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METAL COATED FIBERS AND TREATMENTS THEREFOR

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This invention relates to metal coated fibers and particularly to metal coated fibrous glass and treatments for enhancing the properties thereof.

In an attempt to adapt fibrous glass for certain new uses, the fibers have been coated with metals and alloys of metals such as have been described in copending applications. One or more of the following metals and alloys are applied by a suitable method as disclosed in copending applications having Serial Numbers 380,868; 398,544; 317,678; 318,786; 319,388, now Patent 2,772,-987; 391,184, now Patent 2,848,390; 399,239: lead, zinc, tin, copper, aluminum, silver, Wood's alloy, Rose's alloy, and various other alloys such as zinc-titanium, lead-copper, lead-tin, aluminum-copper, aluminum-gold, aluminum-zinc, aluminum-tin, lead-antimony, cadmium-zinc, copper-cadmium, tin-indium, silver-tin, silver-zinc, copper-zinc, antimony-tin, antimony-zinc, copper-aluminum, Dow metal, brazing and soldering alloys and the like. Metal coated fibers having secondary and tertiary coatings of electrodeposited metal are likewise treated by the methods and materials of this invention. In order to facilitate processing of metal coated fibers, it has been found necessary to treat the fibers with various agents to provide handleability.

Treatments for bare fibrous glass used in the textile arts have been described in the literature and generally comprise the application of size and binder compositions and the like. Some of these compositions are adapted for use with metal coated fibrous glass; however, a number of treatments especially suited for metal coated fibrous glass have been discovered.

It is an object of this invention to provide treatments for enhancing the properties of metal coated fibers.

It is an object to provide novel decorative effects on fibrous glass and products thereof.

It is an object to reduce the coefficient of friction of metal surfaces of fibers which slide one over the other.

It is a further object to provide methods of improving the physical properties and handling characteristics of metal coated fibrous glass in the form of textile materials.

It is an object to provide surface protective coatings for metal coated fibers.

The objects of this invention are attained by treating metal coated fibers with specific materials within the classification of lubricants, sizes, coating materials, acids, bases, oxidizing agents, adhesives or mixtures of one or more of these materials.

To improve the handling characteristics of metal coated fibers which are to be used in reinforcing other materials, it is necessary to group together a sufficient number of fibers in the form of a strand, yarn, roving or the like in order to obtain sufficient bulkiness so that the strand or other form can be handled in processing steps which follow the forming operation, i.e., twisting, plying and so forth. If a strand comprising a plurality of fibers is to be handled, it is generally necessary that some sort of a size or lubricating material be applied to provide strand integrity. The treating material must hold together individual fibers within a single strand with sufficient strength to provide integrity. However, adjacent strands should not be so firmly adhered one to another within a package that the package cannot be unwound.

It has been found that various lubricants may be used to treat the fibers or strands or yarns of fibers which have been metal coated. Application of a lubricant reduces the number of broken fibers in the strand and tends to hold any broken fibers adjacent to unbroken fibers in the strand and thereby provides strand integrity. Lubricants may be applied to the individual fibers as they are being formed but before they are gathered into a strand or they may be applied to the strand, cord, yarn or bundle of fibers during subsequent steps in the process of producing textile materials. Lubricants fall generally into one of several classes including liquid metals, various organic materials, metal films, inorganic materials, oils with or without additives and the like.

Included with the organic materials used as lubricants are those materials such as paraffin oil, solid hydrocarbons, tetrafluoroethylene, polyethylene, polystyrene, liquid fatty acids and the like. The fatty acids which may be used in treating metal coated fibrous glass include acetic, propionic, valeric, caproic, pelargonic, capric, lauric, myristic, palmitic, stearic and others. Such paraffins as nonane, decane, hexadecane, docosane and triacontane may be used. The alcohols which may be used include butyl, octyl, decanol and cetyl alcohol. Any of these organic materials may be applied by themselves or in mixtures such as in water dispersions or solutions or in solution in various solvents.

