

Jan. 6, 1959

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2,867,552

METALLIZED FILAMENTARY MATERIALS

Filed June 1, 1954

2 Sheets-Sheet 1

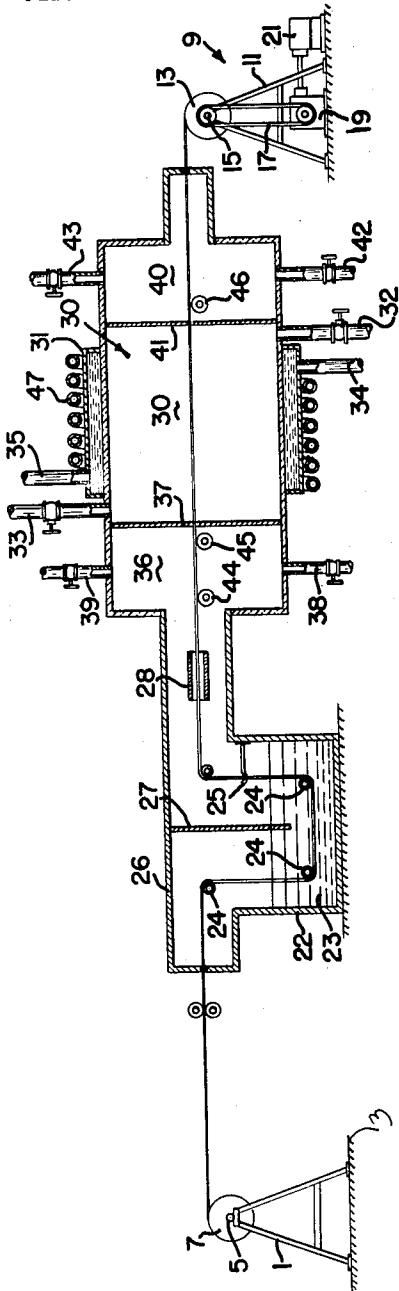


FIG. 1

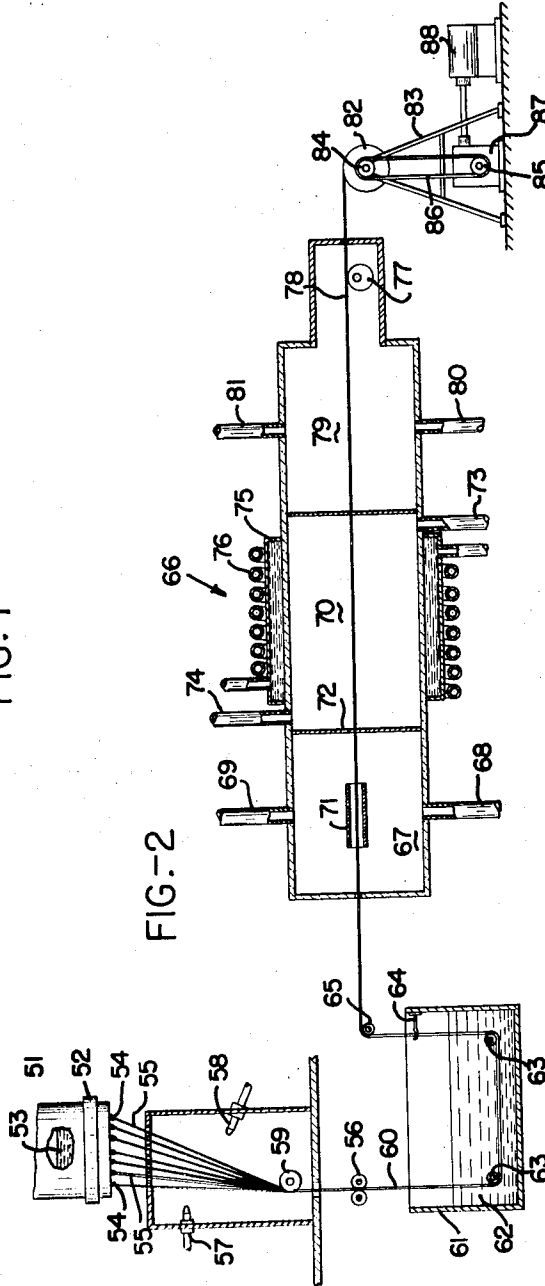


FIG. 2

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2 Sheets-Sheet 2

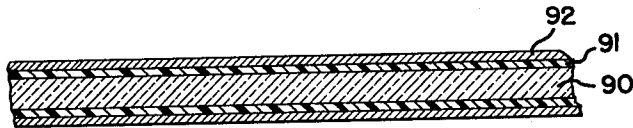


FIG-3



FIG-4

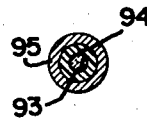


FIG-5

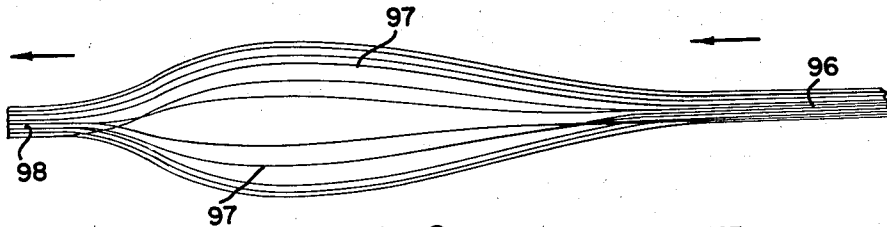


FIG-6

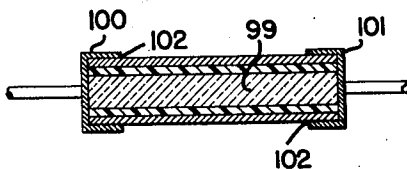


FIG-7

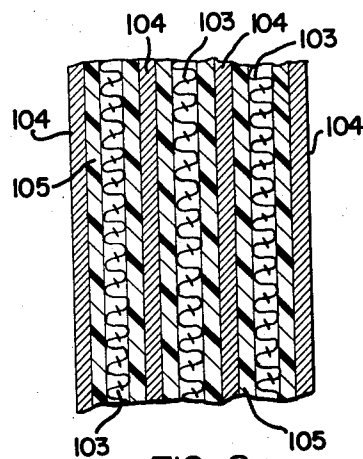


FIG-8

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METALLIZED FILAMENTARY MATERIALS

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Application June 1, 1954, Serial No. 433,510

2 Claims. (Cl. 117—217)

This invention relates to the production of composite bodies having particularly utility with electrical components.

The principal object of the invention is the production of a novel material, the rigidity of which and the electrical conductive characteristics of which may be readily controlled.

An important object of the invention is the novel and new processes for the production of materials having controllable degrees of rigidity and electrical conductivity.

The invention particularly contemplates the provision of a material having an electrically non-conductive base or core in fibrous form which is impregnated with a thermosetting resin and thereafter coated with metal. Such materials may be light in weight, relatively rigid or relatively flexible, have a high degree of strength and are particularly resistant to ageing and corrosion under the most severe of atmospheric conditions.

The process of invention is adapted to permit control of the electrical conductivity of the product and in general contemplates the coating of the non-conductive fibrous base with a thermosetting resin and then the deposition of metal on the resin by thermal decomposition of a heat decomposable metal bearing gaseous compound in contact with the resin coated heated base.

While glass fibers, yarns and fabrics are preferable in the practice of the invention, due to the readiness with which they are freed of moisture, other fibers and fabrics such as cotton, nylon and acetate-rayon are extremely useful.

The latter materials have a distinct advantage in being relatively light in weight; for example, individual cotton fibers have a specific gravity of about 1.5, and a yarn formed of the fibers, due to the interstices and porosity created, may have a density approaching one. Similarly, nylon has a low density in filamentary form, usually between 1.10 to 1.4; while the acetate-rayon is somewhat heavier, having a specific gravity of 1.5. Consequently where lightness in weight is the primary factor the latter base materials are preferred to glass.

