SIZING COMPOSITION FOR GLASS FIBERS

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ABSTRACT
An aqueous sizing comprising a starch mixture comprising a high viscosity starch and a low viscosity starch cooked at a temperature sufficient to solubilize at least 50% of the high viscosity starch and to solubilize at least 50% of the low viscosity starch. Glass fiber strands formed from glass fibers at least partially coated with the sizing composition of the present invention can exhibit good fliability and insertion time properties when used in an air jet loom.
SIZING COMPOSITION FOR GLASS FIBERS

FIELD OF INVENTION

[0001] The present invention is directed to sizing compositions for glass fibers.

BACKGROUND

[0002] Glass fibers are typically treated after forming with a sizing composition that can impart desired properties. As used herein the term “size”, “sized”, “sizing” means a coating composition applied to the glass fibers after formation of the fibers. After their formation and treatment, the sized glass fibers can be gathered into bundles or strands comprising a plurality of individual fibers. The strands may be wound into a spool or “forming package.” The forming packages can be dried to remove moisture from the fibers. For certain uses, the fibers are typically wound onto a bobbin via conventional textile twisting techniques such as a twist frame.

[0003] A sizing composition can serve several functions. It can function as a lubricant and binding agent and can protect the fibers from abrasion with each other.

[0004] A sizing composition can also improve the performance of the fibers during further processing. For example, a weaving process may involve removing the fiber from a bobbin and guiding the fiber over or through a series of guide bars and other points of contact where wear can occur.

[0005] A sizing composition can also improve the performance of the fibers in an air jet loom used for high speed fabric weaving. In an air jet loom, one or more warp yarn feed systems deliver, i.e. insert, warp yarn into a shed formed by warp yarns using a main air jet nozzle assisted by groups of relay nozzles disposed across the warp shed, as is well known to those skilled in the art.

[0006] As air jet looms have increased in speed, glass fibers have been modified such that the amount of air needed to pass a weft yarn across the warp shed is reduced (“flexibility”) and/or the period of time to cross the warp shed is reduced (“insertion time”). As used herein, the term “flexibility” refers to the amount of yarn delivered in a specified time through a loom air jet nozzle held at a fixed air pressure. As used herein, the term “insertion time” is the elapsed time from the start of the weaving cycle for yarn to traverse the width of the fabric and pass the selvage or edge of the opposite side of the fabric from the air jet nozzle of the loom. Open strands or zig-zagging strands can reduce the Liability and insertion time for particular yarns. However, open strands and/or zig-zagging strands can reduce the quality of the final fabric product.

[0007] Thus, it would be advantageous to provide a fiber glass sizing composition that can improve the performance of the fiber glass in an air jet loom.

SUMMARY OF INVENTION

[0008] The present invention is directed to starch-oil type sizing compositions for glass fibers. The sizing compositions can provide glass fiber strands having a variety of advantageous properties including high flexibility and low insertion time in weaving. Glass fiber strands treated with the sizing composition may withstand a wide variety of further processing operations such as twisting, chopping, forming into a bundle, roving, chopped mat or continuous strand mat or weaving or knitting into a cloth. Such strands can be useful in a wide variety of applications, such as cloth for printed circuit boards.

[0009] In an embodiment, the present invention provides a sizing composition for glass fibers comprising a starch mixture comprising a high viscosity starch and a low viscosity starch cooked at a temperature sufficient to solubilize at least 50% of the high viscosity starch and to solubilize at least 50% of the low viscosity starch.

[0010] In another embodiment, the present invention provides a glass fiber at least partially coated with the sizing composition.

[0011] In another embodiment, the present invention provides a method of producing an at least partially coated glass fiber comprising applying to a glass fiber a sizing composition.

[0012] In another embodiment, the present invention provides a method of weaving comprising feeding a plurality of warp yarns into a loom to form a shed; feeding a plurality of glass fiber strands into the shed formed by the warp yarns, wherein the glass fiber strands comprise a plurality of glass fibers at least partially coated with the sizing composition.

DETAILED DESCRIPTION

[0013] For the purposes of this specification, unless otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, and so forth used in the specification are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0014] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

[0015] It is further noted that, as used in this specification, the singular forms “a,” “an,” and “the” include plural referents unless expressly and unequivocally limited to one referent.

