

May 8, 1962

A. MARZOCCHI ET AL

3,033,719

FIBROUS GLASS AND METHOD OF MAKING

Filed Feb. 6, 1958

3 Sheets-Sheet 1

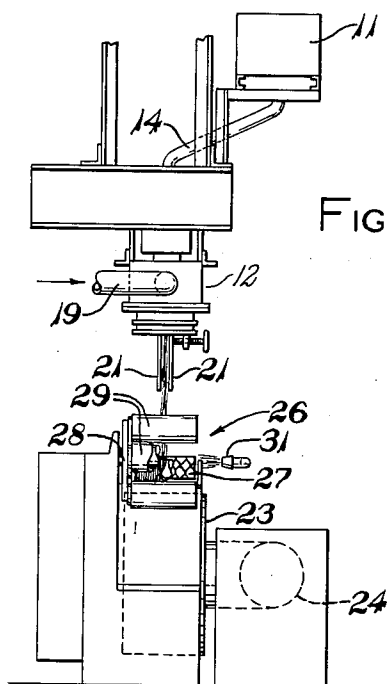


FIG. 2



FIG. 6

FIG. 1

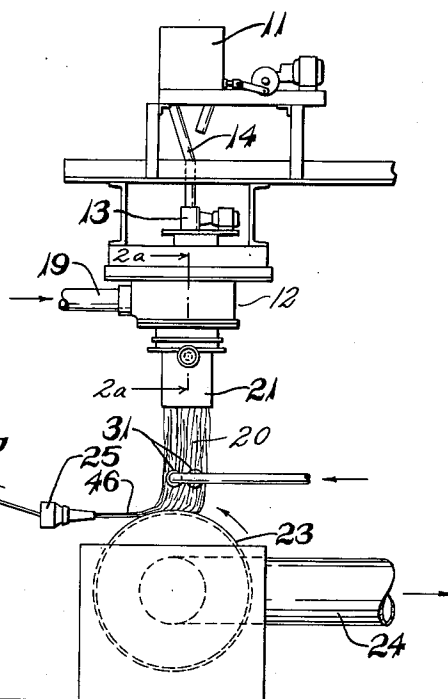
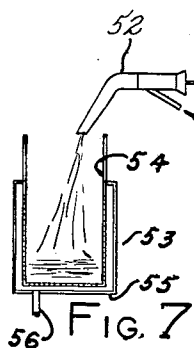


FIG. 7

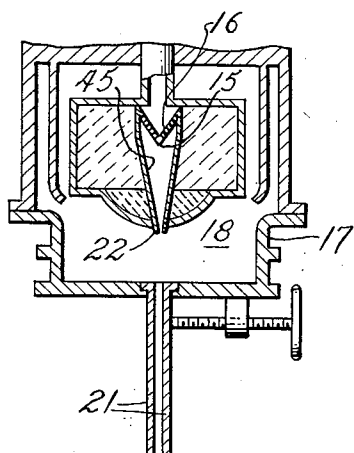


FIG. 2a

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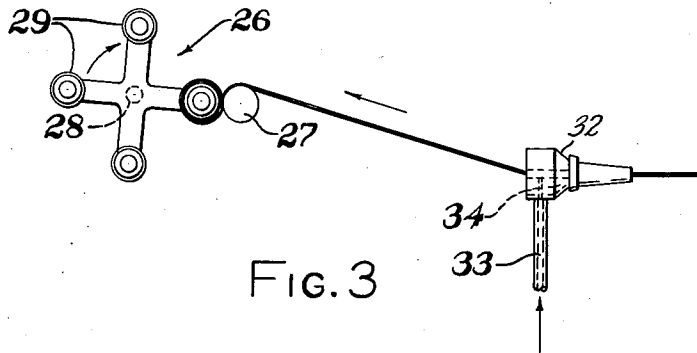
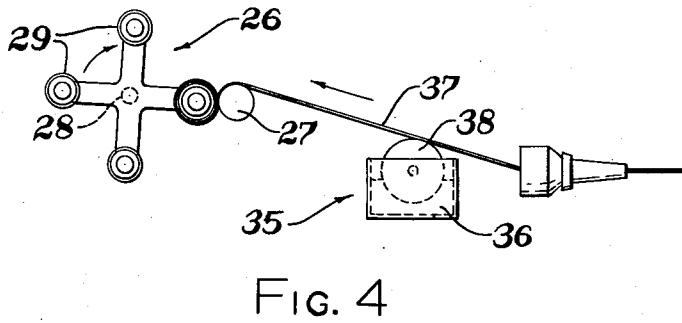
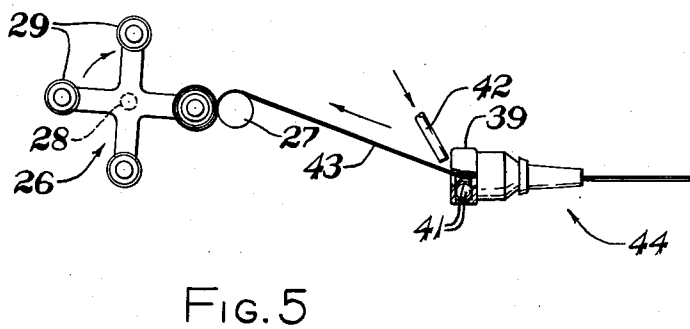
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3 Sheets-Sheet 3