The thermosetting resins useful in the practice of the invention include phenol aldehyde, ureaformaldehyde and furfural-formaldehyde coating resins, as well as those polyesters which are normally useful in application to glass fibers and the formation of laminates. Such polyesters include particularly those formed from components which include as acids phthalic and maleic, and which include as alcohols or glycols, aryl alcohol, the glycols such as ethylene glycol and di-ethylene glycol; also suitable modifiers for the alkyd or polyester may be included such as succinic, adipic and sebacic, for example. However, since high adherence to metal of the polyesters is a factor, it is preferred to employ polyesters such as those described in co-pending application of M. J. Hiler and P. Q. Peake, Serial No. 338,155, filed February 20, 1953, assigned to the same assignee as the present invention, and wherein blends of an alkyd resin with a vinyl-substituted

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heterocyclic tertiary amine, such as a composition comprising an alkyd resin and 2-vinylpyridine are set forth.

Nickel carbonyl is preferred as the heat decomposable gaseous metal bearing compound as it is relatively low in decomposition temperature and therefore suitable with most electrically non-conductive base materials in the practice of the invention. It is also available commercially and presently relatively cheap in contrast to other members in the class. However, other compounds such as copper acetylacetonate, molybdenum, titanium carbonyls are eminently suitable.

It has been found to be most satisfactory to employ a carrier gas for the nickel carbonyl as the same serves to dilute the carbonyl and to permit control of the concentration thereof; further the use of the carbonyl tends to dilute gases of decomposition and to inhibit the formation of unwanted products such as carbides. For the purpose it is preferred to use carbon dioxide, although other gases which are inert in the process, such as argon or nitrogen, may be utilized.

The product of invention is characterized by a high degree of coherence of the constituents, a substantially corrosion free metal surface, and its adaptability for formation into electrical components of various shapes having desired degrees of electrical conductivity.

The invention will be more fully understood by reference to the following detailed description and accompanying drawings wherein:

Figure 1 is a schematic elevational view of apparatus useful in the production of metallized resin coated fibrous material;

Figure 2 is a schematic elevational view of apparatus particularly useful in the formation of glass base materials;

Figure 3 is a sectional view of a metallized resin coated fabric produced in accordance with the principles of invention;

Figure 4 is a view of a yarn strand resin coated and metallized in accordance with the invention;

Figure 5 is an end view of the structure of Figure 4;

Figure 6 is a plan view illustrating glass fiber rovings in a spread and resin coated condition adapted to receive the deposit of metal thereon;

Figure 7 illustrates an electrical resistance element produced in accordance with the invention; and

Figure 8 illustrates a condenser element.

Referring first to Figure 1, there is indicated at 1 a stand supported on a base 3, the stand being provided with a shaft 5 which rotatably supports a bobbin of glass yarn 7. Shown at the right hand end of Figure 1 is take-up mechanism indicated generally at 9 and comprising a stand 11 which supports a bobbin of metallized resin coated yarn 13 being wound thereon, the shaft 15 which supports the bobbin 13 being driven through belt 17 and gear box 19 by motor 21.

The resin coating on the glass yarn 7 is effected by drawing the yarn rightwardly in Figure 1 through a tank 22 containing a phenol-formaldehyde coating resin 23, the yarn being supported on pulleys 24 for passage through the bath. At the exit end of the bath at 25 a wiper blade extends from the tank 22 and engages against the yarn to remove any excess resin therefrom.

A housing portion 26 extends over the bath 23 and has a depending flange 27 which extends into the resin to form a gas seal therewith. Rightwardly the housing 26 at 28 encloses a Chromolox electrically energized resistance heater through which the coated yarn passes to be raised to a temperature of approximately 350° F., which heating serves to partially set the phenol-formaldehyde resin on the glass.

Rightwardly in Figure 1 there is indicated at 30 a plating chamber preferably constructed of glass and being

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surrounded over a portion of the length thereof with a water jacket 31. Inlet conduit 32 supplies the plating gas which may consist of equal volumes of nickel carbonyl and carbon dioxide to the plating chamber 30, and outlet 33 is connected to a source of vacuum to rapidly remove from the plating chamber gases of decomposition as well as any undecomposed metal bearing gases; preferably the latter are recovered for reuse.

