April 19, 1966 W. SHULVER ETAL 3,247,020

ELECTRICALLY-CONDUCTIVE ELEMENTS AND THEIR MANUFACTURE

Filed Jan. 2, 1962 2 Sheets-Sheet 1

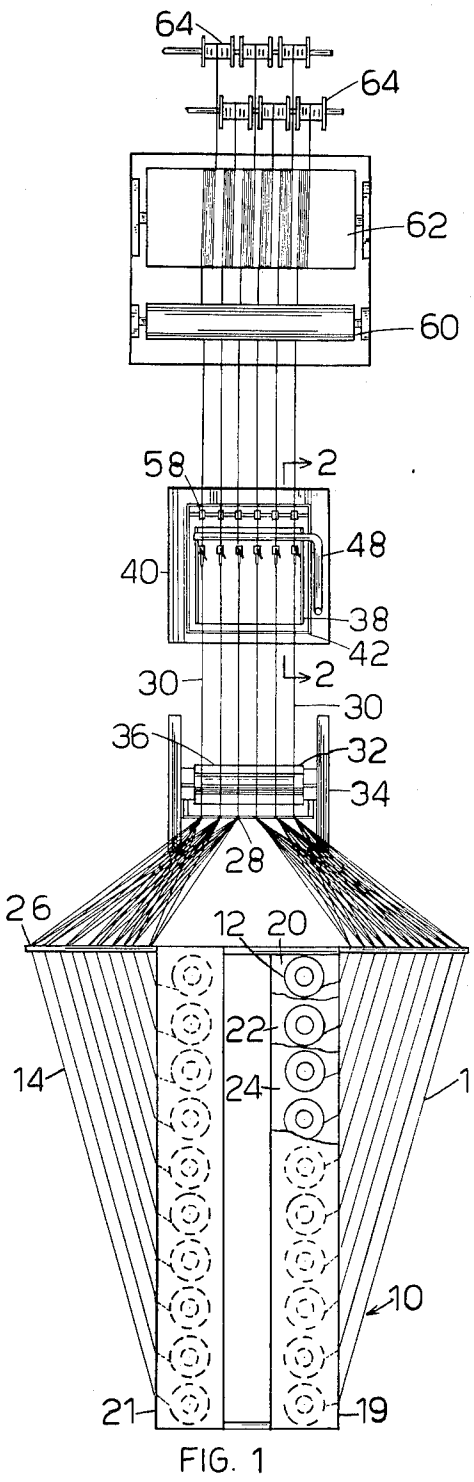


FIG. 1

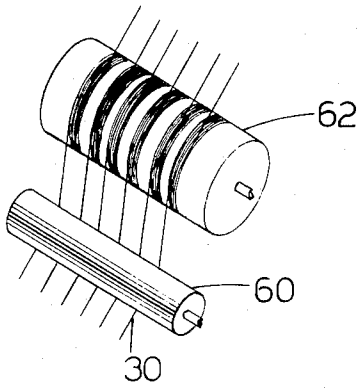


FIG. 3

