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BINDER AND COATING MATERIALS AND
METHOD OF PRODUCING THE SAMERussell E. Palmateer, Emporium, Pa., assignor
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Mass., a corporation of MassachusettsNo Drawing. Application March 18, 1935,
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This invention relates to coating methods and coating preparations, and more particularly to the coating of articles with materials which require the use of binders.

A principal object of the invention is to provide a method of coating articles by employing a binder which after suitable heat treatment possesses characteristics similar to the characteristics of the final coating material proper.

Another object of the invention is to provide an improved method of coating articles which are intended for use in a vacuum, such for example as in lamps, radio tubes or the like.

Another object is to provide an improved method of providing an article with a coating which is intended to be used at incandescence.

While the invention is not limited to the coating of any particular article or material, it is peculiarly advantageous in the coating of wire and also in the coating of insulators. Heretofore in coating wire whether in filamentary or ribbon form, it has been the common practice to employ a binder material carried by a liquid or liquids consisting for the most part of organic materials, such for example as nitro cellulose carried in amyl acetate or the like. I have found that such binders are undesirable, and in certain cases actually detrimental, particularly where the article to be coated is to be used or processed at a relatively high temperature. For example in the case of incandescent filaments which are provided with an insulating coating or with an electron-emissive coating, the carbonaceous constituents of the usual binders in many instances are not completely removed and even if entirely removed, the heat of processing causes some reaction with the metal of the filament whereby the latter becomes brittle and loses, to an appreciable degree, its tensile strength. Furthermore the carbonaceous products which are not entirely removed are undesirable when the filament must have a uniform insulator coating.

Accordingly another principal object of this invention is to provide a method of providing a filament, whether in wire or ribbon form, with a coating which is substantially entirely free from organic materials.

Another object of the invention relates to an improved binder and process of preparing the same.

Another object relates to a binder consisting substantially entirely of inorganic material or materials, and also to the process of preparing the same.

Another object is to provide a method of pro-

viding an article with a coating of material having specially chosen electrical characteristics, by employing a bonding agent for the said material and a binder, which binder responds to heat treatment to provide a constituent which has substantially the same electrical characteristics as those of the final coating material proper.

A feature of the invention relates to the method of preparing an inorganic binder liquid having substantial stickiness or tackiness, and comprising in part at least a metal and an acid radical.

Another feature relates to an inorganic liquid having substantial stickiness or tackiness suitable for binder purposes, the liquid having a pH range of the order of from 3.9 to 5.1.

A feature of the invention relates to a method of preparing a coating of metallic oxide employing an inorganic binder which binder comprises, in part at least, a metal having substantially the same electrical properties as the metal of the oxide coating.

Another feature relates to a liquid having substantial stickiness or tackiness suitable for binder purposes, and consisting mainly of a hydrolyzed inorganic metallic salt.

A further feature relates to the method of preparing an inorganic liquid metallic salt having substantial tackiness or stickiness, which when dry is mechanically strong, and when ignited leaves a residue having high electric insulating properties.

A further feature relates to an inorganic friable material having the apparent composition of a hydrolyzed nitrate.

A further feature relates to the method of preparing hydrolyzed aluminum nitrate for use as a binder in the coating of articles generally.

A still further feature relates to the organization and succession of steps whereby an improved insulator or electron-emissive coating may be produced.

Other features and advantages of the invention not specifically enumerated will be apparent after a consideration of the following detailed description and the appended claims.

While the invention will be described herein in connection with the coating of a wire or ribbon filament, and the coating of a mica insulator, it will be understood that this is done merely by way of explaining the inventive concept and not by way of limitation to these particular materials.

More particularly considered the invention contemplates the utilization of a binder consist-

ing for the most part of a material having the apparent composition of a hydrolized metallic nitrate but which is so prepared that when subjected to drying treatment it retains its stickiness and tackiness. In achieving this result it has been found that there are certain limits to the proportions of constituents necessary in the preparation so that when heated the material neither crystallizes or gels but does retain its tackiness or stickiness. Thus the preferred procedure is to add to an acid a metal in respective molar proportions in excess of those necessary to produce a normal or neutral salt of the metal and acid. As one typical example metallic aluminum preferably, although not necessarily, in comminuted form may be treated with nitric acid in the proper amount so that there results a viscous solution having the apparent composition of a hydrolized nitrate of aluminum. Upon continued evaporation of this liquid, it becomes correspondingly more viscous and finally assumes a clear non-crystallized solid state. This clear solid upon further drying over a water bath becomes brittle and cracks so that it may be readily comminuted or reduced to powdered state, this powder being readily soluble in water or in an alcohol to produce a viscous liquid. This water or alcohol solution may then be used for any purpose for which a liquid binder is ordinarily used, for example to hold the particles of insulating material or electron-emissive material on a support or article to be coated, while the latter is being subjected to heat treatment. The powder upon being ignited leaves a residue of aluminum oxide equal approximately to 41% of the weight of the powder.