Conduit 34 provides for entry of water to the cooling jacket, which water flows out through conduit 35; the cooling jacket is effective to maintain the interior wall of the plating chamber cool and to inhibit the deposition of metal bearing gases thereon.

The chamber 30 has integral therewith at the left hand end a compartment 36 which is separated from the plating chamber itself by a baffle 37 having a small aperture therein for the passage of the yarn therethrough. An inert gas preferably carbon dioxide is passed through the compartment 36 under pressure from inlet conduit 38 to the outlet conduit 39.

A similar compartment is provided at 40 separated from the plating chamber by an apertured baffle 41 and carbon dioxide is passed through this chamber under pressure from inlet conduit 42 to outlet conduit 43.

The compartments 36 and 40 serve to provide gas seals to prevent the ingress of air to the plating chamber 30. While carbon dioxide may contact the heater 28 or even the resin 23 such is not deleterious to the operation.

The resin coated heated yarn suitably supported by rollers 44, 45 in compartment 36 and roller 46 in compartment 40 is passed through the baffle 37 from compartment 36 to the plating chamber 30 where it is contacted by the heat decomposable nickel carbonyl and a film of nickel immediately results on the glass.

Surrounding the plating chamber is an induction heating coil 47 which serves to heat the partially metallized yarn further and to effect increased deposition of the metal on the yarn. The heating induction coil 47 may suitably be effective to raise the temperature of the yarn to about 425° F. when the plating gas contains nickel carbonyl. The resin coated metallized yarn passes from the equipment outwardly through compartment 40 to be wound up as at 13.

It is to be noted that in the practice of the invention the usual precautions to effect adequate plating are to be taken, that is the plating chamber itself should be evacuated of air and preferably should contain an atmosphere of carbon dioxide prior to the start of the plating operation.

Similarly the compartments 36 and 40 should contain carbon dioxide under pressure before the resin coated yarn is passed to the plating chamber. Valves appropriately positioned in the conduits leading into the apparatus are effective to permit the attainment of this initial condition.

The nickelized resin coated yarn may have an electrical conductivity as low as about 100 ohms per inch or by controlling the metal deposit, that is by reducing the thickness thereof resistance of several thousand ohms per inch may be attained.

The phenol-formaldehyde resin will normally be partially set only in the passage through the plating apparatus and this partially set material may be cut into suitable lengths and formed into desirable configurations to produce, for example, electrical resistance elements. The rigidity of the element may be controlled by completing a cure of the resin after formation to shape.

It is also to be understood that while the procedure outlined in connection with Figure 1 has been specifically set forth with relation to a yarn, a fabric or tape could be passed through similar apparatus in the same manner to effect a complete impregnation of the fabric with resin and complete coating of the resin with metal. Such fabric may then be cut into suitable sections and formed into electrically condensive elements, the broad thin metal-

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lic coating serving as an excellent plate of the condenser.

Referring now to Figure 2, there is shown therein apparatus for the resin coating and the metallizing of glass filamentary strands as they are produced from the molten glass body. Thus there is shown at 51 a platinum pot heated through electrical conductors indicated at 52 from a source (not shown) to maintain a body 53 of molten glass at a temperature of about 2100-2200° F. The glass exudes from this pot to form at 54 small glass pools from which filaments 55 are drawn by means of rotating rollers 56 powered from a source (not shown). The filaments in their passage to the rollers are subjected to resin sprays at 57, 58 and each filament receives a complete coating of resin before it passes over the guide 59 which groups the coated filaments into a single strand 60. Strand 60 passes into a tank 61 containing a urea-formaldehyde resin 62, the strand being supported for its passage over pulleys as at 63.

A wiper element 64 is supported below pulley 65 over which the single heated strand passes to the metallizing apparatus indicated generally at 66. The metallizing apparatus is constituted by a first compartment 67 through which carbon dioxide passes through inlet 68 to outlet 69 continuously to provide a seal against the entry of air into the plating chamber 70. Compartment 67 also contains a Chromolox heater 71 provided with energy from a source (not shown). An apertured baffle 72 separates the compartment 67 from the plating chamber 70 and the yarn passes through the aperture thereof as described in connection with Figure 1.