One Edge
of Sliver

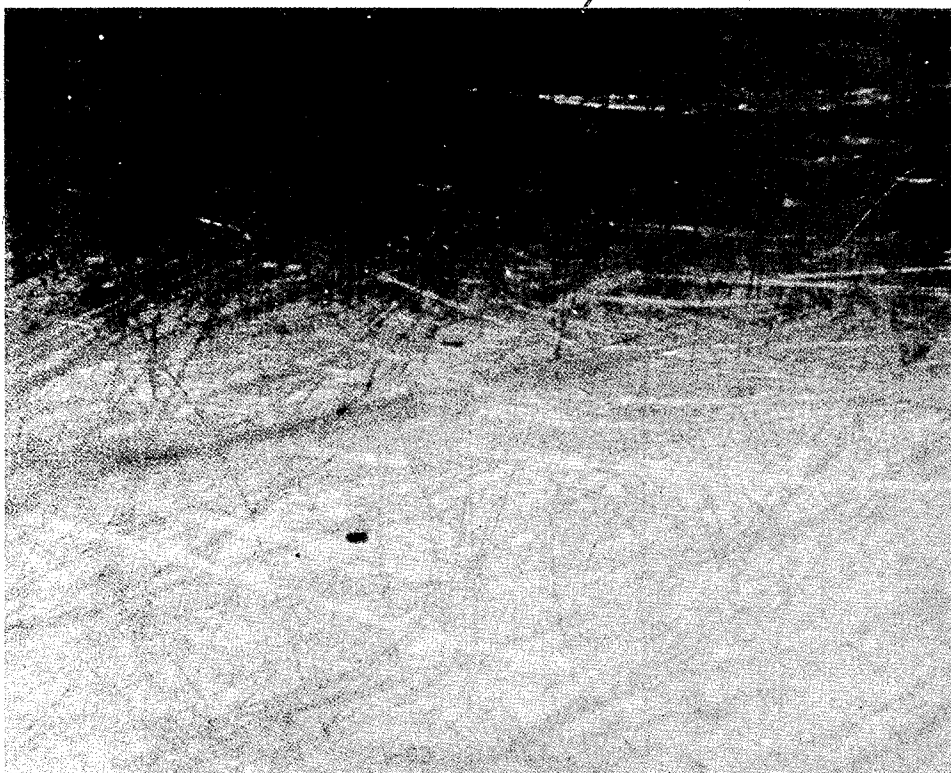


FIG. 8

Central
Portion
of Sliver

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FIBROUS GLASS AND METHOD OF MAKING
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ning Fiberglas Corporation, a corporation of Delaware
Filed Feb. 6, 1958, Ser. No. 714,460
5 Claims. (Cl. 154—43)

This application is a continuation-in-part of our appli-
cation having Serial Number 531,486, filed August 30,
1955, now abandoned.

This invention relates to fibrous glass staple products
and particularly to treatments for staple fibers and to a
process of making bonded staple products.

It is an object of this invention to provide a bulky, low
cost textile product.

It is a further object to provide loosely woven fabrics
especially adapted to be coated with or reinforced by
resins, elastomers, and the like.

It is also an object to provide a textile sliver of staple
fibers which can be woven without first twisting the sliver.

It is also an object to provide an improved staple textile
material having good integrity but remaining open and
adapted for absorption of materials to be added thereto.

