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D. H. GRIFFITHS

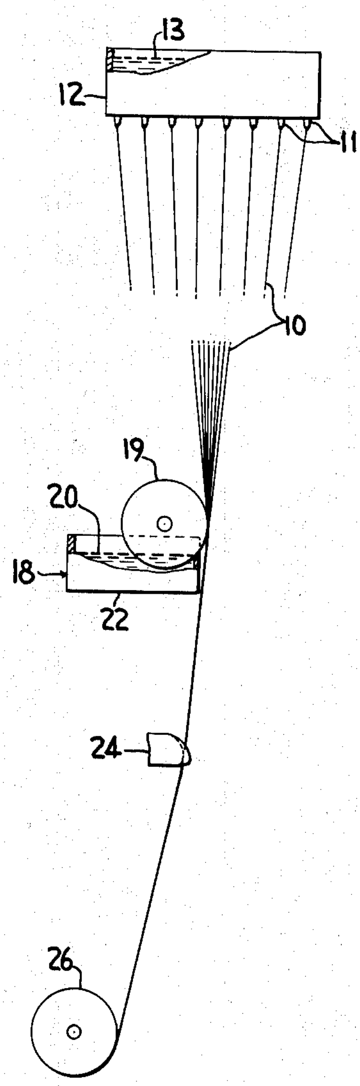
3,227,192

SIZED GLASS FABRIC AND METHOD

Filed April 2, 1962

2 Sheets-Sheet 1

FIG. 1



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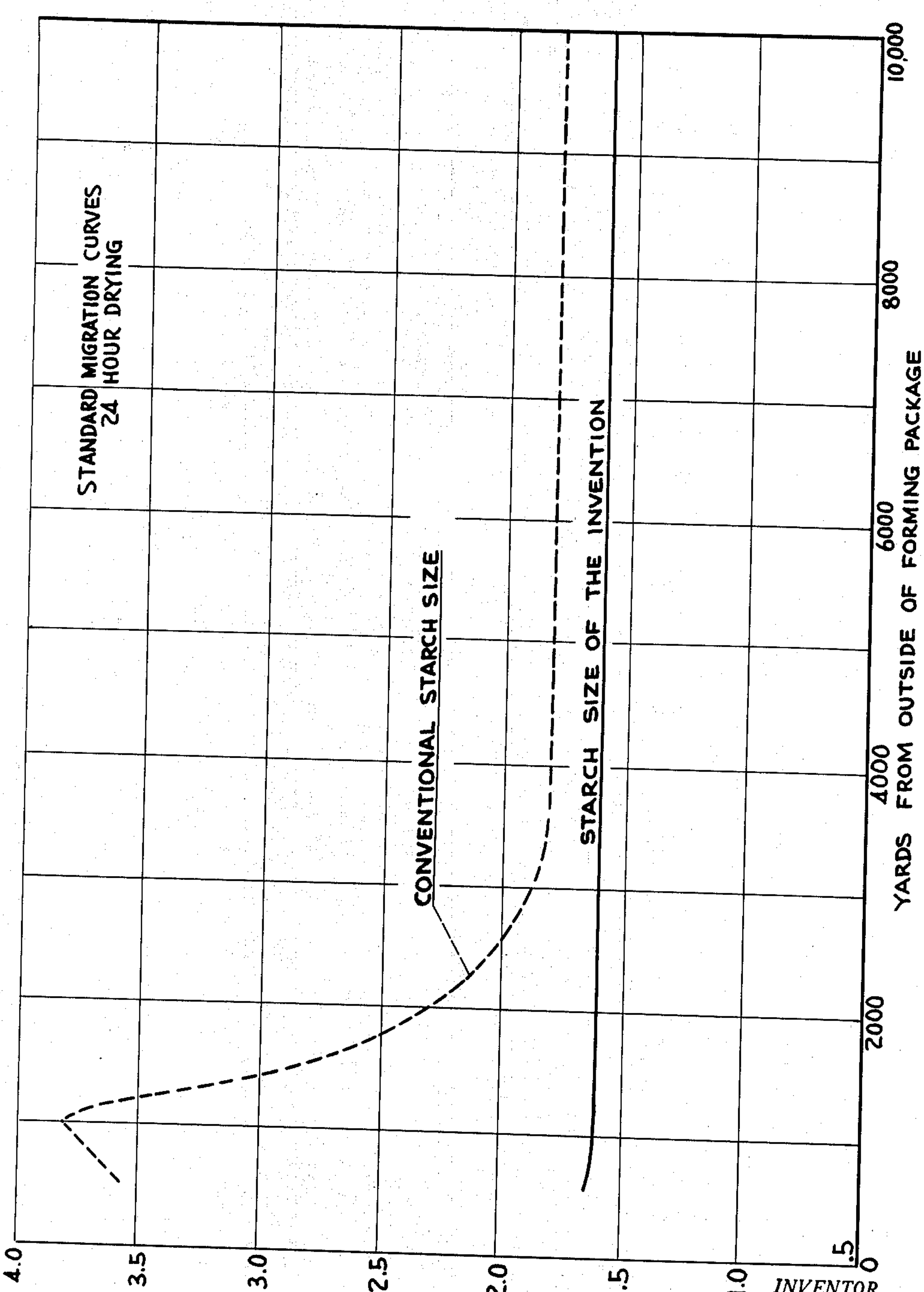

FIG.2

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SIZED GLASS FABRIC AND METHOD

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Filed Apr. 2, 1962, Ser. No. 184,405
11 Claims. (Cl. 139—420)

This invention is directed to a process for preparing glass fibers, and it has particular relation to the application of a size to continuous filament glass fiber strand during the formation of the strand.

