

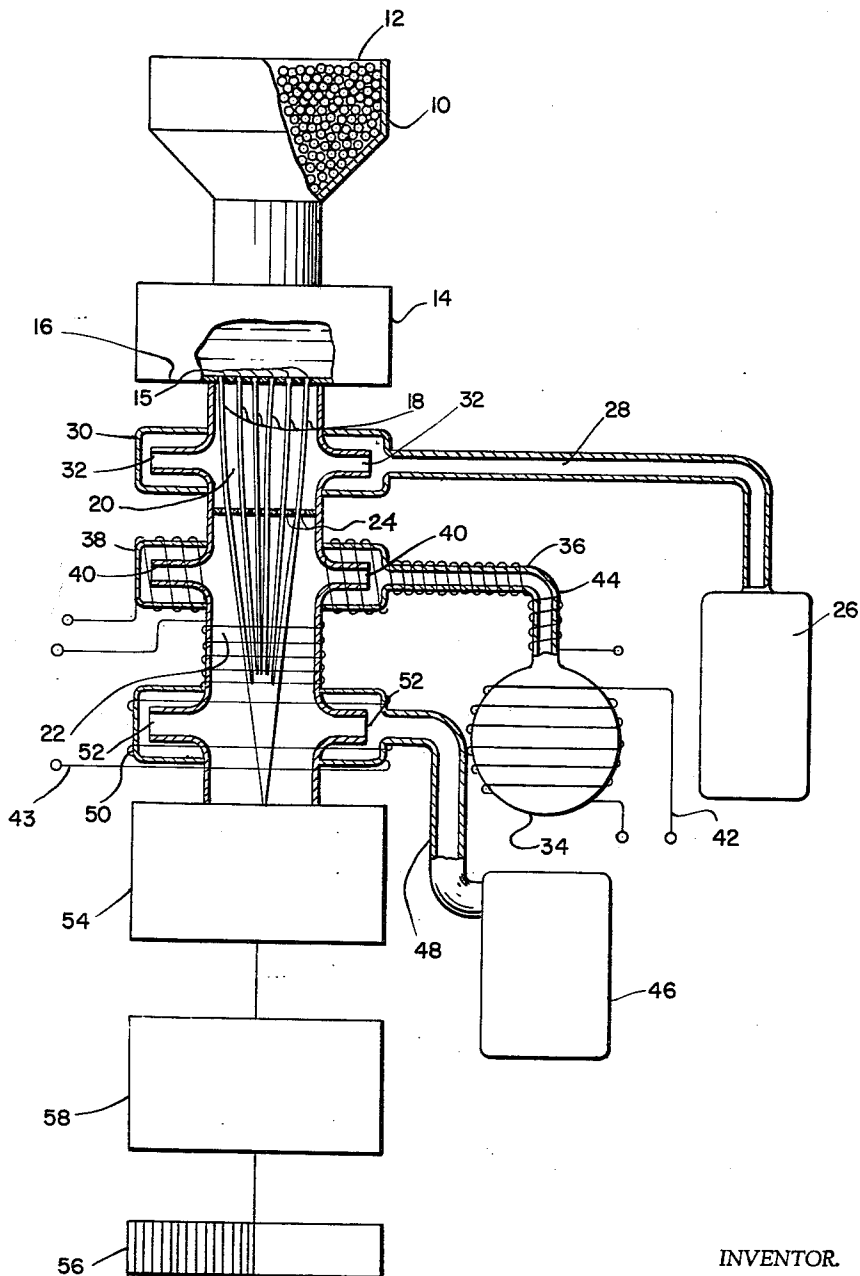
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PROCESS OF COATING VITREOUS FILAMENTS

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PROCESS OF COATING VITREOUS FILAMENTS
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The present invention relates to the manufacture of vitreous fiber products and, more particularly to processes and products involving vitreous fiber materials, particularly glass fiber materials, of unusual strength.

