

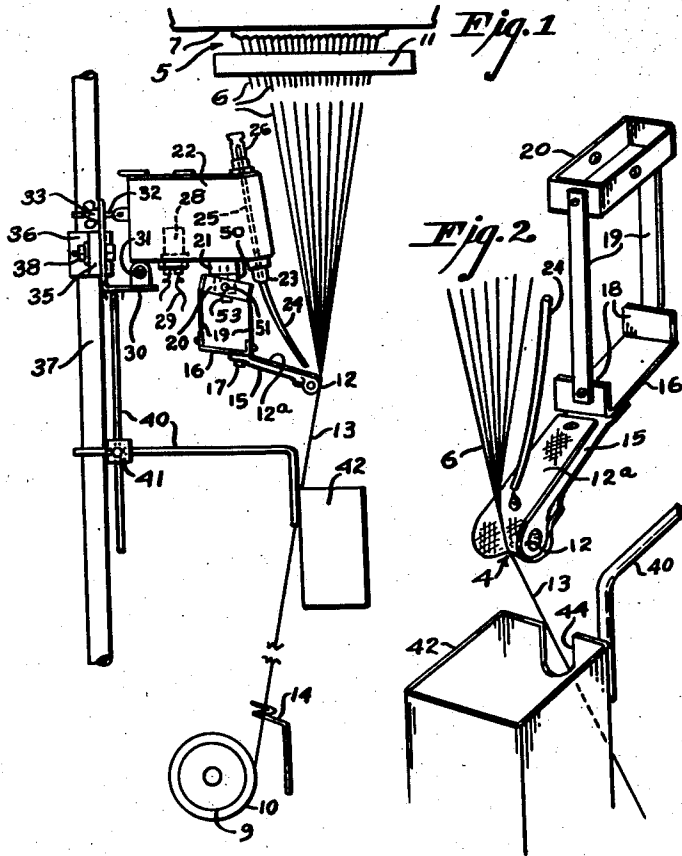
Nov. 28, 1950

J. F. HYDE

2,531,571

MANUFACTURE OF GLASS YARN

Filed April 21, 1945



Inventor

JAMES FRANKLIN HYDE

*Haight & Fowler*

Attorneys

## UNITED STATES PATENT OFFICE

2,531,571

## MANUFACTURE OF GLASS YARN

James Franklin Hyde, Corning, N. Y., assignor, by  
mesne assignments, to Owens-Corning Fiber-  
glas Corporation

Application April 21, 1945, Serial No. 589,688

7 Claims. (Cl. 28-74)

1

The present invention relates to coatings for glass fibers particularly when grouped in strand or yarn form.

This application is a continuation-in-part of my copending applications Serial Number 490,517, filed June 11, 1943, now Patent No. 2,439,689, dated April 13, 1948, and Serial Number 505,833, filed October 11, 1943, now Patent No. 2,390,370, dated December 4, 1945.

It is the purpose of the present invention to provide coatings for glass fibers that facilitate the formation of strands of the fibers, that assure ready fabrication of the strands into yarns and woven fabrics, and that improve the handleability of strands, yarns, and slivers and lend new properties to the finished article.

In the mechanical drawing method for the production of a plurality of extremely fine, long, continuous fibers, as, for example, by the method illustrated and described in the Slayter and Thomas Patent No. 2,234,986 dated March 18, 1941, it has been found that the speed of attenuation and production of fibers was limited by the speeds at which the fibers could be formed into strands and wound on packages in such a manner that the strands could be unwound and processed thereafter in the conventional textile machines. When the bundle of fibers is drawn from the molten glass flowing from the hot bushing, it is pressed against a pad continually saturated with a liquid called a "binding fluid." The fibers pick up this binding fluid as they pass over the pad at very high velocities. The fluid must be able to impart lubrication to the fibers as they are drawn over the pad and also it must lubricate the fibers against themselves to prevent breakage by abrasion during twisting and winding operations. Also this fluid must contain adhesive ingredients for binding all the individual filaments from one bushing (100-400) into one strand. This strand must function as a single fine thread during the twisting process. If this strand is not well bound, it will tend to separate into many small strands or filaments which divide and make its removal from the original winding tubes almost impossible.