In the production of continuous filament glass fiber strands, a number of individual glass filaments are drawn from an electrically heated, platinum alloy bushing containing a molten supply of the glass. The glass passes through tips which define orifices in the bottom of the bushing and form inverted cones of glass at the ends of the tips. Individual filaments are drawn from the cones of glass at a high rate of speed, i.e., 5,000 to 20,000 feet per minute, and are grouped into a strand as they pass over a suitable guide. The strand is thereafter wound on a rapidly rotating forming tube.

There is no twist in the strand as it is thus formed, and an aqueous size composed of an aqueous dispersion of a binder and a lubricant, such as dextrinized corn starch and a vegetable oil, is applied to the individual filaments prior to the time they are grouped into the strand and wound on the tube in order to bond them together and maintain the integrity of the strand. The strand is wound on the tube with a slight traverse so that succeeding turns cross each other at an angle rather than being parallel to each other so that the strand can be more easily removed from the tube.

One problem which occurs in the manufacture of continuous filament strand in this manner is that of "size migration." "Size migration" is a phenomenon which occurs in the strand after it is wound on the forming tube. As stated above, the size normally employed in the prior art is an aqueous dispersion of dextrinized corn starch and vegetable oil. The solids content of the size is about 12 percent by weight with the remainder being water. Some of this water must be removed from the strand before it is twisted to form yarn. This water is removed from the strand by drying the strand after it is wound upon a plastic forming tube. As the sized strand dries on the plastic forming tube, the water moves from the inside of the forming package next to the tube to the outside of the forming package. In cases where paper (cardboard) forming tubes are used, the water moves both in and out. This movement of the water carries with it some of the starch and oil of the size so that the strand in the outside layers of the package has a much higher size solids content than the strand in the layers beneath the surface.

Size migration creates a number of problems in subsequent fabrication of the strand. In twisting, plying, warping, quilling and weaving of glass fiber yarn there are a number of winding and unwinding operations where the tension exerted on the yarn is important. The tension exerted on the yarn during these operations must be relatively constant. If the tension on the yarn is uneven during these operations, the individual filaments making up the yarn are likely to be broken and produce fuzzy yarn. Fuzzy yarn clogs up the fabricating equipment and causes

yarn break out. Uneven tension on the yarn can be created by non-uniform size contents on the yarn throughout its length. Thus, it is desired that the size content on the yarn be uniform throughout its length.

Another fabricating operation where uneven size content on a yarn is troublesome is in the process of texturing yarn. Textured yarns are those continuous filament yarns which have been bulked by an air jet, such as described in U.S. Patent No. 2,783,609. The size content of the yarn which is textured determines the resistance of the yarn to being textured or bulked by the air jet. A variation in size content along the length of the yarn results in a variation in the degree of bulking. Any variation in the degree of bulking of the yarn shows up in the fabric and may be serious enough to result in rejection of the piece of goods.

An additional problem due to size migration is encountered when woven fabrics are heat treated. The strand with the higher size-solids content shows up differently from the strand with the lower size-solids content when the twisted strand is woven into a fabric, and the fabric is heated to remove the size and set the fibers in the fabric. This heating is conducted at a temperature of about 1200 to 1400° F. for 30 to 40 seconds, and is sufficient to volatilize the solids and remove them from the fabric, and to soften the glass fibers in the glass fabric to set them in their new position. This process is described in greater detail in U.S. Patent No. 2,845,364.

After the heat treatment, the strand from the outside of the forming package which strand originally had the higher size-solids content shows up as a band in the fabric which is colored to an extent different from the rest of the fabric. Sometimes this band exhibits a "moire" effect. This results in an imperfection in the fabric which is of sufficient magnitude to cause rejection of the fabric.

It is not known exactly what causes the difference in appearance in the yarn in the fabric; however, it is believed that it may be due to incomplete removal of the size, or it may be due to a difference in the orientation of the individual filaments in the yarn due to the increased heating activity which occurs in the areas of increased size solids content when the fabric has been sufficiently heated to remove all of the size throughout the fabric. In any event, this difference has definitely been noted, and has been a cause for serious concern with the yarn manufacturers and weavers. The above defects have also occurred in fabrics woven with textured, continuous filament glass yarns.

As can be surmised from the description above concerning the defects in woven fabrics caused by "size migration," this problem has been a most serious problem and has required drastic steps to overcome it. These steps have involved the stripping or running off of the strand on the outside of the forming package to remove that portion of the forming package which contains strands having a higher size content than the remainder of the package. This represents a substantial loss in the production of strand and also requires a costly and undesirable intermediate step between the forming and twisting of the strand.