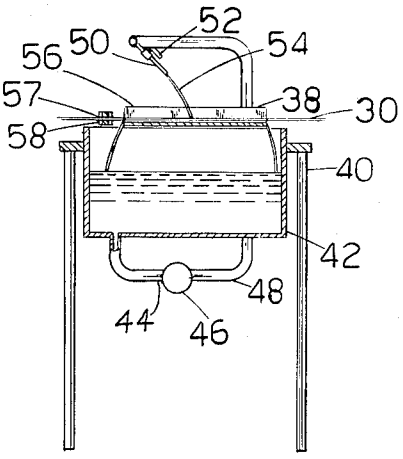


FIG. 2

INVENTOR.
WILLIAM SHULVER WILLIAM H. MILLER
THOMAS L. ATTERIDGE ALFRED MARZOCCHI
BY
Stahlin & Quinman
ATTORNEYS

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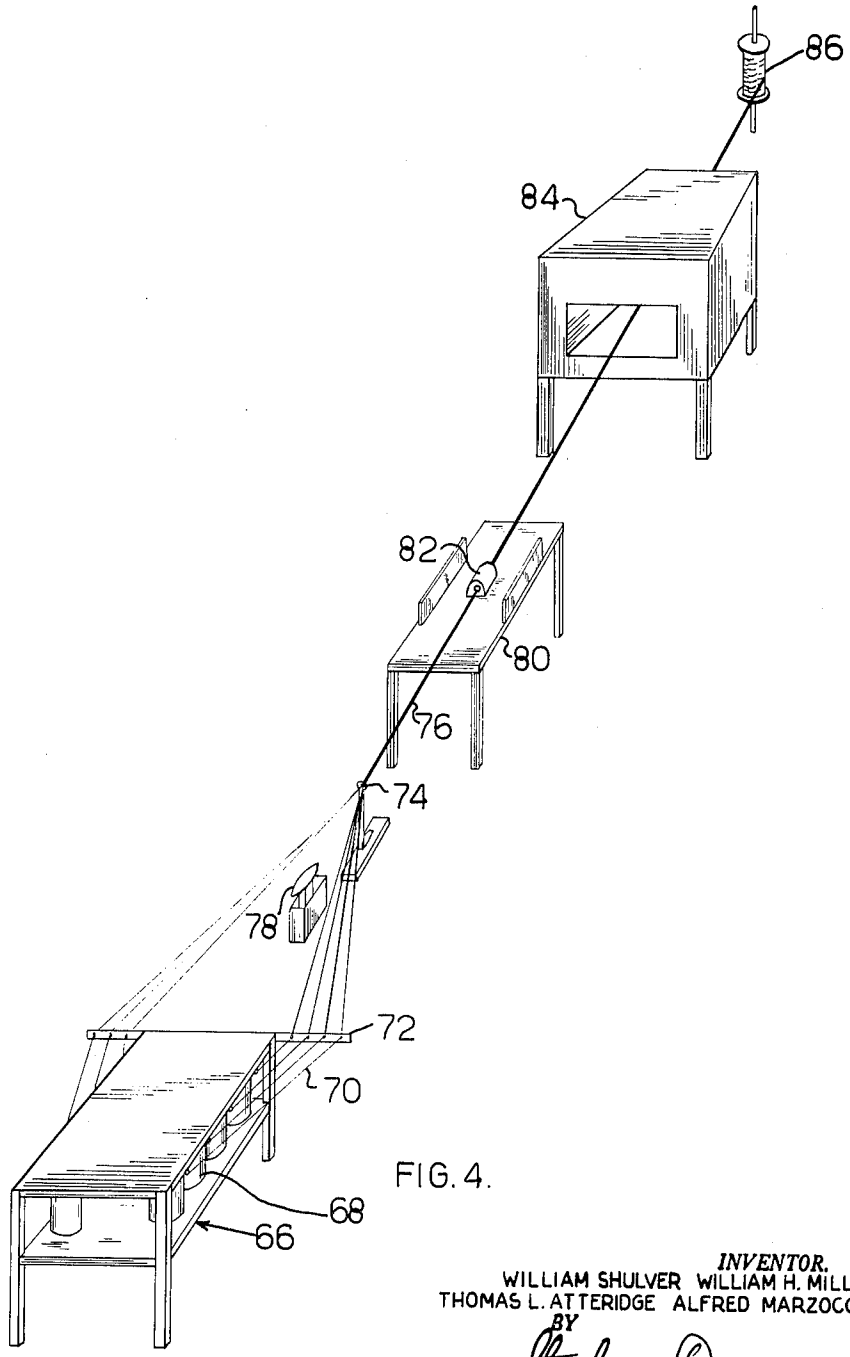


FIG. 4.