The tensile strength of vitreous, particularly glass, fiber may be utilized in a variety of ways. For example, the winding of glass fiber yarn about the circumference of rocket motors or other pressure vessels make substantial weight reduction possible. Ordinarily, however, the occurrence of flaws following of the drawing of glass fiber from the glass melt tends to weaken the glass fiber considerably below its theoretical fracture strength of millions of pounds per square inch. It is well known that glass and other vitreous materials have high compression but low tensile strength. Flaws in such fiber result from the mechanical action of bending stresses and strains and the chemical action of air and moisture. Both this mechanical and chemical action tend to concentrate at the surface of such fiber. The present invention contemplates cladding vitreous fiber in such a way as to reduce the occurrence of such flaws. The cladding material operates mechanically to prevent fracture by applying a compressive load which during bending of the fiber, adds to the residual compressive stress on the concave surface in a manner easily tolerated by the fiber and counteracts the tensile forces on the convex surface in a manner that protects the fiber from fracture. The cladding material operates chemically to seal the surface of the fiber from air and moisture.

The primary objects of the present invention are: to prevent the weakening of vitreous fiber by depositing thereon, immediately upon its formation and before its subjection to mechanical and chemical action, an extremely thin metallic coat from a metal bearing vapor; to diffusion bond such coated vitreous fibers into a yarn; and to provide pressure vessels and like about which such a yarn is wound.

Other objects of the present invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process involving the several steps and the relation and order of one or more of such steps with respect to each of the others, and the apparatus possessing the construction, combination of elements and arrangement of parts, which are exemplified in the following detailed disclosure, and the scope of which will be indicated in the appended claims.

For a fuller understanding of the nature and objects of the present invention, reference should be had to the following detailed description, taken in connection with the accompanying drawing, wherein there is shown a diagrammatic view of an apparatus for performing a process of the present invention.

Generally, the process illustrated herein involves the sequential steps of drawing filaments from a molten mass of glass through die apertures directly into a buffer zone having an atmosphere of a carrier reducing or inert gas, advancing the filaments through buffer apertures into a plating zone provided with a metal bearing vapor, collecting metal coated filaments so formed into yarn, diffusion bonding the filaments of the yarn together, and winding the yarn about a pressure vessel that is intended to withstand high pressures. In conventional fashion, the glass contains silicon dioxide fused with such materials as alkali oxides and alkaline earth oxides. The inert gas

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escapes through the buffer apertures to dilute metal bearing vapor in the plating zone to a desired concentration and to prevent the introduction of the metal bearing compound to the buffer zone and consequent deposition of the metal on the die through which the glass filaments are being drawn. The metal coat, which is deposited by reduction from or decomposition of the metal bearing vapor, ranges from .0001 to .001 inch in thickness. The filaments so coated may be diffusion bonded together in any suitable way such as by brazing. In order to secure a satisfactory bond between the metal coat and the surface to which it is applied, it is desirable that the coat be composed of a substantially pure metal, either elemental or alloyed, it being particularly important that the metal be substantially oxygen free. Preferably, the auxiliary gas is a reducing gas such as hydrogen or an inert gas such as argon or another noble gas or nitrogen. The mixture of auxiliary gas and metal bearing vapor ranges 1,000° C. and ranges in composition by total weight from 1 to 30% of the metal bearing vapor and from 99 to 70% of the auxiliary gas.