An improved staple has been provided by treating staple
fibers with a size during the forming operation. The
treatment with the size compositions of this invention
has a dual purpose in that the composition acts as a
lubricant and as a binder. As first applied, the treating
composition acts essentially as a lubricant; however, after
the composition attains a cured state, it is essentially a
binder.

The treating compositions used comprise a polymeriz-
able material which acts as a lubricant when unpolym-
erized, an emulsifying agent when needed, and water or
other liquid carrier or solvent.

Examples illustrating the compositions used are as
follows:

Example 1

Ingredient:	Percent by weight
Linseed oil	15.0
Emulsifier	0.5
Water	84.5

The linseed oil as supplied is believed to include a small
proportion of a catalyst such as an organometallic com-
pound or the like. The linseed oil and emulsifier such
as Triton X-100 or one of the quaternary ammonium
compounds generally used as emulsifiers, lubricants and
the like are mixed and the water is added slowly with
rapid agitation. Triton X-100 is an alkyl aryl polyether
alcohol. It has been represented as being an ethylene
oxide condensate of tertiary octyl phenol. When the
mixture becomes fluid, water is added to bring to the final
volume. Constant agitation is important. The linseed
oil may contain a small portion of methyl anthraquinone.

Example 2

Ingredient:	Percent by weight
Linseed oil	10.0
Emulsifying agent	0.5
Water	89.5

The linseed oil as supplied is believed to contain a
small portion of a catalyst such as an organometallic com-
pound or the like. This size was mixed as was that of
Example 1.

Example 3

Ingredient:	Percent by weight
Linseed oil	25.0
Emulsifying agent	1.0
Water	74.0

The linseed oil used is believed to contain a small

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portion of a catalyst such as an organometallic compound
or the like. This size was mixed as was that of Ex-
ample 1.

Example 4

Ingredient:	Percent by weight
Raw linseed oil	20.0
Cobalt naphthenate	0.3
Emulsifying agent	0.5
Water	79.2

These ingredients were mixed together as were those
in Example 1.

Example 5

Ingredient:	Percent by weight
Raw linseed oil	15.0
Japan drier	0.2
Emulsifying agent	0.5
Water	84.3

These ingredients were mixed as were those of Ex-
ample 1.

Example 6

Ingredient:	Percent by weight
Tung oil	15.0
Japan drier	0.2
Emulsifying agent	0.5
Water	84.3

These ingredients were mixed together as were those
of Example 1.

Example 7

Ingredient:	Percent by weight
Tung oil	15.0
Soybean alkyd resin	4.0
Cobalt naphthenate	0.2
Oleic acid	1.0
Ammonium hydroxide (28° Baumé)	1.0
Water	78.8

These ingredients were mixed together similarly as were
those of Example 1, the oil and resin and emulsifier being
mixed and then the water and other ingredients added
slowly thereto with rapid agitation.

Example 8

Ingredient:	Percent by weight
Copolymer of monomeric hydrocarbon and fish oil fatty acid	20.0
Japan drier	0.2
Oleic acid	1.0
Ammonium hydroxide	0.5
Water	78.3

The copolymer, japan drier, which is a mixture of or-
ganometallic compounds including those of cobalt, man-
ganese and lead, and the oleic acid were mixed together
and then water added slowly thereto with rapid agitation.
The ammonium hydroxide was added along with the
water to bring the final volume.

Example 9

Ingredient:	Percent by weight
Phenol-formaldehyde resin	5.0
Oleic acid	0.5
Ammonium hydroxide	0.25
Water	94.25

These ingredients were mixed as were those of Exam-
ple 1.

Example 10

Ingredient:	Percent by weight
Linseed oil	40.0
Japan drier	0.4
Maleic acid	1.0
Ammonium hydroxide	0.5
Water	58.1

The ingredients were mixed as were those of Example

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1, the maleic acid and ammonium hydroxide acting as an emulsifying soap. Japan drier is a mixture of organo-metallic compounds including those of cobalt, manganese, and lead.

Example 11

Ingredient:	Percent by weight
Tung oil.....	3.0
Japan drier.....	0.2
Oleic acid.....	0.25
Ammonium hydroxide.....	0.13
Water	96.42

Example 12

Ingredient:	Percent by weight
Titanium lactate.....	1.0
Lubricant (tung oil).....	5.0
Water	Remainder

The lubricant was heated to 100° F. and the titanium lactate added thereto and then the water added to bring to the desired final volume. An organometallic catalyst is added as in former examples.