INVENTOR.
WILLIAM SHULVER WILLIAM H. MILLER
THOMAS L. ATTERIDGE ALFRED MARZOCCHI
BY
Stachin & Quirman
ATTORNEYS

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3,247,020 ELECTRICALLY-CONDUCTIVE ELEMENTS AND THEIR MANUFACTURE

William Shulver, Saylesville, William H. Miller, Chepachet, Thomas Le Roy Atteridge, Woonsocket, and Alfred Marzocchi, Cumberland, R.I., assignors to Owens-Corning Fiberglas Corporation, a corporation of Delaware

Filed Jan. 2, 1962, Ser. No. 163,388
9 Claims. (Cl. 117—226)

This application is a continuation-in-part of our former copending application Serial Number 88,542, filed February 10, 1961.

This invention relates to a method of applying an electrically-conductive coating to the outer surface of elongated glass fibers and the resultant products, and more particularly to a method for applying a semi-conducting coating to glass fiber filaments, the conductance of the coating being accurately predetermined in the manufacturing process, the coating being uniform in its character and of substantially constant properties regardless of the conditions encountered during use.

It has been proposed in the past to provide elongated glass fibers having semi-conductive electrical properties. Such coated glass fibers have been proposed for use as resistors, suitable for example as grid leaks or in voltage divider networks. It has been suggested that such fibers may be woven into fabrics and utilized as sheathing for electrical cables used in high-voltage systems to result in a condenser action between the central conductor and the sheathing to avoid localized electrical discharge. Tape, braided or woven from the fibers, may also be used as shielding to reduce the emission of radio interference signals from communication cables and the like. Such shielding may also include copper wire as a carrier.

However, problems have arisen in the manufacture of suitable coated glass fibers. One problem has been to provide coated glass fibers having acceptable flexural strengths. Another problem has been to provide a conductive ribbon in which the fibers are arranged in parallel alignment as opposed to being woven or braided. Such parallel alignment is advantageous in some applications, such as in the communication field for helically wound cable tubing. A further desire has been to provide coated glass fibers which can be utilized as the current carrying core of an electrical line, such as communication and automobile ignition wire. In addition to adequate flexural strengths, conditions of flexing experienced by such flexible structures have tended to yield a rapid loss of the particulate, conductive coating due to an unsatisfactory bond between the inflexible coating and flexible fibrous substrate.

Previous attempts to provide acceptable fibrous glass, semiconductive structures have included the coating of the fibrous strands with colloidal suspensions of the conductive medium, similar treatments with suspensions containing an adhesive phase and the in situ formation of the conductive medium by means of the carbonization or pyrolysis of a carbonizable, but uncarbonized coating.

All of these attempts have resulted in products which proved unsatisfactory for one reason or another. For example, most of these products possessed a coating which flaked or powdered off upon the slightest flexing of the substrate. Others were plagued by great reductions in flexural and tensile strengths due to prolonged exposure to high temperatures or moisture which was inherent in the processes necessary for their preparation. Another common defect comprised nonuniform electrical characteristics or characteristics which could not be consistently reproduced.

Additionally, it has been desired to provide a method

for manufacture of such coated glass fibers which is efficient and inexpensive.

These problems are alleviated in the present invention in which it is an object to provide a method for manufacturing elongated glass fibers having an electrically-conductive coating thereon.

An additional object is the provision of glass fibers possessing a uniform coating of a controlled quantity of an electroconductive material which is strongly adhered to the glass fibers to yield a structure having outstanding properties of semi-conductivity, durability and strength.

Another object of the invention is to provide a method for the uniform distribution of electrically-conductive particles on glass filaments.

A further object of the invention is to provide a method for manufacturing coated glass fibers of predetermined electrical conductivity.

Yet another object of the invention is to provide a process for producing coated glass fibers in which the semi-conductive electrical properties may be readily varied.

Another object of the invention is to provide a method for baking the electrically-conductive coating onto the glass fibers by utilizing a heated drum which is more efficient and occupies less space than the conventional oven.

A further object of the invention is to employ such a heated drum to flatten a bundle of individual glass filaments during baking of the conductive film to result in a conductive ribbon in which the individual filaments are in planes substantially parallel to one another.

Another object is to provide an electrically-conductive flat tape by the above-mentioned process in which the individual filaments are parallel rather than woven or braided.