Fatty acids are especially adapted for application to metal coated fibers. The fatty acids listed above and preferably lauric or stearic acid are applied in combination with paraffin oil to provide a surface having a low coefficient of friction which is desirable for improving flex life and handling characteristics of fibers in the form of a strand or yarn.

Liquid metals such as mercury may be applied in minute quantities to provide a marked reduction in friction when silver coated fibers slide over adjacent silver coated fibers. The mercury wets the silver and forms an amalgam which acts as a lubricating surface.

Thin metal films may be formed upon the thicker coating of metal already on the fibers to provide a lubricant layer which gives longer flex life and improved strength. For instance, a thick silver coat may first be applied to the fibrous glass and then a relatively thinner deposit of lead or lead-tin or lead-indium alloy provides a metal film which lubricates the fibers. A thin film of copper can be formed upon a zinc coated fiber by including a small proportion of copper-sulfate in a size or treating solution which is applied to the zinc coated fiber. Replacement of part of the zinc with copper takes place. The copper-sulfate may be applied along with any conventional size such as a gelatine or starch size which includes wetting and emulsifying agents.

Conventional fibrous glass sizes are well adapted for treating metal coated fibers to provide the desired lubricity. The sizes used on bare fibrous glass include those having generally the following ingredients: a film former such as polyvinyl acetate or gelatine, a suitable lubricant, emulsifying and wetting agents and a liquid carrier which is preferably water. Water systems are generally preferred over solvent systems, since they are less expensive, less toxic and less dangerous.

Certain inorganic materials provide the lubricity necessary for improving handling characteristics, integrity and other physical properties of metal coated fibers in the form of strands or yarns.

Finely divided carbon, graphite, molybdenum disulfide and mica dispersed in suitable liquid carriers including oils, various petroleum fractions, water and the like are applied to provide a low friction surface. All of these materials provide a low coefficient of friction on the metal surface so that the flex life and the handling character-

istics are greatly improved. The liquid component of the dispersion may be a size or binder composition.

Oils may be applied including those classified as mineral, vegetable and animal oils. The mineral oils are especially adapted for application to metal coated fibers and certain materials which are classified as additives for oils are included in the treating materials for metal coated fibers. Long chain organic polymers including polybutenes, polyethylenes, vinyl polymers, polystyrenes and methacrylates may be added and the silicone materials including the short chain and ring polymers may be added to enhance the lubricating properties provided by the oils themselves.

Certain fluorolubes such as tetrafluoroethylene may be applied to the metal coated fibers either in a finely divided state or by passing the metal coated fiber or strand over a rod of tetrafluoroethylene while the metal coated fiber or strand is at an elevated temperature.

Chlorolubes may likewise be applied to the metal coated fibers as may other halogenated compounds. For instance, ethyl benzene which has been chlorinated under intense ultraviolet light may be applied to metal coated fibers to provide lubrication.

It has also been found beneficial to form metal soaps in situ upon the metal coated fibers or groups of fibers by application of a fatty acid to the metal surface and then heating. One percent lauric acid in paraffin oil is applied to the metal coated fibers at an elevated temperature. A hot bath of the paraffin oil is preferably used although the metal coated fiber may be at an elevated temperature also. Reactive metals such as copper, cadmium and zinc form metallic soaps which are very good lubricants. The metal soap and not the fatty acid provides the lubricity in this instance.

Although metal soaps formed in situ are greatly preferred since they are linked to the metal surface, metallic soaps as such are applicable in paraffin oil. For instance, one percent cadmium mercapto-palmitate in paraffin oil is applied to fibers coated with cadmium with a greatly reduced coefficient of friction resulting. Likewise, cadmium stearate, copper laurate, zinc laurate, or copper stearate may be applied to lubricate metal coated fibers. Soaps which are applied as such break down at lower temperatures than the softening point of the soap due to their increased solubility in the paraffin oil at elevated temperature and the weak attachment to the metal. Metallic soaps formed in situ are more firmly attached to the metal surface and can withstand appreciable deformation so that they are very protective to the surface.