Example 13

Ingredient:	Percent by weight
Glyceryl monoricinoleate.....	15.0
Ethylene oxide condensate of tertiary octyl phenol	0.5
Water	Remainder

These ingredients were mixed together as were those of Example 1. An organometallic catalyst is also added in a proportion of from about 0.005 to 0.3%.

Example 14

Ingredient:	Percent by weight
Mixture of cottonseed fatty acid esters.....	10.0
Ethylene oxide condensate of tertiary octyl phenol	1.0
Water	Remainder
Up to about 0.3% catalyst is also added.	

These compositions are intended to illustrate those which might be used; however, the invention is not to be limited thereto for various other materials which act as lubricants prior to polymerization and as binders after cure can be used. For instance, various resins including the alkyd, epoxy, polyester, modified phenolic resins, or mixtures of these resins with each other or with various other resins may be used.

Other oily type polymerizable materials may be applied besides those in the examples. For instance, emulsified phenolic resins, fish oil such as the addition product obtained by reacting a fish oil fatty acid with an unsaturated monomeric hydrocarbon, oil from menhaden fish reacted with dicyclopentadiene, soya fatty alcohols, linseed fatty alcohols and the like may be used.

Many polymerizable materials including cottonseed fatty acids, cottonseed fatty acid esters, ricinoleates, such as glyceryl, monoricinoleate, polyethylene glycol fatty acid derivatives, linolenic acid and its derivatives, polyester resins and many others can be used. A polymerizable material such as linseed oil may be present in the composition in proportions of from 2 to 45% by weight. A material such as japan drier or other catalysts such as zinc chloride or cobalt acetate or others may be present in proportions of from 0.005% to about 0.3% by weight.

The catalysts may be cobalt naphthenate, manganese naphthenate, calcium naphthenate, lead naphthenate, and the like. Sometimes no catalyst or heat is required. For instance, if 0.3% by weight of linseed oil is sprayed on the sliver, the oil will cure without the application of heat. The linseed oil will polymerize slowly at room temperature and become cured. The use of a catalyst is preferred and the sizes generally will include a catalyst. An emulsifying agent is generally used in proportions of from 0.5 to 5.0% by weight. The remainder of the com-

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position is water which is generally present in proportions of from about 65 to 95% by weight.

These compositions are especially adapted for use as a binder composition for staple products. The compositions are applied by various means as will be described by reference to the drawings, in which:

FIGURE 1 is an elevational view of apparatus for producing staple fiber;

FIGURE 2 is an end view in elevation of the same apparatus;

FIGURE 2a is a cross-sectional view on line 2a—2a of FIGURE 1;

FIGURE 3 is a view of the air turbine having means for introducing binder to the staple product;

FIGURE 4 is a view of roll applicator apparatus for applying binder to the staple;

FIGURE 5 is a view of ball bearing apparatus for applying binder to the product;

FIGURE 6 is a view of a product of this invention;

FIGURE 7 is a view of collection apparatus for producing an improved product; and

FIGURE 8 is a magnified photograph of a bonded staple sliver.

The invention will be described with special reference to method and means for producing fibrous glass staple products. In FIGURE 1 the apparatus comprises a marble hopper 11, a glass melter 12 and associated with the glass melter, a marble feeding device 13. A marble chute 14 interconnects marble hopper 11 and glass melter 12. The glass melter comprises a chamber 15 having platinum walls and within this chamber a screen 16, see FIGURE 2a. An outer housing 17 defines a chamber 18 into which air is introduced at low pressure through inlet 19. The outer housing 17 is provided with a pair of skirts 21, 21 at its lower extremity. Positioned above the pair of skirts 21, 21 are a row of orifices indicated by numeral 22.

Disposed below the melter 12 is a collecting drum 23 provided with an exhaust duct 24 adapted for removing air from the surface of the perforated collecting drum 23. Adjacent to the collecting drum is air turbine 25 and the collecting mechanism 26 comprising a winder traverse 27 and a four spindle winder 28. The four spindle winder 28 is rotatable upon its axis so that any one of the four tubes 29, 29 can be put into the winding position immediately adjacent to the winder traverse 27.