Another problem generally present when sizing glass fibers with conventional starch sizes is that of "shedding," also known as "powdering." "Shedding" is the removal of small pieces of binder size which is caused by a peeling of the size from the glass fibers as the sized glass fibers (e.g., sized glass fiber yarn) pass over some contact surface or point during a fabrication step, e.g., when sized strands are being warped. "Shedding" leaves an accumulation of powdery size on fabricating equipment, mostly on those parts of the equipment which contact the sized fibers.

The starch sizing composition of this invention has good shedding properties in that very little shedding occurs during fabrication steps, such as twisting, plying, warping, weaving etc.

Moreover, the starch sizing compositions of the instant invention demonstrate excellent runability and good wet out properties for warp sizes with almost complete freedom from binder "throw-off" and strand "break outs" (breaking of filaments) during fabrication operations.

It is, therefore, an object of this invention to provide an aqueous size which can be easily applied to glass fiber strand during its formation in uniform, controlled amounts and whose non-aqueous constituents will not migrate significantly in the strand forming package upon drying of the package on the forming tube.

It is a further object of this invention to provide such a size which will permit the strand to be twisted, uniformly textured if desired, quilled or warped, and woven into cloth with uniform tension and with a minimum of broken filaments in these various fabricating operations.

It is also an object of the invention to provide an aqueous size whose solids constituents can be readily and completely removed from a woven fabric by the conventional heat treatments which are applied to fabrics to remove the size ingredients and set the fibers in the article.

The objects of this invention are achieved by application to the strand during its formation of an aqueous size containing as the binder ingredient an amylose containing starch mixture having an amylose content of about 35 to 45 percent by weight and formed by admixing approximately equal proportions of:

(A) A high amylose starch fraction, viz., one containing about 50 to 60 percent by weight of amylose with the greater portion of the remainder being amylopectin, and

(B) A water repellent low amylose starch fraction, viz., one containing about 20 to 30 percent by weight amylose with the greater portion of the remainder being amylopectin.

The size also contains other ingredients such as a vegetable oil, as a lubricant, a fungicide of the metallo organic-quaternary type, e.g., tributyltin oxide ammonium complex, softening agents and a wetting agent. Small amounts of additional film forming ingredients other than the previously mentioned amylose containing starch mixture can also be included, such as for example, gelatin, polyvinyl alcohol, etc., to make a more durable strand.

THE STARCH MIXTURE

The basic starch components of the amylose containing starches employed in the starch mixture can be derived from any starch sources including corn, wheat, potato, tapioca, waxy maize, sago, rice, hybrid starches, etc. Conveniently, however, the starch component having the high amylose content, viz., 50 to 60 percent by weight, is derived either from potato starch or a hybrid corn starch having over 50 weight percent amylose, and the starch component having the low amylose content, viz., 20 to 30 percent by weight, is derived from corn starch. The overall amylose content of the starch mixture can vary from 35 to 45 percent by weight based on total starch content.

The high amylose starch component preferably contains about 55 percent by weight of amylose with the remainder being amylopectin. This component serves to impart the non-migratory characteristics while at the same time providing the sized glass fibers with better wet out properties for warp sizes which are subsequently applied thereto prior to the completion of the fabrication steps, e.g., weaving, quilling, etc. The high amylose component can constitute from about 45 to 55 percent by weight (based on total starch content) of the starch mixture. Preferably the high amylose component constitutes about 50 percent by weight of the starch mixture. When the high amylose component is employed in amounts significantly in excess of 55 percent by weight, it becomes increasingly difficult to mix (blend) the two starch components, especially in aqueous media, and the viscosity characteristics are deleteriously affected. Moreover, the "burn-off" (volatilization) of the binder becomes more difficult and expensive.

The low amylose content starch component is a water repellent starch which preferably contains from 25 to 27 percent amylose with the remainder being amylopectin. Instead of pure starch, the low amylose content component can and preferably does contain cross links. Thus, preferably the low amylose content component is a lightly cross-linked corn starch having an amylose content of from 25 to 27 percent by weight. This starch component provides the sizing composition with bulk and imparts strand integrity to the sized glass fibers thus diminishing the development of fuzz, which can lead to strand breakage. The low amylose component, being of a viscous nature, can also be viewed as contributing to the non-migratory nature of applicant's sizing compositions. The low amylose component constitutes from 45 to 55 percent by weight of the mixture (based on total starch content) and preferably about 50 percent by weight thereof.

The term "starch mixture" as used herein is intended to be descriptive of the fact that a plurality of different starches, each having different amylose content, are employed in the instant sizing composition, and not to preclude the possibility of chemical interaction between the starch molecules of each of the starch components. In fact, some chemical bonding can be present between the molecules of both the high amylose starch and the low amylose starch, and such starch mixtures possessing intermolecular bonding between the starch components are considered to be within the realm of this invention.

Also considered to be included within this invention are starch mixtures wherein the low amylose component and the high amylose components are lightly cross-bonded to provide a weakly knit yet three-dimensional composite starch network which is water soluble or water dispersible.