Fatty acid esters are applied to metal coated glass surfaces to provide low friction surfaces. These esters react with the base metal to form a fatty acid by hydrolysis. For instance, ethyl stearate in a dilute benzene solution is applied to the metal coated fibers and by hydrolysis a small amount of fatty acid is formed which attacks the metal surface forming the metal stearate or other metal soap corresponding to the fatty acid ester used. These esters can lubricate metal surfaces at temperatures greater than the melting point of the ester itself. Other solvents than benzene which may be used with ethyl stearate include cyclohexane, octane and hexane.

It is believed that treating a metal surface with a fatty acid forms a monolayer which is relatively thin and wherein the acid chain is oriented so that it is normal to the surface of the metal provided the acid chain contains twelve or more carbons. Probably eight carbons are enough to provide the oriented, perpendicular chains if the metal surface is one of the reactive metals. The layers on top of this monolayer crystallize into typical crystalline forms of fatty acid and the hydrocarbon chains therein are inclined at an appreciable angle to the surface normal. These first monolayers are more firmly attached and it is believed that they are the most effective lubricating and protective means.

It has been noted that water and oxygen must be present before the metal is lubricated by the fatty acids such as lauric acid used as a one percent solution in paraffin oil. Clean metal surfaces are not lubricated and those subjected to air alone are generally not lubricated. Air saturated with water is believed to be necessary in order to provide an oxide film with which the fatty acid reacts to form the metal soap. The fatty acid soaps can be formed with magnesium, cadmium, zinc, copper, iron, aluminum and the like.

Phosphide protective films provide lubrication for metal coated fibers. Tricresyl phosphate reacts with metal to form phosphides which affect the frictional properties of the metal surfaces. One and one-half percent of tricresyl phosphate in white mineral oil is applied to metal coated fibers to provide a reduction in friction. Tricresyl phosphate may also be applied by including it as one of the ingredients in a conventional size or lubricating material. Very small proportions of tricresyl phosphate in the order of one percent or two percent or less provide the desired phosphide layer. Tricresyl phosphate is also applied along with either copper oleate or mesityl heptadecyl ketone in white oil.

Chloride and sulfide protective films likewise provide good lubrication. Copper or cadmium coated fibers which are exposed to dry chlorine gas and then covered with paraffin oil to protect the relatively thick coat of chloride have good lubricating properties. Ammonium polysulfide solution is used to treat metal surfaces to form a sulfide layer and then paraffin oil and better yet paraffin oil having a small percentage of fatty acid is used to protect the sulfide layer. A dilute solution of sodium sulfide may be used instead of the ammonium polysulfide to form the sulfide film. These sulfide layers provide low coefficients of friction up to 160° C. or higher.

Certain long chain paraffinic halides including octadecyl chloride, cetyl bromide and cetyl iodide may likewise be used to treat metal coated fibrous glass in order to improve the lubricity thereof.

Long chain acid chlorides, such as stearyl chloride applied in dilute solution in paraffin oil, provide low friction with metals even at 275° C. or higher.

A 0.1 percent solution of B,B' dichlor dicetyl selenium dichloride is applied to metal coated fibers and then heated to about 175° C. This lubricant provides a large reduction in friction. One percent of B,B' dichlor dicetyl selenium dichloride and one percent of stearic acid in paraffin oil is applied to metal coated fibers to provide a large reduction in friction. Other compounds containing the selenium chloride group seem to give like results. These materials are good for use with copper and cadmium coated fibers of glass.

Sulfurized oleic acid and sulfurized cetene may be applied advantageously to metal coated fibers such as silver coated fibers to materially reduce the coefficient of friction between the metal surfaces. These materials provide a low coefficient of friction between adjacent fibers within a strand over a wide range of temperatures, i.e., from about 20° to 300° C.

Pure long chain sulfur compounds containing a replaceable hydrogen atom such as cetyl mercaptan, cetyl sulfonic acid, di-thio tridecyclic acid, alpha mercapto palmitic acid and the like provide lubrication on copper and cadmium coatings on fibrous glass.