A spray gun 31 is positioned between the glass melter 12 and collecting drum 23 so that it sprays upon the fibers 20 emitting from the skirts 21, 21 as they pass downwardly to the collecting drum 23.

Instead of using spray gun 31 shown in FIGURE 2, an air turbine 32 having binder inlet 33 terminating in a small diameter inlet 34 may be used, see FIGURE 3. The binder compositions of this invention are applied satisfactorily with a roll applicator 35 such as that shown in FIGURE 4. The reservoir 36 contains the binder composition which is transferred to the staple 37 by transfer roll 38.

In FIGURE 5 is shown another embodiment of a binder applicator suitable for use with the apparatus of this invention. The binder applicator comprises a rotatable race 39 within which ball bearings 41, 41 are free to rotate. The race 39 is a part of the rotatable cylindrical part of the air turbine. The binder applicator is provided with an inlet 42 which directs the binder into the race 39 in which balls 41, 41 are disposed. As the staple 43 passes through turbine 44 the staple product passes through the binder applicator in such a manner that the staple touches one or more of the ball bearings 41, 41 within the rotating race 39. The binder is transferred from the ball to the staple when the staple product comes into contact with the ball bearings. The balls rotate on their own axis when they contact the sliver so that they present a binder covered surface at all times as the staple passes through the binder applicator.

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In operating this apparatus shown in FIGURES 1, 2, 2a, the glass marbles from the marble hopper 11 are introduced into the melter and current is supplied to the melter, the platinum walls 45 and platinum screen 16 acting as resistance units to bring the glass up to melting and operating temperature. After the melter reaches an equilibrium temperature and the glass is flowing through the orifices 22, 22, air is introduced through inlet 19 at a low pressure of from about 2 to 5 pounds. The air comes down around the melter through chambers 18, 18, past the orifices 22, 22, and through the chamber defined by skirts 21, 21. The air passing through skirts 21, 21 attenuates the glass streams emitting from the orifices 22, 22 to form long staple fibers which pass downwardly toward collecting drum 23. Air is evacuated from the perforated collecting drum 23 through exhaust duct 24 so that the fibers collect on the periphery of the collecting drum in the form of a web 46.

The web 46 is pulled from the collecting drum which is rotated on its axis in the direction shown by the arrow in FIGURE 1 and passed through air turbine 25. Air is introduced into the air turbine so that an inner-cylinder of the air turbine rotates rapidly. As the web passes through the air turbine, any loose ends are gathered and wrapped into the staple product forming a more integral sliver 47 which is brought up over the winder traverse roll 27 and around the tube positioned on the spindle of the winder which is adjacent the winder traverse 27. A package of sliver is collected on tube 29 and after a package of suitable size has been collected, the collecting mechanism 26 is rotated so that a new tube 29 on another one of the spindles is put into winding position. The winder traverse 27 is rotated by a suitable drive means and the tube 29 which is in contact with the winder traverse turns as a result of its contact with the winder traverse. It has been found desirable to provide a high degree of turbination to assure that all loose ends of fibers are wrapped into the sliver. The sliver travels within the "Yankee Screw" slot of winder traverse 27 and is thereby traversed as it winds upon tube 29.

Any polymerizable material which can be applied to the staple sliver at forming may be used. The sliver is then aged or heated to polymerize the binder, thus producing a product which can be braided onto wire or cable, served onto a magnet wire, or woven into a fabric without the sliver first being twisted into a yarn. A bulky untwisted sliver has many advantageous characteristics and, of course, the savings realized by it being unnecessary to twist make the method and apparatus much more valuable.

The sliver so produced is cured by placing the packages in an oven at 150° F. for 20 hours and then in an oven at 250° F. for 4 hours. The size of the package apparently does not effect the curing time. It has been found that the polymerization of linseed oil can be accomplished by omitting the pre-cure and simply heating the packages at 250° F. for 4 hours or at 150° F. for 44 hours. It is preferred to use a pre-cure, however, to prevent burning of the packages during the curing cycle. When using linseed oil, from 6 to 10% of binder is applied and the binder remains from 6 to 10% of the final weight of the product even after cure. It is believed that during the preheating, oxygen atoms are added to the linseed oil to form epoxy-type groups. During the final cure the double bonds are replaced with peroxide linkages.

The curing of the coated sliver is carried out by heating at from about 145° to about 155° for 20 hours and then heating at from about 240° to 255° F. for another 4 hours.