The binding fluid must be able to stick the fibers together to form the strand, but it must not stick the strand to the application pad. The lubricant part of the binder must be able to lubricate the fibers against abrasion from each other in the final yarn, but it should not inhibit the sticking properties of the binder. An over lubricated strand cannot be removed in the proper man-

2

ner from the winding tubes in the twisting operation. A tightly bound strand without proper lubricant breaks very quickly under friction and abrasion during twisting and winding. Thus, the problem resolves itself into balancing two opposing effects: (1) that of sticking the fibers together, and (2) that of lubricating them against themselves and against abrasion from fabricating equipment. It is an object of this invention to provide a coating that permits glass fibers to be produced at extremely high speeds, as, for example, above 5,000 or even 20,000 feet per minute, and yet enable the fibers to be gathered into strand form and packaged into a useful article.

The present invention is also applicable to slivers of staple-type fibers made by the process of the Tucker and Lannan Patent No. 2,264,345, of December 2, 1941. In this process molten glass streams are attenuated by a gaseous blast and the fibers as they are formed are collected in a web which is elongated and narrowed into the form of a sliver. For some uses the sliver lacks sufficient integrity and handleability and the loose fibers and fiber ends are found objectionable.

One of the primary purposes of the coating itself is to bond the fibers together in strand form prior to twisting without fraying or subdividing. Once extremely fine fibers, that is, below .0004 inch and particularly below about .0002 inch in diameter, have been intertwisted into a thread, they will retain their coherence and strength without fraying or subdividing and without the necessity of an adhesive coating material. Before twisting and when in strand form without proper adhesive, it is difficult to handle the strands and process them through the conventional textile machines.

It is a further object of the present invention to provide a coating for the fibers that will bind the fibers in the sliver and bind down loose fiber ends and facilitate subsequent fabricating operations such as twisting and weaving.

It is a further object to provide a strand of glass fibers wherein the individual fibers are provided with a coating which permits relative movement of the fibers in the strand, thereby preventing breaking of the fibers as the strand is twisted and woven or braided.

Another object of the coating material is to retain the loose ends of any broken fibers in the strand without permitting them to break away and form a fuzz. This feature is particularly important when attempting to unwind a strand from a wound package thereof, owing to the fact

that a loose fiber continues to break away from the main body of the strand as it is unwound and produces a fuzz around the package as the loose fiber is broken by the subsequent unwindings of the main body of the strand. This causes other fibers to be broken away from the strand until the package is destroyed.

Another object of the invention is to provide a coating substance which will readily distribute itself uniformly over the fibers at extremely high speeds.

It is also an object of this invention to provide a coating which will not have to be removed where the glass yarn is to be subsequently impregnated with insulating varnishes.

Other objects and advantages of the present invention will become apparent from the following description taken in conjunction with the drawing, in which—

Fig. 1 is an elevational view of an apparatus for attenuating a multiplicity of fine glass fibers of substantially continuous length, grouping them in strand form, and applying a coating thereto in accordance with the present invention; and

Fig. 2 in a fragmentary perspective view of the apparatus shown in Fig. 1.

In accordance with my invention, I have discovered that the foregoing objects are realized if the individual fibers in the strand are provided with a coating comprising one or more hydrolyzable organo-silanes. These serve admirably as coatings for the individual fine glass filaments and enable the production and fabrication thereof to be carried on at high speeds.

By hydrolyzable organo-silanes, I mean derivatives of  $\text{SiH}_4$ , which contain readily hydrolyzable radicals such as halogens, amino groups, alkoxy, aroxy, and acyloxy radicals, etc., and organic radicals that are joined to the silicon atoms through carbon atoms. Examples of such organic radicals are as follows: aliphatic radicals; such as methyl, ethyl, propyl, isopropyl, butyl, amyl, hexyl, heptyl to octadecyl and higher; alicyclic radicals such as cyclopentyl, cyclohexyl, etc.; aryl and alkaryl radicals such as phenyl, mono- and poly-alkyl phenyls as tolyl, xylyl, mesityl, mono-, di-, and tri-ethyl phenyls, mono-, di- and tri-propyl phenyls, etc.; naphthyl, mono- and poly-alkyl naphthyls as methyl naphthyl, diethyl naphthyl, tri-propyl naphthyl, etc.; tetrahydronaphthyl, anthracyl, etc.; aralkyl such as benzyl, phenylethyl, etc.; alkenyl such as methallyl, allyl, etc.; and heterocyclic radicals. The above organic radicals may also, if desired, contain inorganic substituents such as halogens, etc.

The coating materials of my invention are generally applied in the form of solutions in organic solvents, the nature of the solvent depending upon the specific characteristics and properties of the compound or compounds involved. The concentration of the solution also depends upon the particular compositions being employed by the optimum concentration may be readily determined by preliminary tests. I have also found that other substances may be added in small amounts such as waxes and vegetable oils in order to improve the binding or lubricating effect. The coating materials may be applied to the glass fibers by any suitable means, such as a pad, groove, roller, or other suitable methods. The glass fibers are passed through the coating material, or films thereof, picking up the proper amount, and producing a flexible, coherent strand which may be easily wound into a package. In winding the

strands over a package, it is preferable to traverse the strand as it is being wound in order to wind the strand uniformly and evenly and in a manner which facilitates easy unwinding.