It is desirable to improve the tensile strength of the final cord or strand by a tensioning treatment after applying one of the above disclosed lubricants. The individual metal coated fibers are aligned and compacted by such means, the alignment and orientation of the fibers being facilitated by the presence of a suitable lubricant on the surface of the fibers. After the fibers are aligned, each of them is in a position to carry its share of any load which may be imposed on the cord or strand.

In order to lower the coefficient of friction, it is desirable to form an outer layer of oxide upon the metal coated fibers. The coefficient of friction is reduced when

the metal surface is allowed to form an oxide; therefore, it is desirable in certain instances to direct oxygen to the metal coated surface which has been newly formed in order to accelerate the oxidation. The fibers having oxidized surfaces may be used as formed or may be further treated with lubricants or other coatings. Anodizing of aluminum surfaces provide decorative oxide coatings on fibrous glass. Oxidation of other metals by electrochemical methods provides beneficial properties. Oxidation of copper coatings has provided increased flex life for fibers.

Acids or bases may be used for treating the metal surfaces of fibers. For instance, a mineral acid may be used for etching a metal coated fiber. Chromium is etched with dilute sulfuric acid to form pockets which are suitable for holding a lubricant such as mineral oil or the like. This oil provides boundary lubrication when adjacent fibers within a strand rub together. It is desirable in other instances to etch the metal surface in order to form small nodules upon the metal surface to materially reduce the contact area between adjacent contacting fibers. After etching, it is desirable in some instances to coat the etched surface with the same or an unlike metal. The second metal is preferably a hard metal such as chromium.

The application of secondary coatings of metal by electrodeposition or other suitable means onto the metal coated fibers is desirable in order to provide a strong underlying body of metal over which lies a thin film of a metal that acts as a lubricant. For instance, chromium and rhodium give exceptionally good frictional resistance, and for this reason, are especially adapted as coating materials for other metal undercoats such as aluminum, nickel, zinc and others.

Various textile sizes are used in treating metal coated fibers and fibrous products. A size comprising about five percent gelatine, five percent vegetable oil or animal oil, a small proportion of emulsifying agent and the remainder being water is well adapted for treating metal coated fibers within a strand to provide integrity and good handling characteristics.

The disclosed lubricants including the organic materials such as the liquid fatty acids, the inorganic materials including graphite and the like, the oils including the mineral oils and the silicones etc., the chlorolubes and fluorolubes, the metal soaps and the like may be added to size materials which act as the carrier, the lubricants being an additive or a major ingredient as may be desired.

Other fibrous glass textile sizes having as an ingredient such materials as synthetic latices, polyamides, vinyl polymers, siloxanolates, silicones, tetrafluoroethylene, methacrylato chromic choloride, stearato chromic chloride and others may be used as the carrier for the lubicants disclosed. Generally the sizes used are water systems; however, solvent systems may be used.

Certan sizes have been found to be especially adapted for giving integrity to metal coated strand.

A size comprising one-half percent dodecyl amine acetate and one-half percent gelatine is applied to metal coated fibers in the forming operation. This size allows unwrapping of the packages of strand formed of the metal coated fibers without attendant ringers caused by fibers which become detached from the strand and snarls caused by broken fibers protruding from the strand. A small quantity of 0.01 N or 0.001 N copper sulfate may be added to the above size in order to replace part of the metal already deposited on the glass. For instance, zinc coated fibers can be provided with a very thin outer film of copper by including a small proportion of copper sulfate in the size.

A size comprising the following ingredients by weight is used in treating zinc coated fibers:

Example I

Ingredient	Proportion, percent	Range
Gelatine	0.5	0.25 to 0.5
Polyethylene glycol (Carbowax 1500)	0.25	0.1 to 0.5
Propylene glycol	0.05	0.025 to 0.15
Water	99.2	

The propylene glycol may be replaced with other humectants such as glycerine or any suitable glycol. The water is necessary in order to plasticize the gelatine so that the gelatine does not form a hard cake which hinders unwinding of the package.

The following sizes have been applied to 102 filament strands coated previously with zinc or zinc alloy.