A continuous curing process is used when preferred. The staple product coming from the air turbine is directed into a heated tube after the binder has been applied to the staple. As the binder coated staple passes through the heated tube, the temperature is elevated sufficiently so that an exothermic reaction starts the polymerization

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of the binder. The polymerization proceeds to completion without the application of further heat resulting in a full cure. The material emitting from the heated tube is then wrapped by the use of a winding device as shown in the drawings.

Steam or hot air can also be used as the heat source for curing the binder on the staple. The curing step can be carried out on packages of the staple product by placing the packages in an oven or by directing hot air or steam into a perforated tube upon which the package is formed. Electrical heating elements likewise can be used either with perforated tubes or with packages formed on plain tubes.

The bonded sliver so produced has many good properties with the result that many uses are made possible. The sliver formed is such that resins readily permeate the sliver so that fabrics produced from the sliver or the sliver itself can be used to reinforce resin. The sliver can be braided without first being twisted and lends itself for use in the wire insulation field. The product is bulky and open or fluffy and can be produced at low cost. It has been found that bonded staple adheres very well with vinyl polymers and such combinations are well adapted for use in making pipe and tubing. As an indication of the bulkiness of the sliver, a package of unbonded staple weights about 3 pounds and a package of continuous textile strand of the same size weighs about 4 pounds while the bonded staple in the same size package weighs only 2 pounds. One of the greatest advantages of the bonded staple product is that sufficient strength is imparted to the staple sliver by the binder to enable the untwisted material to be woven. The apparent savings in cost are very important; however, in addition, the characteristics of the fabric open up many new uses for the products.

It is sometimes advantageous to add fibers of other materials to the staple fibers in the form of a web on the collection drum. Such fibers may comprise polyvinyl alcohol, polyvinyl acetate, rayon, cellulose acetate, polyvinyl chloride, vinylidene chloride, or combinations of these and other materials.

Uses of the bonded staple sliver include reinforcement for resin and plastic materials, braiding on electrical wires, backing for rugs, sliver for making fabric, wicking tape, cable tape base, aircraft and industrial duct base, reinforcement for asbestos yarn, gasket base fabric, electrical apparatus padding, cable splicing tape, cable wrapping tape, or any other use where staple sliver is generally employed.

Fabric produced from the sliver was dyed successfully without heat cleaning the fabric prior to applying the dye. Many colors have been successfully applied by padding the dye solution onto the fabric.

It has been found extremely desirable to form the package on a collapsible collet upon which a thin walled tube has been placed. The thin walled tube can then be removed after curing of the package with the result that a cake of bonded sliver is available from which the sliver can be removed from the center of the cake. The sliver removes very easily from the center of the package whereas the sliver is removed rather difficultly from the outside of the package. When the package is formed on such a thin walled paper tube the cure comprises heating the package at from 150° F. to 180° F. for 40 hours. An even color results in the sliver in the package and higher quality is thus achieved. Five and ten pound packages have been produced using the removable tubes of thin cross section.

It has been found that the treating material to be used should preferably be a good lubricant as applied and should be a strong bonding agent and a good lubricant after cure. Adding a lubricant makes it possible to draft or to spin the sliver with ease. By drafting or spinning the sliver before curing, a very fine, lightweight drafted staple is provided which can be used without plying after the binder is set. The staple fibers 48 within the sliver shown in FIGURES 6 and 8 are generally parallel one to another

due to the manner in which they are collected on the drum and due to the drafting which takes place as the web is removed from the collecting drum; however, there are many haphazardly arranged fibers in the central portions of the sliver as is readily ascertained by a study of photomicrographs of the product. Some of the fibers close to the surface of the sliver tend to loop outwardly from the main body of the sliver and then return to the sliver at their opposite end. All loose ends of individual fibers are wrapped back into the sliver by the action of the air driven turbine and are held in such position after the binder is set. The jackstraw arrangement of the interlaced, internal fibers of the final product provides strength which is complemented by the adhesive bond provided by the cured binder. The binder forms a more or less uniform coating on the fibers and collects occasionally in the form of droplets at non-uniform intervals along the length of the fibers.