The individual starch components can be blended, e.g., by mechanical mixing in the "dry" state, and the mixture can then be added to water and cooked; or the starches can be dumped dry into a mixing tank containing water, mixed and then cooked in the same tank; or the individual starch components can be mixed with water separately, then admixed to form an aqueous slurry and then cooked; or the individual starch components can be mixed with water separately, cooked separately and then be admixed. The aforementioned starch mixtures, when formulated into aqueous systems with the addition of other adjuvants, such as lubricants, fungicides, and various softening and conditioning agents, are emmiently suitable as aqueous sizing compositions for application to glass fiber strands during their formation to impart non-migratory characteristics and superior abrasion resistance thereto. It is also observed that by the application of aqueous sizing compositions containing amylose starch mixtures of the aforesaid composition, the problems of "shedding," "break out" and binder "throw off" are substantially eliminated. Moreover, the instant invention allows the uniform application of the aqueous sizing composition with good runability throughout the sizing process, viz., the sizing composition can be applied to the glass fibers easily without clogging the apparatus. In addition, due to its non-migratory characteristics, the said sizing composition can be easily and uniformly removed from the glass fibers (after the fabrication has been completed, e.g., after the strands have been woven into fabric) during the "burn-off" procedure without leaving unsightly yellow or brown bands which cause variance in the light reflecting properties of woven glass fabric. Thus, by use of the present invention, "rejects" can be substantially reduced by avoiding the aforementioned defects of non-uniform size application, size migration, variance in light reflectance, etc.

PREPARATION OF AQUEOUS SIZE COMPOSITIONS

The aqueous size compositions suitable for use as non-migratory, abrasion resistant starch sizes for glass fiber strands in accordance with this invention are conveniently prepared in the following manner. The individual starch components, viz., the high amylose content and low amylose content starches are added to water which has previously been placed in a mixing tank. Preferably the high amylose content starch is added first with agitation followed by the addition of the low amylose content starch component. The agitation is continued until substantially all the lumps of starch are dissolved. Then more water is added to the mix tank to form an aqueous slurry, and this slurry is then heated (cooked) at a temperature of from about 190° to 260° F., and more preferably of from about 200° to 230° F., in a pressure cooker, e.g., of the jet, auger or batch type, at a pressure of from about 5 to about 40 p.s.i. (gauge) for a sufficient period of time to allow the said components to go into the aqueous system, e.g., for a period of from about 0.5 to 1.0 minutes per pound of starch.

The term "aqueous systems" as employed herein is intended to be generic to aqueous solutions, aqueous dispersions and combinations of both since it is immaterial insofar as the present invention is concerned whether the starch is present in solution or in suspension or a combination of both.

A film forming adjuvant material having plasticizing properties, such as polyvinyl alcohol, polyethylene glycol having an approximate molecular weight of about 300, etc., can be added to the cooked slurry. Then a textile softening material, previously dispersed in water, is added to the sizing batch, and the thus formed aqueous system is agitated. Then a wetting agent, such as an ethylene oxide derivative of a sorbitol ester, is added to a processing oil, such as a hydrogenated vegetable oil, by adding the wetting agent to the processing oil and then emulsifying this mixture with hot water maintained at a temperature of from 140 to 180° F. and mixing. A small amount of the aqueous starch solution can be included in the emulsion before adding it to the main portion of the aqueous size. Then the wetting agent-processing oil emulsion is added to the main mixture, and the remaining amount of water is added to bring the aqueous sizing composition up to its desired volume. When a fungicide or bactericide, such as a metallo-organic-quaternary compound, is employed, it is usually added at some time after the addition of the starch components and prior to the addition of the wetting agent-processing oil emulsion. The fungicide is generally added in sufficient amounts to prevent mold or bacterial attack on the starch components of the sizing composition.

The aqueous sizing composition, as thus prepared, is adjusted to a pH of about 4 to 6. The aqueous sizing composition has a viscosity of about 1 to 40 centipoises at 20° C., and a starch content of about 3.0 to 8.0 weight percent based on total sizing composition. Instead of cooking the high amylose content starch component and the low amylose content starch component together as indicated previously, each component can be mixed with water and preliminarily cooked separately, e.g., by cooking the individual starch components with water at sufficient temperatures and for a sufficient period of time to render them readily incorporated into the aqueous system. They can then be admixed together and the remaining ingredients of the sizing composition added in the manner specified above.

The aqueous sizing composition of this invention is applied to glass fiber strands during their formation. While a certain amount of drying of the sized strands will occur during the forming procedure, the sized strands are "conditioned" (dried for about 20 hours at a temperature of about 75° C.) to reduce their average moisture content from about 9 percent to about 6 to 7 percent on the forming package prior to twisting the strand.

The amount of size solids on the strand (binder content) can vary from about 0.7 to about 2.0 percent by weight, and preferably from about 1.2 to about 1.7 percent by weight. One of the distinct advantages attendant to this invention resides in the fact that lesser amounts of size solids can be deposited on the glass fibers to accomplish the function of a starch size binder, viz., hold the glass fibers together in strand form until the fabrication of the strands has been completed. In the case of prior art starch sizes, solids contents of from 1.7 to 2.5 percent on the glass fibers (add on—dry basis) were customarily required to insure adequate film strength and binding. However, in accordance with this invention, the same objectives can be secured with the use of solids contents of from 1.2 to 1.7 percent, thus facilitating the removal of the size solids by volatilization during the subsequent heat treatment, viz., "coronization" or "burn-off." While solids content in excess of 1.7 percent can be used, no beneficial results are secured thereby, and this merely creates more of a problem in volatilization. Moreover, the glass fiber sizing compositions of the present invention are easier to remove, not only on a solids burn-off percentage basis, but also on a material burn-off basis since there is less difficulty in coronizing the instant sizing compositions than is encountered with conventional starch sizes.