A still further object of the invention is to apply the initial conductive coating to the glass fiber filaments by means of a bath containing suspended electrically-conductive particles, and in which the electrically-conductive particles are continuously recirculated to result in a uniform coating on the glass fiber filaments.

A further object of the invention is to provide a die for maintaining an even distribution of electrically-conductive particles on the glass fibers.

Another object of the invention is to provide means for coating glass filaments with graphite linters and a resin coating to result in a product having superior conductive properties.

A still further object of the invention is to provide a method of coating the electrically-conductive glass fibers with a plastic or similar film-forming material to result in improved abrasion resistance.

Other objects of this invention will appear in the following description and appended claims, reference being had to the accompanying drawings forming a part of this specification wherein like reference characters designate corresponding parts in the several views.

In the drawings:

FIGURE 1 is a top plan view of an apparatus utilized in one embodiment of the process of the present invention;

FIGURE 2 is a side elevational view in section of the coating bath taken substantially along the line 2—2 of FIGURE 1 looking in the direction of the arrows;

FIGURE 3 is a perspective view of the heated drum and idler roll utilized to dry and bake the coated glass fiber in the FIGURE 1 process; and

FIGURE 4 is a perspective view of apparatus utilized in a second embodiment of the present invention.

Before explaining the present invention in detail, it is to be understood that the invention is not limited in its application to the details of construction and arrangement of parts illustrated in the accompanying drawings, since

the invention is capable of other embodiments and of being practiced or carried out in various ways. Also, it is to be understood that the phraseology or terminology employed herein is for the purpose of description and not of limitation.

Referring to FIGURE 1, it may be seen that a creel **10** is provided to hold a plurality of rotatable rolls **12** of glass fiber strands. A strand is defined for the purpose of this invention as a primary bundle of continuous glass fiber filaments combined in a single compact unit without twist. Preferably, the filaments are precoated with a starch or similar sizing as is conventional in the manufacture of glass filaments and which normally comprises 0.5 to 15% by weight of the coating composition. The sizing aids in the handling of the filaments and the starch is apparently caramelized during the present process to form part of the conductive-coating. This thermal conversion of the precoating and the consequent improvement of the bond between the fibers and the conductive coating will be subsequently discussed in greater detail.

The creel **10** has two vertical stacks **19, 21** having three levels **20, 22, 24**, each level holding ten rolls **12** to total sixty rolls. The strands **14** are directed from the creel through guide openings in guide structure **26** and thence to central eyes **28** wherein ten strands are gathered together to form rovings **30**.

Each roving **30** passes over roller **32** which is rotatably mounted in support structure **34**. The lower portion of the roller **32** dips into water contained in pan **36** and wets the roving passing thereover. Alcohol in amounts of from 2 to 5% may be added to the water to provide an improved prewetting mix. Other wetting agents may be added to the mix as desired.

The roving then passes through a pan **38** which contains, in liquid suspension, small particles of electrically-conducting material. The particles adhere to the roving as it passes therethrough to form a thin electrically-conducting film on the roving. Each individual filament of the roving will be so coated.

As will be noted in FIGURE 2, the pan **38** is supported on a table structure **40**. The table **40** also supports a reservoir **42**. Fluid is pumped from the bottom of reservoir **42** through conduit **44** by pump **46**. Conduit **48** extends from the pump upwardly to a point above the pan **38**. Spouts **50** having closure valves **52** direct streams of fluid **54** into the pan and over the rovings. The pan **38** is canted slightly and the fluid **54** constantly runs out of the pan through the open front end **56** back into the reservoir **42**. The purpose of continuously pumping from the reservoir into the pan and then allowing the fluid to flow back into the reservoir is to keep the fluid in a well-mixed condition to prevent settling of the electrically-conducting particles. In this way, a uniform coating on the roving is assured. The reservoir **42** is constantly replenished from an external source (not shown).

The coated rovings each pass through openings **57** of predetermined size in dies **58** provided on the table **40**. The dies wipe off the excess particles and fluid to maintain a uniform coating thickness. Additionally, the dies force the individual filaments together to achieve some degree of mechanical bond therebetween.