The gaseous metal bearing compounds preferably are selected from: carbonyls such as ferric carbonyl, molybdenum carbonyl, nickel carbonyl, chromium carbonyl, tungsten carbonyl and cobalt carbonyl; halides such as chromium chloride, tungsten chloride, molybdenum chloride, aluminum chloride, aluminum bromide, aluminum iodide, cobalt bromide, cobalt chloride, ferric chloride, germanium bromide, germanium chloride, manganese fluoride, chromium fluoride, nickel bromide, nickel chloride, tin bromide, tin chloride, tin fluoride, and titanium chloride; alkyls such as aluminum diisobutyl, aluminum triisobutyl, aluminum triethyl and molybdenum ditoluene; aryls such as chromium dibenzene, molybdenum dibenzene, vanadium dibenzene and vanadium di-mesitylene diiodide; olefins such as bis-cyclopentadienylnyls of iron, manganese, cobalt, nickel, rhodium and vanadium; esters such as cupric acetylacetonate, manganic acetylacetonate, titanyl acetylacetonate, platinum acetylacetonate, nickel acetylacetonate, dibutyl tin diformate copper formate and copper acetate; nitro compounds such as copper nitroxyl and cobalt nitrosyl carbonyl; hydrides such as antimony hydride, copper hydride, aluminum hydride, and tin hydride; and combinations and mixtures thereof such as alkyl and aryl carbonyls including benzene chromium tricarbonyl, phenanthrene chromium tricarbonyl, naphthalene chromium tricarbonyl, o-xylene chromium tricarbonyl, naphthalene chromium tricarbonyl, naphthalene chromium tricarbonyl, o-xylene chromium tricarbonyl, benzene molybdenum tricarbonyl, cyclo-octadiene molybdenum tricarbonyl; biscyclopentadienyl chlorides, bromides and diiodides of titanium, zirconium, hafnium, vanadium, molybdenum, tungsten and tantalum, cyclopentadienyl carbonyls such as cyclopentadienyl manganese tricarbonyl, bis-cyclopentadienyl carbonyls of molybdenum, tungsten or iron, carbonyl halogens such as sodium carbonyl bromide, ruthenium carbonyl chloride, and organo hydride compounds such as aluminum diethyl hydride and aluminum dimethyl hydride.

The drawing illustrates diagrammatically apparatus for forming glass yarn in accordance with the present invention. This apparatus comprises a funnel 10 containing a multiplicity of glass marbles 12. From funnel 10, marbles 12 are directed into an electric furnace 14 where they are heated to a molten liquid that is drawn through orifices 15 in a die 16 to produce filaments 18. The diameter of any filament 18 is accurately determined by regulating the viscosity and temperature of the molten mass, the size of orifices 15 and the rate of speed at which the filaments are drawn through the die. From the die, the fibers are advanced through a buffer zone 20 into a plating zone 22 through orifices 24. The auxiliary

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gas is supplied to zone 20 from a container 26 through a conduit 28 and a manifold 30, which communicates via a plurality of entrance ports 32 with buffer zone 20. Metal bearing vapor is supplied to plating zone 22 from a container 34 through a conduit 36 and a manifold 38, which communicates with plating zone 22 via a plurality of entrance ports 40 with plating zone 22.

The metal bearing vapor is produced in container 34 ordinarily by heating a decomposable metal bearing compound therewithin, as by means of a suitable electrical heating coil 42, and maintaining this vapor at predetermined temperature as by means of a suitable electrical heating coil 44 which envelops conduit 36 and manifold 38. The pressure of the auxiliary gas in buffer zone 20 is sufficiently great to prevent the entry of metal bearing gas from plating zone 22 through orifices 24 into buffer zone 20. A suitable pump 46, which communicates with plating zone 22 through a conduit 48 and a manifold 50 via exit ports 52, serves to remove the auxiliary and metal bearing gases from plating zone 22 after they have deposited metal on filaments 18. Plating zone 22 is heated as by means of a suitable electrical heating coil 43. In order to avoid imparting mechanical stress or strain to the filament, aperture 24 is of larger diameter than the filament. In other words, aperture 24 is of larger diameter than aperture 15 which is of the same diameter as the filament.

Gathering of filaments 18 into a yarn is effected by advancing the filaments within a gathering station 54 in contact with a pad (not shown) to which the filaments converge. Finally, the yarn is wound tightly as a helix about a pressure vessel 56. The filaments of the yarn are bonded together either in a heating chamber 58 in which they may be brazed or after they have been wound as a yarn upon pressure vessel 56.