Plating gas is supplied to the plating chamber through conduit 73 and the gases of decomposition together with any undecomposed gases are exhausted through conduit 74 under vacuum pressure. A water jacket 75 surrounds the plating chamber 70 and an induction heater 76 serves to maintain the temperature of the resin coated stranded filaments above the thermal decomposition point of nickel carbonyl.

It is to be noted that the resin treatment in bath 62 serves to bind the filaments together into the strand quite completely and in order to metallize the individual filaments it is necessary that they be exposed individually to the plating gas. To effect this purpose a motor driven cam is provided at 77 which operates at a rotational speed of about 2000 cycles per minute and serves to contact the strand at 78 to cause the same to vibrate rapidly. The strand under the influence of the cam action is caused to assume a condition in the plating chamber such as that shown in Figure 6 and the small filaments are each coated with nickel; metallizing in this manner provides a product of extremely low electrical resistance, due to the plurality of electrical paths formed in the total strand.

The plated product passes outwardly through compartment 79 which contains a continuously flowing atmosphere of carbon dioxide, the compartment being fed with the gas through conduit 80 and the gas passing outwardly through conduit 81. The product is wound up at 82 where a reel is rotatably supported on stand 83 and driven by the combination of pulleys 84, 85, belt 86, gear box 87 and motor 88.

Figure 3 illustrates a fabric which has been resin coated and metallized in accordance with the principles of the invention and there is shown at 90 a glass fabric having an impregnation of resin 91 and a coating of metal 92.

Figures 4 and 5 illustrate a yarn 93 which may be of nylon and which has thereon a coating of urea-formaldehyde 94 and an overlayer of metal 95, for example molybdenum.

In the structure of Figure 6 wherein the filaments are spread apart to receive the metal, it is to be noted that the direction of passage of the filaments is indicated by the arrows and that the resin treated filaments are closely compacted at 96 and separated at 97 under the influence

of the vibrator to be substantially rejoined at 98. The reformation of the filaments into strand form is induced by the very fineness of the metallized coated filaments.

Further with respect to the apparatus shown in Figure 2, it is to be noted that if it is desired to produce a strand of filaments which are coated as a unit with metal, the vibrator cam 77 may be eliminated from the apparatus and sufficient resin may be applied with the sprays 57, 58 to eliminate the bath 62 also.

Under this procedure the single strand formed at 59 will pass from the drawing rolls 56 directly to the plating chamber; with this mode of operation strands having a resistance value of 100 ohms per inch are readily producible, while metallizing of the individual filaments in accordance with the practice briefly described in connection with Figure 2, results in strands which have a resistance of as low as about one ohm per inch, the plurality of paths facilitating the high conductivity.

In either mode of operation of the structure of Figure 2 the resin will normally be only partially set and complete curing to a rigidized product may be readily effected by subjecting the product after formation to desirable configurations to temperature of only about 300° F. for several hours.

Referring now to Figure 7 wherein the complete product is illustrated, a rigidized metallized coated strand of glass fibers is indicated at 99 and caps 100, 101 are silver soldered to the same as at 102 to form the complete resistor.

A condenser is indicated in Figure 8 and comprises a plurality of elements each constituted by a rigidized metallized resin coated fabric, the fabric being indicated at 103, the metal at 104 and the resin at 105.

Referring now to the utilization of the products, the metallized resin coated strands such as shown in Figures 3 and 4 may be cut into small strips and utilized in the same manner as aluminum stripping to interfere with the transmission of high frequency energy which is particularly important with relation to effecting the transmission of intelligence, as for example, with radar signals.

A nylon core coated with nylon itself, for example, is particularly useful in the field as nylon is very light, flexible, and not much affected as to its flexibility by the metal coating thereon, and may be applied in the general manner indicated hereinbefore. Due to its lightness it is supported readily in the air and is twisted into various configurations as it falls towards the ground to produce an excellent pattern for high frequency interference. The glass core material may also be employed, but is not as light and accordingly is not as useful except in those instances where the pattern is desired to be created for only a limited length of time.