The ability of applicant's invention to impart the desired binding power and fabrication properties to glass fibers while depositing fewer solids on a percentage basis is significant. This facilitates size removal because there is less size to burn off the fibers. Moreover, the coronizing equipment can handle more fabric in a given length of time, thereby permitting an increased productivity of the coronizing equipment.

APPLICATION OF THE AQUEOUS SIZING COMPOSITIONS

The aqueous glass fiber sizing compositions of the present invention are applied to the glass fibers during their forming while the sizing composition is at an elevated temperature, i.e., 115° to 125° F., and more preferably at a temperature of about 120° F. This is necessary in order to keep all of the ingredients of the size, especially the hydrogenated vegetable oil, uniformly dispersed in the size. If the size is allowed to cool to, say for example, room temperature and allowed to stand for extended periods of time, some of the ingredients tend to separate from the size.

The method of adding the size to the strands and analysis of the amount of size on the strand after forming and conditioning is further described in conjunction with a description of the drawings in which:

FIGURE 1 is a diagrammatic elevation of a continuous filament, glass fiber strand operation; and

FIGURE 2 is a graph illustrating the improvement of the present invention over the prior art with respect to size migration.

In FIGURE 1 of the drawing there is shown a glass melting furnace or forehearth thereof containing a supply of molten glass **13**, and having an electrically heated, platinum alloy bushing **12** attached to the bottom of the furnace. The bushing is provided with a series of orifices in the form of tips **11** through which the glass flows and forms in small inverted cones suspended from the bottoms of the tips **11**. The tips are usually formed in a number of rows, for example, 4 to 20 or more rows, having a great many tips in each row so that the total number of tips is about 200 to 400 or even more in number.

Glass filaments **10** are pulled from the cones of glass at a very high rate of speed, i.e., 5,000 to 20,000 feet per minute and wound up on a rapidly rotating forming tube **26**. The glass filaments are grouped into a strand as they pass over the guide **24** prior to their being wound on the tube **26**. As the strand is wound on the tube **26**, it is rapidly traversed by means of a traverse (not shown). The size is applied to the individual filaments in the strand prior to the time they pass over the guide. The size is supplied to a reservoir **18** which has a rotating roller or belt **19** mounted so as to dip into a bath **20** of the size in the reservoir. The size is transferred from the rotating roller or belt to the filaments as the filaments pass over the surface of the wetted roller or belt. A suitable size applicator is shown in U.S. Patent No. 2,873,718.

The sizes of the present invention are easily applied to the strand during its formation, and the strand forming proceeds smoothly. After each forming package containing, for example, about 3 to 8 pounds of 150 strand is formed (204 filaments having a diameter such that there are 15,000 yards to the pound of strand), the forming tube and package are removed from the winder and the end of the strand is found on the forming package. The forming package, containing about 9 percent by weight moisture, is then allowed to sit in an atmosphre of about 75° to 85° F. and 45 to 55 percent relative humdity for about 21 hours in order to reduce the moisture content on the strand to a range of about 5 to 7 percent by weight. Thereafter the strand is removed from the forming package and twisted into yarn. The twisting is accomplished on conventional textile apparatus with very few broken filaments. The twisted yarn is warped or transferred onto quills for weaving, and the yarn weaves very well with very few broken filaments. The woven material can be heat treated satisfactorily.

In FIGURE 2 the graph shows a size solids content of the strand in the forming package produced according to the present invention as compared with the prior art. The ordinate shows the per cent of size solids on the strand after 24 hours conditioning at 45 to 55 percent relative humidity and a temperature of 75° to 85° F. The abscissa shows the number of yards of strand as it is removed from the outside to the inside of the forming package. The dotted line represents an average migration curve plotted from 30 to 50 forming tubes showing the average amount of solids of a conventional dextrinized corn starch-vegetable oil size. The solid line represents an average migration curve plotted from 30 to 50 forming tubes showing the average amount of solids of the amylose containing starch mixture of the present invention as defined above exhibited by the size set forth below in Example IV at various points along the strand in the forming package after conditioning as described above.

It will be noted from this graph that virtually no size migration has occurred with the said starch mixture whereas considerable migration of the conventional dextrinized corn starch size occurs in the outside 4,000 yards of strand. Equivalent sizing and binding can be obtained with lower amounts of the said amylose containing starch derivative compared to the results secured with use of the conventional starch size. The uniform amount of size solids on the strand as permitted by the amylose containing starch mixture of the present invention provides uniform low tension in the strand during the various winding and unwinding fabricating steps necessary to transform the strand into yarn and into a woven product. During these various fabricating steps, the strand (or yarn) handles well, and there are very few filaments broken during these fabricating steps. The yarn as sized according to the method as described above is exceptionally useful for bulking by means of the texturing air jet described in the above-mentioned patent. The uniformity of size content on the yarn permits uniform conditions in the texturing operation and the production of acceptable textured yarn. The size does not blow off of the yarn during the texturing as does the conventional dextrinized corn starch-oil size. Heat treated fabrics woven from twisted strand formed in accordance with the present invention are free from the appearance defects discussed above which are due to size migration in the strand forming package.