Examples of hydrolyzable organo-silanes which I have found to be particularly useful in the practice of my invention are the following when dissolved in either Stoddard solvent or toluene to yield approximately ten per cent solutions: laurylsilicon trichloride ( $\text{C}_{12}\text{H}_{25}\text{SiCl}_3$ ), tetradecylsilicon trichloride ( $\text{C}_{14}\text{H}_{29}\text{SiCl}_3$ ) and octadecylsilicon trichloride ( $\text{C}_{18}\text{H}_{37}\text{SiCl}_3$ ). Other examples of hydrolyzable organo-silanes which may be employed in practicing my invention are as follows: methylsilicon trichloride, dimethylsilicon dichloride, trimethylsilicon chloride, methyltriethoxysilane, dimethyldiethoxysilane, trimethylethoxysilane, methyldichlorsilane, dimethylchlorsilane, ethylsilicon trichloride, diethyldiethoxysilane, phenylmethyldiethoxysilane, and diphenylsilicon dichloride. In general, I prefer to employ those hydrolyzable organo-silanes having the general formula  $\text{RSiCl}_3$  where R is an alkyl radical having from 10 to 31 carbon atoms. Such compounds, I have found to possess unusual waterproofing and lubricating properties.

By way of illustration the preparation and properties of certain of the silanes of my invention are described in the following examples.

#### EXAMPLE 1

##### Dodecyl silicon trichloride

95 parts (0.43 mol) of lauryl chloride ( $\text{C}_{12}\text{H}_{25}\text{Cl}$ ) dissolved in 68 parts (0.92 mol) of anhydrous ethyl ether were added slowly to 12.5 parts (0.51 mol) of magnesium turnings under 35 parts of ethyl ether. The latter was in a 3-necked glass flask provided with a stirrer, a condenser, and a dropping funnel, respectively. The addition of the chloride was accomplished through the dropping funnel. Reaction was initiated by the addition of a little bromide in ether. The addition of the chloride was such thereafter as to maintain a gentle reflux of the ether. After all the chloride had been admitted, the reaction mass was stirred for another hour with the temperature being held at reflux. The stirring was then stopped and the mixture allowed to stand to permit settling of the salt and cooling to room temperature. The supernatant liquor was then carefully siphoned into a closed dropping funnel on the coupling reactor which, likewise, was a 3-necked flask provided with the aforementioned funnel, a stirrer, and a condenser.

The Grignard reagent so produced was added to a twofold excess of 140 parts of silicon tetrachloride (0.83 mole) in 150 parts of benzene. The reaction mass was stirred for 3 hours and then heated to reflux temperature for another 3 hours with stirring being continued. The product was filtered and the filtrate was then fractionally distilled, yielding a fraction at  $162\text{--}171^\circ\text{C}$ . at 18 mm. in an amount corresponding to 67% of theory. An analysis of this fraction was as follows:

	Per Cent C	Per Cent H	Per Cent Cl	Per Cent Si
Found.....	47.7	8.52	34.2	9.02
Theory.....	47.4	8.23	35.2	9.22

## EXAMPLE 2

*Tetradecylsilicon trichloride*

Tetradecylsilicon trichloride ( $C_{14}H_{29}SiCl_3$ ) was prepared in a manner similar to the preparation of the dodecylsilicon trichloride of Example 1 with the exception that the Grignard reagent which was prepared from myristyl bromide ( $C_{14}H_{29}Br$ ) was diluted with ether to a relatively low concentration prior to coupling with silicon tetrachloride. The crude coupling product was directly distilled and a fraction collected in the range of 131–132° C. at 0.8 mm. This fraction was identified by analysis as  $C_{14}H_{29}SiCl_3$ . The yield was 50% of the theoretical.

## EXAMPLE 3

*Octadecylsilicon trichloride*

Octadecylsilicon trichloride was likewise prepared in a manner similar to that described in Example 1. The Grignard reagent was made from pure stearyl bromide ( $C_{18}H_{37}SiBr$ ). An ether solution containing 3.54 mols of the Grignard reagent was slowly introduced into a coupling reactor containing 7.3 mols of silicon tetrachloride and 1.5 liters of benzene. The coupling product was filtered in the usual manner and the filtrate fractionally distilled in vacuo. A fraction boiling at 159 to 162° C. at 13 mm. was identified by analysis to be  $C_{18}H_{37}SiCl_3$ . Its density was 0.95 g./cc. at 22° C.