[0016] The present invention provides an aqueous sizing for coating glass fibers. The aqueous sizing comprises a starch mixture comprising a high viscosity starch and a low viscosity starch.

[0017] The present invention also provides glass fiber strands including at least one glass fiber, and typically a plurality of glass fibers, having a coating or sizing composition applied to at least a portion of the surface of the glass fiber(s). In one embodiment, the coated glass fibers are woven into a fabric.
Glass fiber strands formed from glass fibers at least partially coated with the sizing composition of the present invention can exhibit good Liabilities and insertion time properties when used in an air jet loom. Glass fiber strands formed from glass fibers at least partially coated with the sizing composition of the present invention may also be used in other looms such as a shuttle loom or a rapier loom.

The starch mixture of the sizing composition comprises a high viscosity starch and a low viscosity starch. The starches of the starch mixture are cooked at a temperature sufficient to solubilize at least 50% of the high viscosity starch and to solubilize at least 50% of the low viscosity starch. In an embodiment, the starches of the starch mixture are cooked at a temperature sufficient to solubilize at least 80% of the low viscosity starch.

The starches of the starch mixture may be cooked at a temperature that solubilizes one starch to a greater degree than the other. In another embodiment, the starches of the starch mixture are cooked at a temperature sufficient to solubilize at least 75% of the high viscosity starch and to solubilize at least 80% of the low viscosity starch. In another embodiment, the starches of the starch mixture are cooked at a temperature sufficient to solubilize at least 80% of the high viscosity starch and to solubilize at least 90% of the low viscosity starch.

As used herein, the term “solubilize” refers to dissolving matter (a solute) in a solvent. As used herein, the term “solubilizes” refers to matter dissolved in a solvent.

As used herein, the term “high viscosity starch” refers to a starch that produces less than 80% solubles when cooked at a temperature of less than 125 °C. As used herein, the term “low viscosity starch” refers to a starch that produces 80% or more solubles when cooked at a temperature of less than 125 °C.

Starches which may be used in the sizing composition of the invention include amylose-containing starches derived from starch sources such as, but not limited to, corn, wheat, potato, tapioca, waxy maize, sago, rice, hybrid starches, etc. Starch components having a high amylose content, e.g., 50 or more percent by weight, can be derived from either corn starch or a hybrid corn starch, while the starch components having a low amylose content, e.g., 20 to 30 percent by weight, are usually derived from either potato or cattie, phosphatized, ethoxylated or etherified corn starch.

Starches useful in the sizing composition can be modified by acetylation, chlorination, acid hydrolysis, derivatizing agents such as phosphatizing, ethoxylating or etherifying agents, crosslinking agents or enzymatic action, for example. Starches can be crosslinked by treatment with difunctional agents which are capable of reacting with hydroxyl groups on two different molecules in the starch granule.

A non-limiting example of a commercially available starch suitable for use in the present invention as a low viscosity starch is Hi-Set® 369 sold by National Starch. Hi-Set® 369 is a propylene oxide modified corn starch with an amylose content of 55%.

A non-limiting example of a commercially available starch for use in the present invention as a high viscosity starch is HYLON® sold by National Starch with an amylose content of 58%.

When starch granules are cooked in water, two main events occur: the starch granules swell and materials inside the granule, such as amylose, leach out. By cooking the starch mixture at a cooking temperature sufficient to solubilize at least 50% of the high viscosity starch and to solubilize at least 50% of the low viscosity starch, a majority of the starch granules in the starch mixture swell and rupture. Because a majority of the starch granules rupture, upon cooling the cooked starch mixture does not significantly increase in viscosity and blends more readily with the ester waxes described below. In the prior art, there is a general belief that the % solubles of a starch or a starch mixture used in the sizing should be limited to keep the viscosity of sizing at high levels and thereby potentially avoid migration of the sizing once applied to a glass fiber. In the present invention, the temperatures used to cook the starch mixture results in a relatively low viscosity sizing. For example, in an embodiment of the sizing comprising Hi-Set® 369 and Hylont®, the viscosity of the sizing is less than or equal to 20 centipoise. Further cooking the starch mixture at a temperature sufficient to solubilize at least 50% of the high viscosity starch and to solubilize at least 50% of the low viscosity starch can improve the miscibility of any oil and/or wax included in the sizing composition.