The invention will be further illustrated by the following examples in which all percentages and parts are by weight unless otherwise indicated.

Example I

Ingredient:	Amount
"Amylon Special 55" (fractionated natural potato starch having 55 percent by weight amylose)	300 pounds.
"National HFS" (corn starch cross-linked with phosphorus oxychloride and having 27 percent by weight amylose)	300 pounds.
"Pureco Oil" (hydrogenated cottonseed oil)	135 pounds.
"Tween 81" (ethylene oxide derivative of a sorbitol ester)	30 pounds.
"Cation X" (alkyl imidazoline reaction product of tetraethylene pentamine and stearic acid)	60 pounds.
"Carbowax 300" (polyethylene glycol having a molecular weight of approximately 300)	72 pounds.
"Igepal CA–630" (octyl phenoxy poly - (ethyleneoxy)ethanol - wetting agent)	2100 ml.
"C–Sn–6" (organo-tin bacteriocide)	54 ml.
Water	Sufficient to bring to a volume of 1360 gallons.

Add cold deionized water to a mixing tank employing 1¼ gallons of water for each pound of starch. Then add both starch components to the cold water with mechanical agitation adding the "Amylon Special 55" first and agitating until most of the "Amylon Special 55" has been added to the water and then adding the "National HFS" to the cold water and continue agitation until substantially all the lumps are dissolved. Then add 40 gallons of water to the mixing tank to form an aqueous slurry, and cook this slurry at 198° to 205° F. in a jet cooker for a sufficient period of time to thoroughly incorporate the starch into the aqueous system. Then add the "Carbowax 300" to the cooked slurry. Then add "Cation X" (textile softener) previously mixed with 10 to 20 gallons of hot water maintained at 170° to 180° F., and agitate the mixture. Add "Tween 81" to "Pureco Oil" and mix these two materials in an Eppenbach homogenizer. Add 5 to 25 gallons of hot water, maintained at a temperature of from 140° to 180° F., during the mixing in the Eppenbach homogenizer. Add the "Tween 81"—"Pureco Oil" emulsion to the main batch mixture and homogenize the mixture at a temperature of 120° F. for 30 minutes. Then add the remaining amount of water to bring up to a volume of 1360 gallons.

Apply this aqueous size composition to glass fibers as they are being formed into a strand. Then wind the sized strands upon a forming package. Condition the forming package for 20 hours at 80° F. and a relative humidity of 45 to 65 percent.

The glass fiber strands sized with the above sizing composition to an add on (dry basis) of 1.6 percent by weight showed practically no migration and had good abrasion resistance.

Example II

Ingredient:	Amount
"National 77–1238" (a 50/50 mechanical polyblend of a cross-linked straight corn starch cross-linked with phosphorus oxychloride and containing 27 percent amylose and "Amylon Special 55")	600 pounds.
"Pureco Oil"	135 pounds.
"Tween 81"	30 pounds.
"Cation X"	60 pounds.
"Carbowax 300"	72 pounds.
"Igepal CA–630"	2100 ml.
"C–Sn–6"	54 ml.
Water	Sufficient to bring to a volume of 1360 gallons.

The procedure of Example I was repeated with the exception that "National 77–1238," a mechanical polyblend of a high amylose starch component and a low amylose starch component, has been employed in place of the unblended individual starch components in Example I. This aqueous size composition had a solids content of 6.5 weight percent. The glass fiber yarn sized with this sizing composition had a binder content of 1.4 percent by weight, yet fabricated well. The glass fiber strands sized with this composition had practically no binder migration. This size formulation showed excellent results in warping trials, and also possessed excellent quilling, weaving and finishing properties. It also had excellent compatibility with additional sizing materials (for example, warp sizes).

Example III

Ingredient:	Amount
"Amylomaize" (hybrid corn starch having an amylose content 55 percent by weight)	330 pounds.
"National HFS"	270 pounds.
"Pureco Oil"	135 pounds.
"Tween 81"	30 pounds.
"Cation X"	60 pounds.
"Carboxwax 300"	72 pounds.
"Igepal CA–630"	2100 ml.
"C–Sn–6"	54 ml.
Water	Sufficient to bring to a volume of 1360 gallons.

The procedure of Example I was repeated with the except that 55 percent by weight of the starch mixture was constituted of the high amylose hybrid starch component, viz., "Amylomaize." This composition had a solids content of 6.5 weight percent, and the glass fiber sized with this sizing composition had a binder add on (dry basis) of 1.6 weight percent, and very little binder migration. This aqueous sizing composition demonstrated excellent fabricating characteristics and the sized glass fiber strands had good abrasion resistance.

Example IV

Ingredient:	Amount
"Amylomaize"	270 pounds.
"National HFS"	300 pounds.
"Pureco Oil"	135 pounds.
"Tween 81"	30 pounds.
"Cation X"	60 pounds.
"Carbowax 300"	72 pounds.
"Igepal CA–630"	2100 ml.
"C–Sn–6"	54 ml.
Water	Sufficient to bring to a volume of 1360 gallons.