The coated rovings extend from the dies **58** over idler roller **60** and thence spirally over heated rotating drum **62**. As will be understood, the roving slides sidewise in its spiral path over the drum. For this reason, it is important to adjust the pressure between the drum and roving to avoid binding of the roving with the drum surface. As shown in FIGURE 3, the roving takes approximately ten turns around the drum. The function of the heated drum is to dry the roving and brake the electrically-conducting particles onto the glass fiber. Additionally, the drum flattens the bundles of glass fibers and, during the baking process, bonds the individual fibers together in substantially parallel arrangement to form a flat ribbon.

As will be appreciate, the drum diameter and temperature and the number of times the roving passes thereover may be varied. It has been found, however, that with the roving travelling at 35 feet per minute drum temperatures in the range of from 550–650° F. are preferred. However, temperatures up to 700° F. may be employed. Temperatures in this range are made possible by virtue of the highly efficient thermal transfer between the drum surface and the coated strands which engage that surface. The heat treatment is probably also enhanced by the gradually increasing thermal gradient which ensues from the presence of an aqueous phase in the coating composition present upon the treated strand. A uniform thermal transfer from the exterior to the interior of the strand is also derived from the intimate engagement of strand and drum and the continual change in the portion of the strand which engages the drum. In addition, the flexibility of the strand is maintained as it is simultaneously exposed to heat and a working or drafting effect.

The idler roller **60** is also preferably heated to a temperature approximating that of the drum **62**. If the idler roller is cool or warm, it will pick up a portion of the coating material from the roving. This is, of course, undesirable because such a pickup will make the thickness of the final coating nonuniform.

After the roving leaves the drum **62**, it is wound up on take-up rollers **64** and subsequently stored.

More than one coating of electrically-conductive particles may be applied. For example, one conductor material was made having three coatings of particles. This material was passed through a 32 foot oven at 600° F. at the rate of twenty-five feet per minute. Its conductivity was 4000 ohms per square inch.

A number of different electrically-conductive particles may be utilized to coat the glass fibers. For example, dispersions or colloidal suspensions of graphite, carbon black, metals and organometallic compositions which decompose under heat to form a metallic electrically-conductive coating may be used. The percentage of electrically-conductive particles in the fluid mixture is varied depending on the desired thickness of the applied coating. Graphite is a preferred material because of its excellent electrical properties and because of its lubricating properties. When graphite coated filaments rub against each other, there is less friction and thus less abrasion. Additionally, elongated carbon particles, such as the graphite linters described hereinafter in conjunction with the second embodiment of the invention, may be included in the mixture of electrically-conductive particles. It has been found that when such elongated particles are used, less electrically-conductive material is necessary in the coating and the flexibility of the coating is improved. This may result from the greater interlinkage and dove-tailing between adjacent elongated elements as compared with the interlinkage of spherical particles.

One suitable commercially available material which has been used with success is sold under the tradename "aquadag." This material is a concentrated colloidal dispersion of pure electric-furnace graphite in water. It is a paste consistency with a solids content of 22%. The average particle size is 0.5 micron and the maximum particle size is 4 microns. The specific gravity is 1.121 and the boiling point is 100° C. The material is completely miscible with water. This material is preferably diluted with water, for example, three parts water to one part aquadag, to obtain a fluid which can be pumped and which will give the desired surface coating thickness.

While various starches, sugars, glucose, sorbitol, glycerol and the like have been suggested as the preferred types of compositions for the precoating, it should be realized that any organic material capable of conversion to a carbonized or caramelized condition upon exposure to temperatures below 750° F. are suitable for the practice of the invention. Specifically, such materials must be thermally transformable at temperatures below 750°

F. The phrase "thermally transformable" is employed to designate the ability of the materials to be partially or completely carbonized or caramelized at the prescribed temperatures. In addition, it should be noted that numerous other compositions, as for example synthetic resins such as polyvinyl acetate, may be thermally transformed or carbonized at the temperatures involved in the inventive processes.