The combination of the high viscosity starch and low viscosity starch can also provide a balance between improved strand stiffness and integrity resulting from the inclusion of the high viscosity starch and strand flexibility and reduced broken filaments resulting from inclusion of the low viscosity starch. In one embodiment wherein the high viscosity starch comprises HYLON® and the low viscosity starch comprises Hi-Set® 369, the ratio of high viscosity starch to low viscosity starch ranges from 1.5:1 to 2:1, respectively.

The total amount of starch mixture in the sizing composition may depend upon several factors, including but not limited to, optimization of the Liability and/or insertion time characteristics of glass fibers or strands coated with the sizing, and compatibility with other components of the sizing. In one embodiment wherein the high viscosity starch comprises HYLON® and the low viscosity starch comprises Hi-Set® 369, the amount starch mixture in the sizing composition is between 50 to 60 weight percent solids.

The sizing composition may also comprise one or more lubricants. Any suitable lubricant known to one skilled in the art may be used. Lubricants may be used to reduce interfillament abrasion and improve Liability and insertion times characteristics of coated strands. Non-limiting examples of useful lubricants are non-ionic and ionic lubricants. Non-limiting examples of non-ionic lubricants useful in the present invention include waxes and oils. Examples of waxes include paraffin wax, animal wax, mineral waxes, petroleum derivative waxes and ester waxes.

Any oil known to those skilled in the art for use in sizing compositions can be used. Non-limiting examples of useful oils include vegetable oils hydrogenated to various degrees, such as cotton seed oil, corn oil, soy bean oil. Other oils useful in the sizing composition include palm oil and coconut oil. Further, blends of various oil are also useful. An example of a commercially available oil useful in the sizing composition is CPF000 oil, which is a soy bean oil, available from C+T Refinery.
In another embodiment, the sizing composition may comprise a non-ionic lubricant comprising an oil and a plurality of ester waxes formed from reacting a monocarboxylic acid and a monohydric alcohol. The monocarboxylic acid and the monohydric alcohol comprise an aliphatic chain having about 8 to about 32 carbon atoms. Use of the plurality of ester waxes in the sizing composition can improve the fluidity and insertion time of the glass fiber strand in an air jet loom.

Non-limiting examples of useful monocarboxylic acids include octanoic acid, capric acid, lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, palmitic acid, margaric acid, stearic acid, nonadecanoic acid, arachidic acid, behenic acid, lignoceric acid, cerotic acid, and melissic acid.

Non-limiting examples of useful monohydric alcohols include lauryl alcohol, n-tridecyl alcohol, myristal alcohol, n-pentadecyl alcohol, cetyl alcohol, margary alcohol, stearyl alcohol, n-nonadecyl alcohol, arachidyl alcohol, ceryl alcohol, and myricly alcohol.

The monocarboxylic acid and monohydric alcohol can be reacted to form the ester by conventional esterification processes well known to those skilled in the art and such as are disclosed in Encyclopedia of Chemical Technology, Vol. 9 (1980) at pages 291-310.

In another embodiment, the plurality of ester waxes has a melting point between 40°C and 70°C. In another embodiment, the plurality of ester waxes comprises ester waxes formed from reacting a monocarboxylic acid selected from the group consisting of octanoic acid, capric acid, lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, and palmitic acid, with a monohydric alcohol selected from the group consisting of myristal alcohol, n-pentadecyl alcohol, cetyl alcohol, margary alcohol, stearyl alcohol, n-nonadecyl alcohol, arachidyl alcohol. In another embodiment, the plurality of ester waxes comprises ester waxes formed from reacting a monocarboxylic acid having between 8 and 14 carbons with a monohydric alcohol having between 16 and 18 carbons. In another embodiment, the plurality of ester waxes comprises hexadecyl octanoate, octadecyl octanoate, hexadecyl laurate, octadecyl laurate, octadecyl myristate, and octadecyl palmitate. An example of a commercially available product comprising a plurality of ester waxes is KESTER WAX 385 available from Koster Keunen Inc. KESTER WAX 385 comprises hexadecyl octanoate, octadecyl octanoate, hexadecyl laurate, octadecyl laurate, octadecyl myristate, and octadecyl palmitate in a ratio of 9:20:20:45:3:40:1, respectively.