The procedure of Example I was repeated with the exception that the starch mixture was constituted of 45 percent by weight of the high amylose content starch component and 55 percent by weight of the low amylose content starch component. Glass fiber yarn sized with this sizing composition had a solids content of 6.5 percent by weight, and a binder content, add on (dry basis) of 1.6 percent, yet fabricated well. The glass fiber strands sized with this sizing composition had very little migtration and good resistance to abrasion.

In various trials of the invention, different amounts of the various ingredients were used in the size. In general, water makes up about 91 to 96 percent by weight of the size. The aforesaid amylose containing starch mixture generally constitutes about 3 to about 8 percent by weight of the size. The lubricant is present in the size in amounts of about 25 to 70 percent by weight based on the amount of the amylose containing starch mixture, and preferably about 45 percent by weight of the said amylose containing starch mixture.

Various textile softeners which are equivalent to "Cation X" can be employed in the size in amounts which are sufficient to provide a softening action to the sized strand, such amounts being, for example, 4 to 15 percent by weight of the said amylose containing starch derivative, and preferably about 10 percent by weight of the said amylose containing starch derivative. Suitable textile softeners are alkyl imidazoline derivatives such as described in U.S. Patents Nos. 2,200,815; 2,267,965; 2,268,273 and 2,355,837.

"Cation X" is an example of such a material wherein the alkyl imidazoline derivative is the reaction product of stearic acid, tetraethylene pentamine and acetic acid. Acid solubilized, water-dispersible stearic amides and anhydrous, acid solubilized, water-dispersible lower molecular weight fatty acid amides, as well as anhydrous, acid solubilized, polyunsaturated, lower molecular weight fatty acid amides can also be used as a softener. Some of these softeners also serves as wetting agents, for example, the alkyl imidazoline derivatives.

Non-ionic wetting agents can also be used. They are not as surface active as cationic wetting agents, and therefore are generally used in greater amounts to provide the same degree of wetting. Examples of suitable non-ionic wetting agents include polyalkylene derivatives of esters, fatty acids, fatty alcohols, fatty amides, alkyl phenyl ethers, e.g., Igepal CA–630, and other derivatives. Alkyl phenyl ethers are the preferred class of wetting agents.

Various other non-ionic wetting agents can be employed in the size in sufficient amounts to permit adequate wetting of the sizing ingredients to the glass surface with suitable amounts of wetting agent ranging from 15 to 30 weight percent of wetting agent based on the weight of lubricant, and preferably about 22 percent by weight of the lubricant. The "Tween 81" will generally be employed in sufficient amounts to allow ready emulsification of the starch components.

Suitable cationic agents which can be used include cetyl or stearyl monoamine hydrochloride or acetate, dodecyl amine, hexadecylamine and secondary and tertiary derivatives of the same, for example, dodecylmethylamine and salts thereof. Quaternary ammonium compounds, such as trimethyl stearyl or cetyl ammonium bromides and chlorides, and generally any of the amine compounds which dissociate in aqueous systems to provide a positive radical containing a group of more than 10, preferably 12 or more carbon atoms can be employed. These materials are cationic active substances.

A fungicide, such as one of the metallo-organic quaternary type, e.g., C–Sn–6 (tributylin oxide) can be employed in sufficient amount to prevent mold attack on the amylose containing starch derivative. Suitable effective amounts of the fungicide are about 3 milliliters to 75 gallons of the sizing composition.

"Carbowax 300" is believed to serve as a plasticizer for the said amylose containing starch mixture. The polyethylene glycol is preferably present in amounts of about 5 to about 20 percent by weight of the said amylose containing starch mixture, and more preferably in amounts of about 12 percent by weight thereof. The polyethylene glycol has been found to be useful in the size in order to make end-finding of the strand easier and to lessen the brittleness of the strand. Moreover, polyethylene glycol is believed to impart even tension properties to the sized strands.

If desired, the polyethylene glycol can be employed in conjunction with a water-soluble polyvinyl alcohol in the size. This is often desirable because of the added film strength properties which sizing compositions containing this combination impart. The ratio of polyvinyl alcohol to the polyethylene glycol when used in combination ranges from about 1:1 to 2:1. The combined amount of polyethylene glycol and polyvinyl alcohol in the size is about 0.1 to about 0.2 percent by weight of the amylose containing starch component.

In place of the low molecular weight polyethylene glycol, glycerine can be employed in similar weight concentrations either alone or in admixture with polyvinyl alcohol. For most purposes, however, the use of polyethylene glycol is prefered since it is less hygroscopic than glycerine.

The overall solids content of the size can vary from about 4 to about 8 percent by weight. It should be noted that the solids content can be adjusted in accordance with the desired solids content for the specific forming conditions employed. Generally the solids content will range from 5 to 7 percent by weight and preferably from 6.3 to 6.7 percent by weight. By "solids content" is meant the residual solids remaining after drying the sizing composition at 105° C. to constant weight.

Although the present invention has been described with respect to the specific details of certain embodiments thereof, it is not intended that such details serve as limitations upon the scope and spirit of this invention.