Example II

Ingredient: Proportion, percent

- Gelatine ---------- 0.3
- Sulfonated hard fat with humectant ---------- 0.2
- Tetraethylene pentamine stearic acid condensate 0.2
- Remainder water.

Example III

Ingredient:

- 2-chlorobutadiene 1,3 (solids basis) latex---- 0.3
- Tetraethylene pentamine stearic acid condensate 0.15
- Starch ---------- 0.10
- Remainder water.

Example IV

Ingredient:

- Butadiene-acrylonitrile (solids basis) latex---- 0.3
- Tetraethylene pentamine stearic acid condensate 0.15
- Starch ---------- 0.10
- Remainder water.

These sizes are very satisfactory for the purposes of this invention and is should be understood that they may be used with various other metals than zinc with equally good results.

Various other coatings may be applied to the metal coated fiber when the fiber or strand is to be combined with materials such as resins, rubber and the like. Certain size compositions are applied to give strand integrity and good handleability as disclosed. To the size compositions may be added other dispersions of resin-like or rubbery polymerization products obtained by polymerizing monomeric materials such as butadiene-1,3, isoprene, 2-chlorobutadiene-1,3, isobutylene or interpolymers of these monomers with interpolymerizable monomers such as styrene, acrylonitrile, methacrylonitrile, methyl methacrylate, methyl acrylate, ethyl methacrylate, 2-vinyl pyridine, and others.

Butadiene-styrene copolymers are generally rubbery but copolymers high in styrene (styrene-butadiene copolymers) tend to be tougher and more resin-like. Either the resin-like or rubber-like compounds may be used as additives for the size compositions.

Resinous products such as phenol formaldehyde may likewise be added to the size compositions, preferably in the form of finely divided dispersions.

Metal coated fibers or bundles of fibers which may or may not have been treated with a size are coated with adhesive compositions before they are combined with rubber, resin or other materials which are to be reinforced. Rubber adhesives comprising a rubbery component and a resinous component in solvent systems are utilized to treat metal coated fibers before they are combined with rubber to produce glass reinforced rubber products. Conventional rubber adhesives comprising resorcinol-formaldehyde latex are used likewise to achieve the desired bonding effect between the reinforcing fibers and the body or carcass of rubber.

Rubber adhesives are readily applied by dipping the metal coated fiber in a latex or cement bath or by spreading a cement bath upon a fabric woven of metal coated

fibers. The cement which comprises compounded rubber in an organic solvent is directed upon the surface of a woven fabric or a weftless fabric and the excess removed by a doctor blade. The cement is then dried by applying heat to remove the solvent.

A strand or a cord comprising metal coated fibrous glass when passed through an adhesive bath picks up sufficient adhesive to fill the interstices of the strand and provide a coating over the strand itself. The rubbery component of the adhesive may be vulcanized at the same time that the glass reinforced rubber product is vulcanized or molded.

Adhesive compositions comprising natural rubber latex, caustic potash, zinc oxide, sulfur and suitable accelerators and the like are used to treat metal coated fibers and these fibers are then combined with rubber by calendering methods or other suitable means and the resulting product is heated for a sufficient time to effect vulcanization of the rubber in the adhesive and that in the body or carcass of the glass-reinforced rubber product.

Chloroprene latex adhesives comprising zinc oxide, accelerator and neoprene latex likewise may be used.

Good adhesion of metal coated fibers to rubber during vulcanization is also achieved as follows. To the metal coated fibers is applied a metal to rubber adhesive such as Ty Ply Q which is a chemical derivative of rubber dispersed in a volatile solvent. The coated metal is then combined with a suitable sheet of natural or reclaimed rubber and the composite product is heated in a mold under pressure to vulcanize the rubber.

Chloroprene and butadiene-acrylonitrile rubbers are bonded to metal coated fibers during vulcanization by using Ty Ply S which is likewise a chemical derivative of rubber in volatile solvents. Ty Ply S is adapted for use with synthetic rubber.