The amount of nonionic lubricant may depend upon several factors such as, but not limited to, the amount of lubricant necessary to reduce interfilament abrasion, and optimization of the fluidity and insertion time characteristics of glass fibers coated with the sizing. In an embodiment wherein the non-ionic lubricant comprises KESTER WAX 385 and CT7000 oil, the amount of non-ionic lubricant in the sizing is between 25 and 35 weight percent solids and the ratio of wax to oil is between 2:1 and 3:1.

The sizing composition may also comprise a cationic lubricant. In an embodiment, the cationic lubricant comprises alkyl imidazoline derivatives including compounds of the class n-alkyl-N-amido-alkyl imidazolines. These cationic lubricants may be formed by causing fatty acids or carboxylic acids to react with polyalkylene polyamines under conditions which produce ring closure. The reaction of tetraethylenepentamine with stearic acid is exemplary of such a reaction and these imidazolines are described in U.S. Pat. No. 2,200,815. Other imidazolines are described in U.S. Pat. Nos. 2,267,965; 2,268,273; and 2,353,837. A useful imidazoline lubricant is available under the name Alubraspin™ 261 lubricant from BASF Corp., or under the name Cation-X. The amount of cationic lubricant may depend upon several factors such as, but not limited to, the amount necessary to reduce interfilament abrasion of glass fibers coated with the sizing. In an embodiment, the cationic lubricant is present in an amount between 2.0 and 3.0 weight percent solids.

The sizing composition may also comprise a silane coupling agent. Silane coupling agents useful in the sizing composition comprise a functional group which is capable of chemically bonding with the surface of fiber glass and a second functional group which is capable of chemically binding with a starch of the starch mixture. Examples of silane coupling agents useful in the sizing compositions are epoxy-functional silanes. A commercially available silane such as gamma-glycidoxypropyltrimethoxy silane (A-187) from Union Carbide Corporation is useful in the sizing composition. The silane coupling agent may be hydrolyzed to some degree before use by reacting it with an effective amount of a suitable carboxylic acid such as acetic acid. The amount of the silane coupling agent in the sizing may depend upon several factors such as, but not limited to, the type and amount of starch used in the starch mixture, the amount necessary to couple the starch to the glass fiber, the coupling agent’s compatibility with the other components of the size, and optimization of the Liability and insertion time characteristics of glass fibers coated with the sizing. In an embodiment of the sizing composition, a coupling agent comprising gamma-glycidoxypropyltrimethoxy silane is present in an amount ranging from 3.0 to 6.0 weight percent solids.

The sizing composition may optionally comprise a biocide or a fungicide to control organic growth in sizing solutions for glass fibers. Any suitable biocide or fungicide known to one skilled in the art to be compatible with the other ingredients of the sizing composition may be used. In a non-limiting embodiment, a biocide useful in the sizing comprises a chlorinated compound. An example of commercially available biocides is CHEMTREAT CL-2141 (methylene-bis-thiocyanate) available from ChemTreat, Inc.

The sizing may optionally comprise a defoamer to control foaming in sizing composition. Any suitable defoamer known to one skilled in the art to be compatible with the other ingredients of the sizing composition may be used. In a non-limiting embodiment, a defoamer useful in the sizing comprises a polyether-triglyceride. An example of a polyether-triglyceride useful as a defoamer useful in the sizing comprises MAZU® DF-136 defoamer commercially available from BASF Corp.