Referring now more particularly to the drawing, reference character 5 designates broadly to the filamentizing apparatus wherein a multiplicity of individual filaments 6 are simultaneously being supplied continuously from a single source such as a feeder 7 or other supply means and are being drawn and attenuated by means of a revolving spool or drum 9 on which the fibers are wound to form a package 10 thereon. A blower 11 which may be provided in proximity to the feeder 7, is adapted to chill the glass as it emerges from the feeder, although the present invention is not limited to any particular filamentizing apparatus.

The filaments 6 as they emerge from the filamentizing apparatus 5 are grouped together in substantially parallel relation and drawn over a concave guide 12 in the form of a groove or eye which serves to size the filaments and simultaneously group them into a strand 13. In being drawn over the guide 12, the filaments are preferably turned through as small an angle as possible in order to reduce to a minimum the amount of force exerted by the strand upon the guide and the resultant friction. The strand 13 may then be traversed by means of traverse 14 which assists in the formation of the package 10 upon the drum or spool 9.

The gathering and lubrication guide 12 is preferably made from a very light metal, such as aluminum, in order to keep its inertia as low as possible. The free end of the guide is provided with a groove 4 (see Fig. 2) having a rounded outer surface which may be covered by means of a pad 12a composed of suitable porous material such as a felt, muslin, sponge, cloth, or the like. The upper portion 15 of the guide 12 is in the form of an inclined trough upon which the coating substance may be fed and introduced to the groove 4 over which the filaments are drawn. The guide 12 may be fastened to a support 16 by means of a screw 17 or the like. The support 16

is preferably provided with two upstanding flanges 18, one at each end thereof, and each secured to and suspended from yielding means 19 which are preferably in the form of flexible metal tapes, composed, for example, of spring steel or the like. The upper ends of the tapes 19 may be secured to an upper support 20 having dimensions comparable to the lower support 16, whereby supports 16 and 20 and the tapes 19 define a parallelogram which gives approximately straight line motion to the guide 12 as it is moved by the strand 13. The upper support 20 may be mounted upon a lug 50 by means of set screws 51. In order to permit pivoting of the system under the influence of the traversing movement of the strand 13, the lug 50 may be pivotally secured to a bushing 21 which is located at the bottom of a sizing container 22. A bolt 53 may be provided to hold the lug in place and permit the same to pivot in relation to the container 22.

The container 22 is provided with an outlet orifice 23 through which sizing material may be fed. A conduit 24 communicates with the outlet 23 and serves to convey the sizing material to the guide 12 by gravitational means. An adjusting needle 25 fits into the orifice 23 and may be placed in any desired vertical position by means of an adjusting pin 26, similar in design to a conventional oil dripper.

Arranged preferably in the lower portion of the container 22 is a heating means 28, such as an immersion type heater using electrical energy supplied through the electrical connections 29.

The container 22 may be adjustably mounted upon a suitable elbow 30 to which it is pivotally attached for tilting movement by means of a pivot bolt 31. The container is held in any desired position of adjustment by means of a screw rod 32 and wing nut 33.

The elbow 30 in turn may be mounted upon one end of an arm 35 having a collar 36 at the opposite end thereof, fitting around a vertical supporting rod 37. The collar 36 may swing around on the rod 37 and be held in adjusted position by means of the bolt and nut 38.

Depending from the elbow 30 is a system of rods 40 having an adjustable connection 41. Supported at the free end thereof is a cup 42 which is spaced below the guide 12 to receive any surplus drippings of sizing material which may fall from the guide 12. As shown in Fig. 2, the cup may be provided with an opening 44 through which the strand 13 may pass without touching the sides of the cup. When not in operation the cup may be swung about the connection 41 out of the path of the strand 13.

In the operation of the present device, the organosilicon compositions of my invention or mixtures thereof, may be held in the container 22, heated to the desired temperature by means of the heater 28, and fed through the orifice 23 and through the conduit 24 to the guide 12. The pad 12a may be saturated with the coating material, especially the groove 4 around which the filaments 6 are drawn. The filaments in being drawn over the pad 12a are lubricated by the liquid coating material and are simultaneously coated thereby. In traveling from the guide 12 to the package 10, the coating material may be sufficiently solidified that it will not cause the adjacent strands upon the package to adhere to one another. However, when such substances as oils or thin solutions are applied, the coating may remain substantially in a fluid or slightly viscous condition on the package

which, however, does not prevent the strand from being unwound.