In addition to the electrically-conductive particles, a binder material may be added to the suspension to improve the bond of the particles to the glass fibers. Preferably, the binder material, if used, is a carbonaceous material which will decompose to form carbon when heated. For example, sugar, starch, glucose, sorbitol, glycerol and the like may be used. When such materials are heated and thermally decomposed to carbon, they form an electrical bridge between the electrically-conductive particles to result in a continuous electrical path. Quaternary ammonium compounds have also been found useful for this purpose. It is preferable, however, to avoid or minimize the use of a binder material because the resultant electrical properties when a binder is used are not as good as when the binder is not used, due to the requisite heterogeneity of the coating.

Alternative to the use of a heated drum, the roving may be passed through an oven to dry and bake the roving. As will be appreciated, when an oven is used the roving is not flattened, and higher temperatures must be employed in order to derive an equivalent result.

The products derived from the inventive methods exhibit an electrical-conductivity which has been previously unequalled with such materials, in respect to either degree or uniformity. In addition, the conductive coating is so well adhered to the fibrous substrate that the coated structure may be subjected to repetitive, prolonged flexing without an appreciable loss of the coating or decrease in conductivity. Still further, the coated structure does not exhibit a diminution of flexural or tensile strengths.

While it is found that some degree of improvement, within the scope of improvement made possible by the invention, may be attributed to the drum drying technique, it is believed that a major contribution to the realization of the improvements, is derived from the properties of the fibrous substrate employed and the bond which is obtained as the result of the effects of the inventive processes upon these substrates and their precoatings.

The advantages of drum-drying appear to derive from the high efficiency of the conductive transfer of heat from the surface of the drum to the glass filaments, which is attended by rapid and thorough heating. It further serves to provide a structure in a tape-like form with the individual filaments positioned in a relationship ideal for many semi-conductive applications.

However, it is believed that the unusual and improved properties of the ultimate products are primarily attributable to an improved bonding at the fiber-coating interface, which may experience an additional increment of improvement when conductive, as opposed to radiant, heating is employed.

It is further believed that the ideal interfacial condition is the direct result of the presence of a carbonizable, pyrolyzable or caramelizable material upon the surfaces of the fibers prior to the application of the conductive coating and the drying or heat treatment of that coating. This condition is achieved by the conversion of the materials at the interface to a partially or completely, carbonized or caramelized state. It has been demonstrated that film-forming dispersions or solutions of a film-forming material such as starch, sugar, glucose, sorbitol, glycerol and the like, are capable of adhering to the surfaces of glass fibers. In contrast, colloidal suspensions of carbon, graphite, metals and organometals may be deposited upon glass surfaces by dispelling or volatilizing the suspension carrier, but such materials are not actually bonded to the glass and are easily displaced by external contact or the flexing of the glass substrate. This condition is only slightly improved if the conductive suspensions are deposited upon an organic film of starch or the like which is previously formed upon the surface of the glass, since there is no pronounced compatibility or adhesion between such organic films and the conductive deposits.

However, in accordance with the invention, it is believed that a situation favorable to both the compatibility and adhesion of these two dissimilar types of materials is achieved. It has been determined that when organic materials capable of undergoing carbonization, pyrolysis or caramelization at temperatures below the softening point of the glass, are subjected to such temperatures while positioned upon the glass surface, the transformed residues still exhibit a strong adhesion to the glass surfaces. For example, glass fibers coated with dextrinized starch were treated in an oven maintained at 400° F. for three hours and subsequently immersed in boiling water for three hours. It was found that only 50% of the starch was removed despite the severity of this test, and some of that loss is undoubtedly attributable to the thermal treatment rather than the attack of the boiling water upon the bond of the starch residue to the glass surface. In the conduct of the test it was found that the starch began to caramelize at 400° F. and that the effect continued to substantial completion during the three hour heat treatment. This test is cited to illustrate the tenacity of the adherence of caramelized starch residues to glass surfaces.