Metal coated fibers are provided with an outer coating of rubber by electrodepositing rubber thereon by the Sheppard process disclosed in United States Patents 1,589,324 to 1,589,330, inclusive, and others. Rubber is electrodeposited on lead, cadmium, zinc, tin, antimony and alloys of these metals which has been applied to fibrous glass by passing the metal coated fibers through an electroplating bath comprising the following ingredients:

Ingredients:	Percent of total solids
Rubber latex	53.3
Sulfur	2.0
Zinc oxide	10.0
Whiting	30.0
Carbon black	2.0
Paraffin wax	2.0
Tetramethyl thiuram disulfide	0.2
Gum arabic	0.5
	100.0

Rubber so deposited has great strength. Fibers so treated are readily combined with rubber in the carcass of a tire, belt or other rubber product.

The metal coating imparts abrasion resistance and greater strength to the fibrous glass and the electrodeposited outer rubber coating which is very strong adds further to the abrasion resistance of the individual fibers and provides an outer surface on fibers, strands, cords, bundles of fibers or fabrics which is very compatible with rubber. Metal coated fibers having an outer layer of electrodeposited rubber are combined with a rubber carcass by conventional methods such as by applying suitable rubber adhesives to the rubber surfaces to be joined followed by a vulcanization step.

When iron or iron alloys are used to coat the fibrous glass, surface treatments such as nitriding, phosphiding or sulfurizing or combinations of these processes may be used to provide additional surface hardness or other improved physical properties.

Metal coated fibers are provided with an outer coating of plasticized vinyl polymers such as polyvinyl chloride and the like using calendering or extruding processes. Metal coated fibers are coated with plastisols, highly plasticized vinyl polymers, by drawing the fibers through a bath of plastisol and then stripping the excess plastisol by passing the fiber through a die. Solvent solutions of vinyl polymers may be applied by dipping or other coating processes also. Strands, bundles of fibers, yarns or the like may be so treated.

Metal coated fibers are dyed by coating the fibers with a metal such as aluminum, chromium, iron, tin, antimony, copper or any other metal which forms soluble salts. A salt of the metal is then produced by treating the metal coat with the appropriate acid and this metal salt is reacted with a mordant dye to form an insoluble metal compound upon the surface of the fiber.

Various other treatments for metal coated fibers are included within the spirit and scope of the appended claims.

I claim:

1. A size composition suitable for metal coated fibers in a textile strand comprising the following ingredients in the indicated approximate proportions expressed in weight percent, 0.3 percent of a rubber latex, 0.15 percent of tetraethylene pentamine stearic acid condensate, 0.1 percent starch and the remainder water.

2. The size composition of claim 1 wherein the rubber latex is 2-chloro butadiene 1,3.

3. The size composition of claim 1 wherein the rubber latex is butadiene acrylonitrile.

4. Process of treating metal coated filaments to form an integral bundle of filaments for reinforcing an elastomer comprising applying a size to the filaments to form a coating upon the metal coating and to effect a union of the filaments in the form of an integral bundle, said size comprising rubber latex, starch, tetraethylene pentamine stearic acid condensate, and water.

5. Method of treating zinc alloy coated filaments to form an integral bundle of filaments for reinforcing rubber comprising applying a rubber latex size to the filaments to form a coating upon the zinc alloy and to effect a union of the filaments in the form of an integral bundle, said size comprising rubber latex, starch, tetraethylene pentamine stearic acid condensate and water.

6. Method of treating textile strand comprising glass fibers coated with metal comprising applying to the metal coated fibers a size composition which includes 0.3 percent by weight of butadiene-acrylonitrile latex, 0.15 percent by weight of tetraethylene pentamine stearic acid condensate and 0.10 percent by weight starch, the remainder being water.

7. Method of treating textile strand composed of glass fibers coated with metal composed of applying to the metal coated fibers a size composition which includes 0.30 percent by weight of 2-chloro butadiene 1,3 latex, 0.15 percent by weight of tetraethylene pentamine stearic acid condensate and 0.10 percent by weight of starch, the remainder being water.

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