The products of this invention are useful when chopped into short lengths and may be employed even in molding operations, for the metal coating is sufficiently thin and flexible to be shaped, and the metal itself in fact provides a lubricating value between the coated filaments, which inhibits their fracturing under curing pressure.

The metal itself is subject to coating in the usual way with varnishes, paints and the like, and the physical properties of the metal are in general similar to the same metal otherwise produced except for the feature of corrosion resistance which is extremely high with the metals deposited from the gaseous state, probably due to the purity of the metal—iron for example does not rust after long periods of exposure to atmospheric conditions, and aqueous solutions in contrast to the usual cast iron, for example.

With respect to the employment of nylon in the product described it is to be noted that nylon melts at about 482° F., and where employed as either a core material or a coating the temperature in processing should not exceed about 450° F. in order to maintain a suitable factor of safety. Nylon, however, like glass fibers is substantially flame-proof and will not burn except in a direct flame and

the combustion will be extinguished completely upon removal from the flame. Further the nylon is highly resistant to low temperatures and suffer practically no change in strength or elongation in the exposure over a considerable period at minus 112° F. for example.

The selection of the metal for use in the novel product of invention is of course dependent upon the process and product requirements, including the nature of the core and the thermosetting resin, and in general the following compounds are considered most suitable when used with or without inert carrier gases, the temperatures and pressures given in the table being suggested temperatures and pressures and not to be taken as limitations upon the inventive concept:

Plating material	System pressure, mm. of Hg	Temperature range of base material in degrees Fahrenheit
Ni(CO) ₄	0.5-760.0	350-450
Cr(CO) ₆	0.5- 1.8	375-450
Mo(CO) ₆	0.5- 1.8	450-650
W(CO) ₆	0.5- 1.8	525-775
Cu(C ₅ H ₇ O ₂) ₂	0.5- 1.8	400-750
(C ₄ H ₉) ₃ PAuCl	1.0- 3.0	250-400

Tungsten and molybdenum in general in carbonyl form decompose at temperatures which tend to preclude their use with nylon, for example, but are of definite value in conjunction with cotton and glass.

In connection with nylon and cotton, it is to be noted that extremely novel products result from the employment of the polyesters of the M. J. Hiler et al. application referred to hereinbefore, whether or not they are subsequently metallized. Thus nylon itself may be rigidized by the application thereto of a liquid composition comprising an alkyd resin and 2-vinyl pyridine having therein about 2% by weight of benzoyl peroxide. The same may be cured without application of metal at temperatures of between 50 and 200° C. to attain a transparent rigidized material, which may then be coated with metal to produce the product referred to hereinbefore.

The rigidity of the nylon coated material will vary with the time and temperature of cure and may be controlled in order to produce products useful for particular purposes.

The cotton coated with, for example, a polyester comprising a non-modified alkyd resin with 5-ethyl-2-vinylpyridine in which the weight of the alkyd resin to the weight of the vinyl substituted heterocyclic tertiary amine is about 100 parts of the resin to about 40 parts of the amine, the composition containing about 2 percent lauroyl peroxide as catalyst. In this case also the product will be transparent, subject to metallizing, rigidized and attractive in appearance since the cotton will clearly show through the resin.

It will be understood that this invention is susceptible to modification in order to adopt it to different usages and conditions and accordingly it is desired to comprehend such modifications within this invention as may fall within the scope of the appended claims.

I claim:

1. In a method of producing an electrical conductor composite body having a core of electrically non-conductive filaments, the steps of coating a plurality of strands composed of said fibers with a thermosetting resin, said strands being arranged in substantially parallel relation, vibrating the resultant resin-coated strands to spread the strands apart, and while thus separated depositing a coating of metal on the spread apart strands to metallize each strand substantially uniformly, said strands being metallized by depositing metal thereon from a heat-decomposable gaseous metal bearing compound which is brought in contact therewith and heat-decomposed while in contact with said resin-coated strands of material, and

heating the resultant coated strands to thermoset said resin coating.

2. An article of manufacture made in accordance with method of claim 1.

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