The term "caramelize" as used herein is intended to connote a condition short of complete carbonization or pyrolysis, wherein the thermally "caramelized" material may possess some carbonized portions but is generally perceptible as a relatively rigid, plastic, and normally tacky, composition.

If one employs temperatures capable of caramelizing the coating upon the glass fibers while that coating is in intimate engagement with a further coating comprising a colloidal suspension of conductive particles, it is apparent that the coating will be caramelized and the particles will be deposited upon the caramelized surface. It is further apparent that the caramelized material will be strongly adhered to the glass substrate and the particles will be strongly adhered to the caramelized material due to the tacky nature of the latter.

Proceeding further, it is also feasible that a favorable interface will result if the thermal conditions experienced are in excess of those required for mere caramelization, and are adequate for complete or partial carbonization of the material employed to precoat the glass fibers. For example if the heat treatment is adequate to carbonize the surface of the coating and merely caramelize that portion of the coating which is immediately adjacent to the glass surface, a desirable association of glass to caramelized material, caramelized material to carbonized material and carbonized material to inorganic conductive particles is achieved. The factors of compatibility between the carbonized material and the inorganic particles, and the adhesion of the remaining strata, are highly conductive to a well-integrated structure. Even if the material employed to precoat the fibers is completely carbonized, a condition favorable to compatibility is attained wherein the nature of the structure blends from glass to an in situ carbonized region and ultimately to an area comprising deposited carbonaceous or metallic materials which were present and in intimate engagement with the precoating upon the fibers, during the thermal conversion of the precoating to a carbonized condition.

While it is practically impossible to guage or determine the actual nature of the conductive coating to glass interface after subjection to the inventive processes, it is known that starch employed as a size upon glass fibers is caramelized after prolonged heat treatment at tem-

peratures in the range of 400° F., and that short exposures at 700–750° F. will serve to achieve a similar effect while similar exposures at 900° F. in an oven, will result in a substantially complete carbonization of the starch. While it is difficult to assess the effect of the superimposition of an aqueous dispersion of conductive particles upon the precoated strand and the divergent thermal effects of conductive and radiant heat treatments, it is safe to assume that the temperatures which are preferably employed by the inventive processes (550–700° F.) will operate to caramelize the precoating and possibly to partially or completely carbonize the precoating.

While temperatures of 550–700° F. are preferred when the thermal treatment is achieved by means of a heated drum, higher temperatures may be employed with oven treatments. For example, temperatures of as high as 1100° F. may be necessary in the latter type of treatment due to the limited efficiency of thermal transfer. However, temperatures in excess of 1100–1200° F. should be avoided with a conventional glass composition such as E glass, in order to avoid achieving the softening point of the glass.

It should also be noted that the precoating may be transformed to a caramelized condition and the conductive particles may then be powdered upon the resultant tacky surface. However, such a method is not as conducive to the formation of a conductive coating possessing both the quantity of coating material and the continuity of the coating derived from the in situ deposition of the conductive particles from a colloidal suspension.

It has been further found that the electrical properties of the coated glass fibers may be improved if an electric current is passed through the fibers as the fibers are heated to carbonize and bake the coating thereon. The electric current tends to align the graphite and other carbon particles. Such alignment links up the particles and improves the conductivity of the coating.

It will be appreciated that the resultant product may be varied within wide limits. For example, the number of strands and the electrical resistance per foot of the product is capable of being varied as desired. One product produced consisted of 60 strands and had a resistance of 3000 ohms per foot. It has been found that strands having 100 or more filaments and roving having four or more strands are particularly useful.

Another embodiment of a method for applying an electrically-conductive film to glass fibers is illustrated in FIGURE 4. A creel **66** is provided having a plurality of rolls **68** to dispense strands **70** of glass fibers. The fibers extend through guide openings in guide structure **72** and pass to a central collecting eye **74** where they are formed into a roving **76**. At a point just short of entering the gathering eye **74**, the strands are sprayed with electrically-conductive linters by means of a flocking gun **78**. The spray is directed towards the center of the converging strands. The linters are loosely held in the roving by entanglement with the strands.