Should any filament 6 break during its attenuation, an operator may restart the stream flow by means of a bait or the like and after a preliminary attenuation may draw the filament adjacent the others across the groove 4, and as it takes on its allotment of coating material, it joins with the other filaments in the strand and passes on into the package automatically.

It is to be observed that in the process of coating, the guide 12 is supported yieldingly by means of the flexible tapes 19 so that when the strand 13 is subjected to any unusual stresses or irregular pulling forces, even of minute magnitude, the guide 12 will yield, maintaining a substantially uniform friction and force against the strand. Moreover, as the strand is traversed back and forth by the traverse 14, the guide 12 is permitted to follow the sideway movements by oscillating around the axis of the bolt 53, and thus any jerking movements emanating from the packaging process are smoothed out and dissipated. This arrangement has been found to materially assist in the efficiency of the sizing operation.

After the strands have been fabricated into the finished product, as, for example, into a woven, knitted, braided, or otherwise interlaced glass fabric, the coating liquid surrounding each fiber conditions the fibers to provide a soft, supple fabric that is smooth and lustrous. The good electrical properties of the organo-silicon compounds also make the fabrics well suited for use in electrical insulation. Furthermore, the moisture repellent character of the compounds adapts the fabrics to uses where high humidity and other moisture conditions prevail.

For certain industrial applications, it has been found unnecessary to remove the organo-silicon coatings of my invention. In fact, the continued presence of the organo-silicon compounds has been found desirable. For example, if an electrical insulating varnish is to be applied to the glass fibers, the organo-silicon compound not only possesses such electrical properties as not to impair the insulating character of the product, but it also serves to waterproof the glass and to act as a primer for the insulating varnish causing it to adhere much more tenaciously than it otherwise would.

Modifications and variations may be resorted to within the scope and the spirit of the present invention as defined in the appended claims.

I claim:

1. A strand composed of a multiplicity of long, fine attenuated glass fibers that have been coat-

ed with an adhesive and lubricating liquid composition comprising a hydrolyzable organomonosilane, the organic substituents of the silane being alkyl radicals attached to silicon through direct carbon linkage.

2. A strand composed of a multiplicity of long, fine attenuated glass fibers that have been coated with an adhesive and lubricating liquid composition comprising a hydrolyzable organo-silane of the formula  $RSiCl_3$ , where R is an alkyl radical having from ten to thirty-one carbon atoms.

3. A strand composed of a multiplicity of long extremely fine glass fibers that have been coated with an adhesive and lubricating liquid composition comprising lauryl silicon trichloride.

4. A strand composed of a multiplicity of long, extremely fine glass fibers that have been coated with an adhesive and lubricating liquid composition comprising tetradecylsilicon trichloride.

5. A strand composed of a multiplicity of long, extremely fine glass fibers that have been coated with an adhesive and lubricating liquid composition comprising octadecylsilicon trichloride.

6. In the method of grouping glass fibers into a yarn, the step of treating such fibers with a solution of a hydrolyzable organomonosilane in an organic solvent therefor, the organic substituents of the silane being alkyl radicals attached to silicon through direct carbon linkage.

7. In the method of grouping glass fibers into a yarn, the step of treating such fibers with a solution of a hydrolyzable organomonosilane having the general formula  $RSiCl_3$  in an organic solvent therefor where R is an alkyl radical having from 10 to 31 carbon atoms.

JAMES FRANKLIN HYDE.

#### REFERENCES CITED

The following references are of record in the file of this patent:

#### UNITED STATES PATENTS

Number	Name	Date
2,133,238	Slayter et al. ....	Oct. 11, 1938
2,234,986	Slayter et al. ....	Mar. 18, 1941
2,245,824	Roesch .....	June 17, 1941
2,258,218	Rochow .....	Oct. 7, 1941
2,272,588	Simison .....	Feb. 10, 1942
2,306,222	Patnode .....	Dec. 22, 1942
2,380,995	Rochow .....	Aug. 7, 1945
2,380,996	Rochow .....	Aug. 7, 1945
2,439,689	Hyde .....	Apr. 13, 1948

#### FOREIGN PATENTS

Number	Country	Date
543,434	Great Britain .....	Feb. 25, 1942

**Certificate of Correction**

Patent No. 2,531,571

November 28, 1950

**JAMES FRANKLIN HYDE**

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 3, line 63, for the words "employed by" read *employed but*; column 4, line 60, for "mole" read *mol*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 13th day of March, A. D. 1951.

[SEAL]

**THOMAS F. MURPHY,***Assistant Commissioner of Patents.*