The components of the sizing composition, such as the lubricants, can be emulsified through mechanical means or through the use of an emulsiﬁer. Any emulsiﬁer known to those skilled in the art to be useful in emulsifying waxes and
oils may be used. In embodiments of the sizing comprising a non-ionic emulsifier, the emulsifier may be selected based on its hydrophilic/lipophilic balance (HLB) where HLB is the balance of the size and strength of the hydrophilic (water loving or polar) and the lipophilic (oil loving or non-polar) groups of the emulsifier. A low HLB number (below 9) indicates an emulsifier that is lipophilic in character and a high HLB number (above 11) indicates an emulsifier that is hydrophilic in character. An example of a suitable non-ionic emulsifier useful in the sizing composition includes TMAZ 81 emulsifier commercially available from BASF Corp., which is sorbitan mono-oleate which is an ethylene oxide derivative of sorbitol ester with an HLB of about 10. Another example of a useful emulsifier is commercially available as Tween 81. The amount of emulsifier to be used may depend upon the types of lubricants used and the equipment used to mix them. In an embodiment of the sizing composition comprising an emulsifier, the emulsifier is present in an amount between 3.0 to 6.0 weight percent solids.

In another embodiment, the loom used in the method of weaving may comprise an air jet loom. In another embodiment, the glass fiber strands used in the method of weaving have substantially no twist.

As used herein, glass fiber strands having “substantially no twist” refers to strands that have not been twisted after being wound on a forming package. It should be noted that there is some twist in a fiber glass strand in a forming package that results when fiber glass strands are formed and wound into a forming package. In addition, there can be additional incidental twist in the fiber glass strand as it is paid out from the forming package and fed to the loom. Thus, “yarns with substantially no twist” can have some twist in them due to formation and winding and/or due to pay out from the forming package.

In the preparation of the sizing composition, the components are usually mixed with water and prepared separately before being added to the main mixture. For example, the starch mixture may be prepared by mixing the starches together with water and then cooking by any method known to those skilled in the art. Other components are prepared separately and then added to the mixture of starch and water.

The total amount of water in the final composition should normally be sufficient to enable the composition to be effectively applied to glass fibers using conventional equipment and techniques. This usually results in a solids level of less than 15 percent in the final sizing composition. In a non-limiting embodiment, the percent solids of the sizing is between 5 and 7 percent.

The starch preparation method of one embodiment uses a jet cooker which injects steam directly into a starch and water mixture as it travels in a pipe. The downstream temperature is controlled at a specific value by the regulation of the addition rate of steam to the mixture. The mixture is held at the cooking temperature sufficient to solubilize at least 50% of the high viscosity starch and to solubilize at least 50% of the low viscosity starch. Cooking is stopped by cooling the mixture.

The wax, oil and emulsifier may be mixed with demineralized water and emulsified by any suitable means. One method of emulsification is by circulating the mixture through a high pressure homogenizing pump and returning it to the same vessel. By this method, the quality of the emulsion may be monitored until the mixture forms an emulsion with particles within a desired range. Another method of emulsifying the mixture is to agitate it in a tank using a high shear mixer such as an Eppenbach mixer. The emulsion is then added to the starch mixture.

The lubricants may be mixed with water and added to the mixture. The silane coupling agent may be mixed with water and then added, while the other ingredients may be added directly to the mixture.

The sizing composition of this invention may be prepared by any other suitable method known to those skilled in the art and applied to glass fibers using conventional techniques. The sized fibers can be gathered together to form strands by any method known to those skilled in the art and then dried in an oven or at room temperature such that the moisture content of the sizing on the fibers is reduced.
EXAMPLES

Example 1

Table 1 describes a specific example of the sizing composition of the present invention which was prepared from the ingredients listed to produce about 1,000 gallons of the sizing composition.

### TABLE 1

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount (lbs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HYYLON® starch</td>
<td>198.8</td>
</tr>
<tr>
<td>HiSet® 369 starch</td>
<td>124.3</td>
</tr>
<tr>
<td>Kester Wax 385</td>
<td>124.3</td>
</tr>
<tr>
<td>CT-7000 oil</td>
<td>40.7</td>
</tr>
<tr>
<td>TWEEN 81 emulsifier</td>
<td>24.9</td>
</tr>
<tr>
<td>Alubraspin 261 lubricant</td>
<td>37.3</td>
</tr>
<tr>
<td>MAZU® DF-136 defoamer</td>
<td>5.0</td>
</tr>
<tr>
<td>A-187 coupling agent</td>
<td>24.9</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>1.6</td>
</tr>
<tr>
<td>CL-2141 Biocide</td>
<td>50 mL</td>
</tr>
</tbody>
</table>

In the example, the aqueous sizing composition was prepared by adding the starch to an agitated mixing or slurry tank to which was previously added about 300 gallons of deionized water.

