherein the polyglycol is a mixed ethylene-propylene glycol produced from 45 percent to 75 percent of ethylene glycol and 55 percent to 25 per-

cent of propylene glycol, from 2 to 8 percent of tricresyl phosphate, and from about 0.2 percent to about 1 percent of a dispersing agent which is chemically similar to the linear polymer.

3. In a method for producing a fibrous glass of the class described which includes the steps of forming a plurality of fine glass fibers, depositing and accumulating the fibers, and progressively removing and laterally compacting the accumulated fibers, the improvement which comprises spraying onto the fibers, prior to accumulation, an aqueous dispersion containing from about 5 percent to about 25 percent of a linear polyglycol polymer wherein the polyglycol is a mixed ethylene-propylene polyglycol produced from 45 percent to 75 percent of ethylene glycol and 55 percent to 25 percent of propylene glycol, from about 0.2 percent to about 1 percent of a dispersing agent which is chemically similar to the linear polymer, and an amount of tricresyl phosphate, not greater than 25 percent, sufficient that the ratio of tricresyl phosphate to linear polyglycol polymer is at least as high as the minimum non-tacky, tricresyl phosphate to polyglycol polymer ratio.

4. In a method for producing a fibrous glass of the class described which includes the steps of forming a plurality of fine glass fibers, depositing and accumulating the fibers, and progressively removing and laterally compacting the accumulated fibers, the improvement

which comprises spraying onto the fibers, prior to accumulation, an aqueous dispersion containing from about 5 percent to about 25 percent of a linear polyglycol polymer wherein the polyglycol is a mixed ethylene-propylene polyglycol produced from 45 percent to 75 percent of ethylene glycol and 55 percent to 25 percent of propylene glycol, and an amount of tricresyl phosphate, not greater than 25 percent, sufficient that the ratio of tricresyl phosphate to linear polyglycol polymer is at least as high as the minimum non-tacky, tricresyl phosphate to polyglycol polymer ratio.

5. In a method for producing fibrous glass, the improvement as claimed in claim 4 wherein the reactants from which the mixed ethylene-propylene polyglycol polymer is produced consist essentially of ethylene glycol and propylene glycol.

6. A fibrous glass of the class described, the individual fibers of which carry a thin coating of a substantially dry size which is produced by evaporating water in situ on the fibers from an aqueous dispersion containing from about 5 percent to about 25 percent of a linear polyglycol polymer wherein the polyglycol is a mixed ethylene-propylene glycol produced from 45 percent to 75 percent of ethylene glycol and 55 percent to 25 percent of propylene glycol, and an amount of tricresyl phosphate, not greater than 25 percent, sufficient that the ratio of tricresyl phosphate to linear polyglycol polymer is at least as high as the minimum non-tacky, tricresyl phosphate to polyglycol polymer ratio.

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