The following non-limiting examples will further illustrate the present invention:

Example I

In one specific example of the foregoing process effected by the above described apparatus, glass fibers are drawn from the melt at a temperature of approximately 353° C. Hydrogen, heated to approximately 90° C., is introduced into buffer gas chamber 20 and the vapor of molybdenum carbonyl, heated to approximately 90° C., is introduced into vapor plating chamber 22. The partial pressure of the hydrogen is approximately five times the partial pressure of the molybdenum carbonyl. The total pressure is approximately 50 mm. Hg. The vapor deposition chamber is heated to a temperature of approximately 450° C. The flow rate through the vapor deposition chamber is approximately .5 cubic feet per hour. Each increment of glass filament is coated with a molybdenum layer approximately .001 inch thick. Filaments so treated are found to be characterized by a remarkable increase in tensile strength. A multiplicity of these filaments are collected into a yarn, wound about a tube and brazed at a temperature of approximately 1000° C. The end result is a tube capable of withstanding unusually high internal pressure.

Example II

The foregoing process is repeated except that the auxiliary gas is nitrogen and the metal bearing gas is chromium dicumene. After 20 minutes of plating time under otherwise substantially the same conditions as above, it is found that the filaments will not fracture to the extent that they had previously and that these filaments are quite ductile.

Example III

The process of Example I is repeated except that the auxiliary gas is nitrogen and the metal bearing gas is iron dodecacarbonyl, the nitrogen being initially at room temperature and the iron dodecacarbonyl being at a

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temperature of 135° C. Excellent plating on the glass filaments results.

Example IV

The process of Example I is repeated except that the auxiliary gas is nitrogen and the metal bearing gas is aluminum trichloride, both at a temperature of approximately 900° C.

Example V

Example I is repeated except that the inert gas is argon and the metal bearing gas is cyclo-octadiene molybdenum tricarbonyl, both at a temperature of approximately 110° C.

Example VI

The process of Example I is repeated except that the auxiliary gas is hydrogen and the metal bearing gas is copper acetylacetonate, both at a temperature of approximately 300° C. A clean coating resulted.

Example VII

The process of Example I is repeated except that the auxiliary gas is hydrogen and the metal bearing gas is aluminum hydride, both at a temperature of 100° C.

The present invention thus provides a continuous process by which glass filaments can be drawn from a suitable melt through a die in such a way that the die is protected from metal deposition and the glass filaments are subjected to metal deposition before being subjected to mechanical stress or strain or attacked by atmospheric oxygen or other contaminants.

Since certain changes may be made in the above process and apparatus without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted in an illustrative and not in a limiting sense.

What is claimed is:

1. The process of coating vitreous filaments formed from a molten mass in a melt zone, said process comprising the steps of drawing a vitreous filament from said melt zone through a first aperture in a die, advancing said filament from said first aperture directly into a buffer zone, advancing said filament from said buffer zone through a second aperture into a plating zone, advancing said filament from said plating zone into an exhaust zone, said melt zone, said buffer zone, said plating zone and said exhaust zone being disposed sequentially along a path, introducing an inert gas into said buffer zone, introducing a heat decomposable gaseous metal compound into said plating zone, said metal compound being selected from the class consisting of the metal carbonyls, metal halides, organometallics, metal hydrides and mixtures thereof, decomposing said metal compound in said plating zone in the presence of said inert gas in the temperature range from 100 to 1,000° C. in order to coat said filament with metal, exhausting said path at said exhaust zone so that the minimum pressure along said path is in said exhaust zone, said second aperture being larger in extent than said first aperture.

2. The process of claim 1 wherein said metal compound is iron dodecacarbonyl.

3. The process of claim 1 wherein said vitreous filament is composed of glass.

4. The process of claim 1 wherein said metal compound is composed of dodecacarbonyl and said vitreous filament is composed of glass.

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