Cooking of the starch took place by pumping the starch mixture from the slurry tank through a jet cooker in which steam was injected directly into the starch mixture. The steam addition rate was controlled to give a cook temperature of about 126.5 °C (±2.2 °C) and the exit back pressure was controlled at approximately 27 psig (±7 psig). The residence or dwell time of the starch mixture at the cooking temperature was about 11 seconds to cook it, and the exit temperature was no greater than 85 °C.

The starch mixture was then directed to a main mix tank preset to 85.5 °C. Deionized water in an amount of about 80 gallons was used to wash the slurry tank to thoroughly remove the raw starch from the slurry tank as well as to flush any remaining starch from the jet cooker. This wash water was flushed into the main mix tank also. In addition to the above method, any other method of cooking starch, such as open kettle cooking, known to those skilled in the art may be used to solubilize the high viscosity starch and to solubilize the low viscosity starch to the same degree obtained by using jet cooker.

To a separate emulsion tank containing 50 gallons of water at a temperature set at about 80 °C (±2.2 °C) was added the specified quantity of CT7000, Kester Wax 385, and TWEEN 81. The mixture was agitated and the contents of the tank were circulated through a homogenizer set at a pressure of 2500 psi. Once the ingredients had been emulsified to the point where the particle size was in a range of about 1 to 3 microns, the emulsion was transferred through the homogenizer into the main mix tank. The emulsion tank was flushed with water (80 °C).

To another tank, about 30 gallons of warm (approximately 63 °C) deionized water was added and agitation begun. The Alubraspin™ 261 alkylimidazoline derivative lubricant was then added and agitation continued until it dissolved (about 10 minutes), at which point the mixture was transferred to the main mix tank.

The MAZU DF 136 defoamer was added directly to the main mix tank.

To another tank, about 30 gallons of room temperature (approximately 25 °C) demineralized water was added and agitation begun. The indicated amount of acetic acid was then added. The A-187 silane coupling agent was slowly added (a rate not exceeding 1 gpm) and the solution was agitated until it cleared (at least 5 minutes). The mixture was then added to the main mix tank.

The CL-2141 biocide was the last ingredient added to the main mix tank.

Warm (63 °C) demineralized water was then added to the main mix tank in an amount sufficient to bring the total amount of sizing prepared to about 1000 gallons with a solids level of about 6 percent, and agitation continued for at least an additional 10 minutes.

The percent solids of the completed sizing composition was 6.2% (±0.3%), and the viscosity was less than 20 centipoise.

The sizing composition of the example was applied to glass fibers using an applicator. An example of an applicator suitable for this application is shown in U.S. Pat. No. 2,728,972. After the application of the sizing, the fibers were gathered together to form a strand composed of multiple fibers.

Example 2

G-75 glass fibers sized with the composition of this invention can demonstrate improved performance in air jet looms as compared to G-75 glass fibers sized with prior art sizing compositions. For example, G-75 glass fibers sized with the composition in Example 1 required less than 4 bar of air pressure at the main jet nozzle of a ZAX-e air jet loom (Tsukakima Corporation, Japan) while operating at a rate of 1000 picks per minute. Under similar conditions, G-75 glass fibers sized with a sizing disclosed in the examples of U.S. Pat. No. 5,393,335 required approximately 6 bar of air pressure at the main jet nozzle. Accordingly, use of glass fibers sized with the composition of this invention can reduce the amount of air pressure needed at a main jet nozzle of an air jet loom by 20 to 30 percent (i.e. increase Liability).

It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover modifications that are within the spirit and scope of the invention, as defined by the appended claims.

1. An aqueous sizing composition for glass fibers comprising:
   a starch mixture comprising a high viscosity starch and a low viscosity starch cooked at a temperature sufficient to solubilize at least 50% of the high viscosity starch and to solubilize at least 50% of the low viscosity starch.