Subsequent to passing through the eye **74**, the roving **76** passes over table **80** and through applicator **82**. Applicator **82** contains a fluid coating material (supplied from an external source not shown) and a coating is applied to the roving. The resin acts as a binder and also is electrically-conductive.

Subsequent to the application of the fluid coating, the roving is directed into an oven **84** wherein the resin is cured thermally to form a tough coating. The thus coated roving is wound up on take-up roll **86**.

The roving may be directed through a wiping die before or after baking in the oven depending upon the compatibilities of the materials. The die may be either of the rotating or stationary type.

The linters are preferably graphite of a size approximately ⅛ to 1 inch long. However, elongated metallic particles may also be utilized. If metallic particles are used, a reducing agent such as hydrazine, formaldehyde (or hydride) or the like should be added to reduce the resistance between contacting particles. Graphite linters may be manufactured by graphitizing natural or synthetic fibers.

The fluid coating for the roving may be an organosol, plastisol or latex resin, such as vinyl or butyl acrylate which is partially hydrolyzed or it may be a coating composition such as a lacquer. In order to obtain maximum conductivity when using an emulsified resin, it is preferable that the diluents or plasticizers be reduced to a minimum concentration. Additionally, an improved material will result if the conductive particles are adsorbed on the surface prior to application of the resin or coating composition.

The resultant conductive glass fibers will have improved conductivity over that provided by other forms of electrically-conductive materials because of the linear structure of the linters. It has been found that very small amounts of such linear material results in superior conductivity.

In use of the coated linter conductor, current passes through the outer low conductive coating to the core which contains the linters and thence along the core to an exit point such as ground where it again passes through the outer cover.

It is apparent that new and improved conductive glass elements, and methods for their preparation, are provided by the present invention.

It is also obvious that various changes, alterations and substitutions may be made in the present invention without departing from the spirit of the invention as defined by the following claims:

We claim:

1. An electrically conductive element comprising: a glass fiber, oblong particles of electrically conductive material positioned adjacent the surface of said glass fiber with the major dimension of said oblong particles parallel to the surface of said fiber, and a material selected from the group consisting of residues of caramelizable and of carbonizable materials, produced in situ while connecting said glass and particles by thermal decomposition in a controlled oxidizing atmosphere to bond said electrically conductive particles to said glass.

2. An element as described in claim **1** in which said electrically conductive particles are selected from the group consisting of platelets of graphite, and platelets of metals.

3. A method for the preparation of electrically conductive glass comprising:

(a) coating glass with between 0.5 to 15% by weight of a thermally transformable material selected from the group consisting of caramelizable and carbonizable materials,

(b) positioning upon said thermally transformable material while wetted by water electrically conductive particles with their major dimensions generally parallel to the surface of the glass, and

(c) subjecting the so coated glass to a controlled oxidizing atmosphere and a temperature adequate to achieve the in situ thermal transformation of said thermally transformable material without removing said thermally transformable material to bond said particles to said glass by means of the thermally transformed material, said temperature being below the softening point of said glass fibers.

4. A method as described in claim **3** in which electrically-conductive particles are selected from the group consisting of graphite, and metal platelets.

5. A method as claimed by claim **3** in which said thermally transformable material is between 0.5 to 15% by weight of starch.

6. A method as claimed by claim **3** in which said thermally transformable material is between 0.5 to 15% by weight of sugar.

7. A method as claimed by claim 3 in which said thermally transformable material is between 0.5 to 15% by weight of glucose.

8. A method as claimed by claim 3 in which said thermally transformable material is between 0.5 to 15% by weight of a carbohydrate, and said thermally transformed material is heated to a temperature between 400° F. and 750° F.

9. A method as claimed by claim 3 in which said thermally transformable material is decomposed by being held against a surface heated to a temperature between 400° F. and 750° F. and which surface is exposed to the atmosphere.

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JOSEPH B. SPENCER, *Primary Examiner.*

RICHARD D. NEVINS, *Examiner.*