An unbonded staple can be drafted so that the fibers therein become parallel; this staple, however, has no strength unless it is twisted. When unbonded staple is twisted it becomes compacted and has less bulk. Bonded staple need not be twisted; therefore, the bulkiness of the product as formed is retained. The individual staple fibers adhere one to another in several ways. For instance, fibers which happen to be arranged in a side-by-side, generally parallel relationship adhere one to another throughout substantially their whole length. Other fibers may be adhered at only points of contact if they cross one another. Irregardless of what the exact arrangement of the fibers may be, the total effect is one of greatly improved integrity and strength imparted to the staple product.

In FIGURE 7 is shown an apparatus for producing an improved staple product. The forming apparatus is the same as is shown in FIGURE 1 and comprises a glass melter and low pressure air blowing device, a collecting drum, and an air turbine. The collection apparatus shown in the drawings comprises air turbine 49, pull rolls 51, 51, air gun 52, and collection device 53. The collection device 53 comprises a perforated box 54 and a suction box 55 adapted for receiving perforated box 54. Suction box 55 has a vacuum line 56 which is connected to a suitable suction pump or the like. The staple fibers gathered on the collecting drum are condensed to a roving as the web formed on the drum is pulled through air turbine 49 by pull rolls 51, 51. The sliver then passes through air gun 52 which throws the sliver into collecting device 53. A slight suction is used to pack the sliver tightly into the perforated box 54. This apparatus provides a round yarn which is especially adapted for use as a bonded staple product. A treating material such as a binder may be applied immediately prior to the time that the web passes into the air turbine or a binder may be applied at the turbine with apparatus such as that shown in FIGURES 1, 3, 4, and 5. The web collected on the drum may be drafted at it is removed by the action of the pull rolls. A sizing material may be applied to the product before it is introduced to a twisting operation.

Bonded staple sliver has been reinforced with one end 900 denier acetate rayon roving and then this combination treated with acetone so that the rayon partially dissolved and impregnated the glass fibers. After the acetone evaporated, the rayon acted as an additional binder for the sliver. A rather stiff binder was provided thereby.

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

We claim:

1. In a method of producing a bulky, untwisted textile sliver suitable for weaving into fabric without first twist-

ing the sliver which method includes forming a plurality of fine, staple glass fibers, depositing the fibers as a web of fibers in a collecting zone and removing the web of fibers from the zone while compacting them into the form of a bulky sliver, the improvement comprising introducing an aqueous emulsion of an unpolymerized but polymerizable oil onto the fibers as a lubricant and polymerizing the substance to form a binder which bonds the fibers into an integral textile sliver by heating the sliver at 150° F. for 20 hours to precure the binder and then heating the sliver for 4 hours at 250° F. to cure the binder completely

2. In a method of producing an open, bulky textile sliver comprising staple glass fibers which includes forming a plurality of fine fibers, collecting the fibers in a web in a collecting zone, progressively removing the fibers from the collecting zone and compacting them into a sliver, and forming a rolled-up package of sliver, the improvement comprising applying a water emulsion of an unpolymerized but polymerizable oil which acts as a lubricant to the fibers, compacting the fibers and wrapping in loose ends of fibers to form a sliver, forming a package by wrapping the sliver onto a tube, and heating the sliver within the package to polymerize the material on the fibers to bind the fibers into an integral sliver, said heating preferably carried out in two steps comprising precuring at 150° F. for about 20 hours and completing the cure by heating at 250° F. for 4 hours.

3. Method of producing bonded, glass fiber, staple sliver comprising forming a plurality of staple fibers from a melt, collecting the fibers in a web in a collecting zone, progressively removing the fibers from the collecting zone, gathering the fibers as they are removed from said collecting zone into an advancing sliver, applying to the fibers an aqueous emulsion of an oil polymerizable to a set condition, rolling up a package of the advancing sliver, heating said package of sliver at a temperature sufficient to advance the polymerization of the oil but insufficient to build up heat in the package to cause scorching of the oil for sufficient time to cure partially the polymerizable oil, and further heating the package at a temperature greater than the precure temperature to advance the polymerization to completion.

4. The process of claim 3 wherein the emulsion comprises linseed oil and the precure treatment comprises heating the package to a temperature of from about 145° to 155° F. for about 20 hours and the final cure comprises heating to a temperature of from 240° to 255° F. for about 4 hours.

5. A reinforced resin product comprising a vinyl polymer and a fibrous glass reinforcement therefor, said reinforcement comprising a fabric woven of untwisted textile sliver having a dried and cured deposit of an aqueous emulsion of linseed oil on the staple fibers of said textile sliver.

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