2. The aqueous sizing composition of claim 1, wherein the starch mixture is cooked at a cooking temperature sufficient to solubilize at least 80% of the low viscosity starch.

3. The aqueous sizing composition of claim 1, wherein the starch mixture is cooked at a cooking temperature sufficient
to solubilize at least 80% of the low viscosity starch and to solubilize at least 75% of the high viscosity starch.

4. The aqueous sizing composition of claim 1, wherein the starch mixture is cooked at a cooking temperature sufficient to solubilize at least 90% of the low viscosity starch and to solubilize at least 80% of the high viscosity starch.

5. The aqueous sizing composition of claim 1, wherein the high viscosity starch comprises an unmodified starch having an amylose content of >50% and the low viscosity starch comprises a modified starch comprising >50% amylose.

6. The aqueous sizing composition of claim 5, wherein the ratio of high viscosity starch to low viscosity starch ranges from 1.5:1 to 2:1, respectively.

7. The aqueous sizing composition of claim 5, wherein the low viscosity starch comprises a propylene oxide modified starch.

8. The aqueous sizing composition of claim 1, further comprising at least one emulsifier in an amount effective to produce an emulsion in water of said nonionic lubricant.

9. The aqueous sizing composition of claim 1, further comprising a cationic lubricant.

10. The aqueous sizing composition of claim 9, wherein the cationic lubricant comprises an alkylidiamidine.

11. The aqueous sizing composition of claim 1, further comprising a biocide in an amount sufficient to inhibit organic growth in said sizing composition.

12. The aqueous sizing composition of claim 1, further comprising a silane coupling agent.

13. The aqueous sizing composition of claim 12, wherein the silane coupling agent comprises gamma-glycidoxypropyltrimethoxy silane.

14. The aqueous sizing composition of claim 1, further comprising a defoamer in an effective amount to reduce foaming during mixing of the aqueous sizing composition.

15. The aqueous sizing composition of claim 1, further comprising a nonionic lubricant comprising an oil and a plurality of ester waxes formed from reacting a monocarboxylic acid and a monohydric alcohol.

16. The aqueous sizing composition of claim 15, wherein the plurality of ester waxes is a solid having a melting point of from about 40° C. to about 70° C.

17. The aqueous sizing composition of claim 15, wherein the monocarboxylic acid is selected from the group consisting of octanoic acid, capric acid, lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, and palmitic acid.

18. The aqueous sizing composition of claim 15, wherein the monohydric alcohol is selected from the group consisting of myristal alcohol, n-pentadecyl alcohol, cetyl alcohol, margaryl alcohol, stearyl alcohol, n-nonadecyl alcohol, arachidyl alcohol.

19. The aqueous sizing composition of claim 15, wherein the plurality of ester waxes are formed from reacting a monocarboxylic acid having between 8 and 14 carbons with a monohydric alcohol having between 16 and 18 carbons.

20. The aqueous sizing composition of claim 15, wherein the plurality of ester waxes comprises hexadecyl octanoate, octadecyl octanoate, hexadecyl laurate, octadecyl laurate, octadecyl myristate, and octadecyl palmitate.

21. The aqueous sizing composition of claim 20, wherein the amount of non-ionic lubricant in the sizing is between 25 and 35 weight percent.

22. The aqueous sizing composition of claim 20, wherein the ratio of wax to oil is between 2:1 and 3:1.

23. A glass fiber at least partially coated with the residue of a sizing composition comprising:

- a starch mixture comprising a high viscosity starch and a low viscosity starch cooked at a temperature sufficient to solubilize at least 50% of the high viscosity starch and to solubilize at least 50% of the low viscosity starch.

24. The glass fiber of claim 23, wherein the starch mixture is cooked at a cooking temperature sufficient to solubilize at least 80% of the low viscosity starch.

25. The glass fiber of claim 23, wherein the starch mixture is cooked at a cooking temperature sufficient to solubilize at least 80% of the low viscosity starch and to solubilize at least 75% of the high viscosity starch.

26. The glass fiber of claim 23, wherein the starch mixture is cooked at a cooking temperature sufficient to solubilize at least 90% of the low viscosity starch and to solubilize at least 80% of the high viscosity starch.