I claim:

1. A method of forming glass fibers which comprises the steps of:
drawing glass filaments from a molten supply of glass at a high rate of speed;
gathering the filaments and combining them into a strand;
applying a non-migratory aqueous sizing composition to the filaments as they are being drawn, said size being at an elevated temperature at the time of application and consisting essentially of
(1) 3 to 8 percent by weight of an amylose containing starch mixture of
(a) 45 to 55 percent by weight of a high amylose starch component having an amylose content of about 50 to about 60 percent by weight, and
(b) 45 to 55 percent by weight of a water-repellent low amylose starch component having an amylose content of about 20 to about 30 percent by weight,
(2) 25 to 70 percent by weight lubricant based upon the weight of starch mixture,
(3) 4 to 15 percent by weight of textile softener based on the weight of starch mixture, and
(4) 91 to 96 percent by weight water,
said aqueous sizing composition having a viscosity of about 1 to about 40 centipoises at 20° C.;
winding the sized strand on a rapidly rotating forming tube; and
conditioning the strand wound on the forming tube to reduce the moisture content of the sizing composition to an amount which is acceptable for twisting the strand into yarn.

2. The method of claim **1** wherein the said high amylose starch component comprises a hybrid corn starch having an amylose content of approximately 55 percent by weight.

3. The method of claim **1** wherein the said high amylose starch component comprises a fractionated potato starch having an amylose content of approximately 55 percent by weight.

4. The method of claim **1** wherein the said low amylose starch component comprises a cross-linked corn starch having an amylose content of approximately 27 percent by weight.

5. The method of claim **1** wherein the overall solids content of the said sizing composition ranges from about 4 to about 8 percent by weight.

6. A glass fiber strand produced according to the method of claim **1**.

7. A glass fiber strand produced according to the method of claim **2**.

8. A glass fiber strand produced according to the method of claim **3**.

9. A sized, woven glass fabric comprising glass fibers sized with a non-migratory, aqueous sizing composition which is readily removed upon subsequent heating of the sized, woven glass fabric at a temperature effecting thermal destruction of the said sizing composition and volatilization of at least the organic components thereof, said sizing composition prior to heating consisting essentially of the dried residue of a sizing composition consisting essentially of
(1) 3 to 8 percent by weight of an amylose containing starch mixture of
(a) 45 to 55 percent by weight of a high amylose starch component having an amylose content of about 50 to about 60 percent by weight, and
(b) 45 to 55 percent by weight of a water repellent, low amylose starch component having an amylose content of about 20 to about 30 percent by weight,
(2) 25 to 70 percent by weight of a lubricant based on the amount of starch mixture in the size,
(3) 4 to 15 percent by weight of a textile softener based upon the weight of the starch mixture in the size, and
(4) 91 to 96 percent by weight of water, and having a viscosity of about 1 to about 40 centipoises at 20° C., and wherein the binder content of the sized fibers prior to heat removal ranges from about 0.7 to about 2 percent by weight on an add-on, dry basis, based upon the weight of the glass fibers.

10. In the method of forming continuous filament glass fiber strand which comprises the steps of:
drawing glass filaments from a molten supply of glass at a high rate of speed;
gathering the filaments and combining them into a strand;
applying an aqueous sizing composition to the filaments as they are being drawn;
winding the sized strand on a rapidly rotating forming tube;
conditioning the strand wound on the forming tube to reduce the moisture content of the sizing composition to an amount which is acceptable for twisting the strand into yarn,
the improvement which comprises,
applying at an elevated temperature a non-migratory, aqueous sizing composition consisting essentially of
(1) 3 to 8 percent by weight of an amylose containing starch mixture of
(a) 45 to 55 percent by weight of a high amylose starch component having an amylose content of about 50 to about 60 percent by weight, and
(b) 45 to 55 percent by weight of a water repellent, low amylose starch component having an amylose content of about 20 to 30 percent by weight,

(2) 25 to 70 percent by weight of a lubricant based on the weight of the starch mixture,

(3) 4 to 15 percent by weight of a textile softener based on the weight of the starch mixture, and

(4) 91 to 96 percent by weight water,

said aqueous sizing composition having a viscosity of about 1 to about 40 centipoises at 20° C.

11. In the method of forming a glass fiber fabric which comprises the steps of:

drawing glass filaments from a molten supply of glass at a high rate of speed;

gathering the filaments and combining them into a strand;

applying an aqueous sizing composition to the filaments as they are being drawn;

winding the sized strand on a rapidly rotating forming tube;

conditioning the strand wound on the forming tube to reduce the moisture content of the sizing composition to an amount which is acceptable for twisting the strand into yarn,

twisting the strand into yarn,

weaving the yarn into cloth,

heating the cloth to remove the sizing composition and set the fibers,

the improvement which comprises,

applying at an elevated temperature a non-migratory, aqueous sizing composition consisting essentially of

(1) 3 to 8 percent by weight of an amylose containing starch mixture of

(a) 45 to 55 percent by weight of a high amylose starch component having an amylose content of about 50 to about 60 percent by weight, and

(b) 45 to 55 percent by weight of a water repellent, low amylose starch component having an amylose content of about 20 to 30 percent by weight,

(2) 25 to 70 percent by weight of lubricant based on the weight of the starch mixture,

(3) 4 to 15 percent by weight of textile softener based on the weight of the starch mixture, and

(4) 91 to 96 percent by weight water,

said aqueous sizing composition having a viscosity of about 1 to about 40 centipoises at 20° C.

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