27. The glass fiber of claim 23, wherein the high viscosity starch comprises an unmodified starch having an amylose content of >50% and the low viscosity starch comprises a modified starch comprising >50% amylose.

28. The glass fiber of claim 27, wherein the ratio of high viscosity starch to low viscosity starch ranges from 1.5:1 to 2:1, respectively.

29. The glass fiber of claim 27, wherein the low viscosity starch comprises a propylene oxide modified starch.

30. The glass fiber of claim 23, wherein the sizing composition further comprises at least one emulsifier in an effective amount to produce an emulsion in water of said nonionic lubricant.

31. The glass fiber of claim 23, wherein the sizing composition further comprises a cationic lubricant.

32. The glass fiber of claim 31, wherein the cationic lubricant comprises an alkylidiamidine.

33. The glass fiber of claim 23, wherein the sizing composition further comprises a biocide in an amount sufficient to inhibit organic growth in said sizing composition.

34. The glass fiber of claim 23, wherein the sizing composition further comprises a silane coupling agent.

35. The glass fiber of claim 34, wherein the silane coupling agent comprises gamma-glycidoxypropyltrimethoxy silane.

36. The glass fiber of claim 23, wherein the sizing composition further comprises a defoamer in an effective amount to reduce foaming during mixing of the aqueous sizing composition.

37. The glass fiber of claim 23, wherein the sizing composition further comprises a nonionic lubricant comprising an oil and a plurality of ester waxes formed from reacting a monocarboxylic acid and a monohydric alcohol.

38. The glass fiber of claim 37, wherein the plurality of ester waxes is a solid having a melting point of from about 40° C. to about 70° C.

39. The glass fiber of claim 37, wherein the monocarboxylic acid is selected from the group consisting of octanoic acid, capric acid, lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, and palmitic acid.

40. The glass fiber of claim 37, wherein the monohydric alcohol is selected from the group consisting of myristal alcohol, n-pentadecyl alcohol, cetyl alcohol, margaryl alcohol, stearyl alcohol, n-nonadecyl alcohol, arachidyl alcohol.
41. The glass fiber of claim 37, wherein the plurality of ester waxes are formed from reacting a monocarboxylic acid having between 8 and 14 carbons with a monohydric alcohol having between 16 and 18 carbons.

42. The glass fiber of claim 37, wherein the plurality of ester waxes comprises hexadecyl octanoate, octadecyl octanoate, hexadecyl laurate, octadecyl laurate, octadecyl myristate, and octadecyl palmitate.

43. The glass fiber of claim 42, wherein the amount of non-ionic lubricant in the sizing is between 25 and 35 weight percent.

44. The glass fiber of claim 42, wherein the ratio of wax to oil is between 2:1 and 3:1.

45. A glass fiber strand comprising a plurality of glass fibers of claim 23.

46. The glass fiber strand of claim 45, wherein the diameter of the glass fibers is between 8.0 to 11.0 microns and the glass fiber strand comprises from 200 to 800 glass fibers.

47. A method of producing an at least partially coated glass fiber comprising:

applying to a glass fiber the sizing composition of claim 1.

48. (Currently amended) A method of weaving comprising:

feeding a plurality of warp yarns into a loom to form a shed; and

feeding a plurality of glass fiber strands into the shed formed by the warp yarns, wherein the glass fiber strands comprise a plurality of glass fibers of claim 23.

49. The method of claim 48, wherein the diameter of the glass fibers of the glass fiber strands is between 8.0 to 11.0 microns and the glass fiber strand comprises from 200 to 800 glass fibers.

50. The method of claim 48, wherein the loom comprises an air jet loom.

51. The method of claim 48, wherein the plurality of glass fiber strands have substantially no twist.

52. An aqueous sizing composition for glass fibers comprising:

a starch mixture comprising:

a high viscosity starch comprising an unmodified starch having an amylose content of >50%; and

a low viscosity starch comprising a modified starch comprising >50% amylose.

53. A glass fiber at least partially coated with the residue of a sizing composition comprising:

a starch mixture comprising:

a high viscosity starch comprising an unmodified starch having an amylose content of >50%; and

a low viscosity starch comprising a modified starch comprising >50% amylose.

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