As pointed out hereinabove, it is important that the proportions of the acid and the metallic aluminum be so regulated that the clear solid which results from heating is neither crystalline nor in gel state. If too much acid is used the resultant material upon drying, crystallizes and loses its stickiness or tackiness and if such material were used as a binder in coating operations, the coating would not be mechanically strong but would tend to powder off, particularly where the coated article is a filamentary wire or ribbon. On the other hand, if the acid is used in insufficient amount, the material when dried will have an increased tendency to gel. Preferably therefore and in accordance with the invention, the acid and metal are mixed in such a proportion that the resultant dried product when added to water in sufficient amounts is capable of producing a pH in the range between 3.9 and 5.1.

As an example of one proportion of constituents that has been found to produce a product with the desired characteristics may be mentioned, one part by weight of metallic aluminum with 4.55 parts by weight of nitric acid, which is approximately one and one-half times the amount of aluminum necessary to produce a normal solution of $\text{Al}(\text{NO}_3)_3$. Approximately expressed, the preferred proportion is one molar quantity of metallic aluminum with two molar quantities of nitric acid, or 1.95 grams of metallic aluminum to ten cubic centimeters of nitric acid (sp. g. 1.4 and containing 65% nitric acid). Upon completion of the chemical reaction between the aluminum and the nitric acid, there is produced a liquid which upon evaporation forms the brittle solid material described above. It will be understood, of course, that the invention is not limited to the specific proportions of aluminum and nitric acid just mentioned. For

example desirable results may be attained by employing as low as one and one-half molar quantity of aluminum to one molar quantity of nitric acid, and as high as one molar quantity of aluminum to three molar quantities of nitric acid. That is, the aluminum content may be varied from as low as one and one-half to three times the amount of aluminum necessary to produce the normal aluminum nitrate salt. While the exact constitution of the resultant material is not directly ascertainable it shows upon analysis to have a similar composition to hydrolized aluminum nitrate, however the chemical and physical properties indicate that it is probably aluminum hydroxide, peptized by the nitrate ion present.

The brittle material obtained in the manner described is readily soluble in water or in an alcohol to produce a viscous liquid. When dissolved in water the material possesses greater stability than when dissolved in an alcohol, and furthermore the instability of the alcohol solution increases with the degree of dilution thereof.

When an alcohol solution of sufficient concentration to prevent gelling is used, this solution may be subsequently diluted with an alcohol saturated with aluminum nitrate, without any substantial danger of the solution gelling when heated. In the case of water solutions, it is possible to carry the concentration of the solution to as low as one gram of aluminum to 2.5 grams of nitric acid. While the viscous liquid resulting from the aluminum and nitric acid may be maintained at approximately 100° C. for a considerable period of time, long-continued heating at this temperature may induce a slight decomposition of the brittle material and it may be necessary to digest the remaining undecomposed material with water for some time before dissolving.

While the alcohol or water solution of the powder previously prepared as above described, may be used as a binder, it will be understood that this solution may also be used without any additional materials to provide an insulator coating. This results from the fact that when the solution is sprayed, brushed, dipped or otherwise applied to the metal to be insulated, and the coating is raised to the ignition temperature, or to a temperature sufficient to drive off water and the oxides of nitrogen and other gases produced by the heat, there results a uniform coating consisting substantially entirely of aluminum oxide which possesses high electrical insulating properties.

When the alcohol solution is to be used as a binder it may have incorporated therein a comminuted material or materials preferably in finely powdered form. The choice of these materials will depend to a large extent upon the characteristics desired in the finishing coating. For example if a high electrical insulation coating is desired such as is required in the heaters of certain types of radio tubes, a quantity of powdered insulating material is added to the previously prepared solution. For this purpose an oxide or mixture of oxides of aluminum, beryllium, titanium, zirconium may be employed; or a silicate or silicates of magnesium, aluminum, beryllium, titanium, zirconium, may be employed. Preferably the major part of the said insulation material comprises one or more of the above-mentioned oxides and a smaller quantity of one or more of the silicates mentioned. Thus for example when the solution is formed by the action of aluminum and nitric acid in the proportions

specified, the added insulating material may consist of aluminum oxide and magnesium silicate, care being taken that the proper amount of insulating material is added so as to provide the desired consistency to the coating liquid. This consistency will of course be determined by the particular method of coating employed viz. spraying, dipping, cupping, brushing, etc., and also by the size of the area to be coated.

After the coating has been properly applied, the coated article is heated to a suitable temperature for a sufficient time to drive off the water content and any gases that are produced. When the article being coated is a wire filament such as is ordinarily employed in radio tubes, preferably the heating is effected in air at a temperature at approximately 730° C., although any other well-known heating procedure may be employed. Thus the coated article may be fired in a hydrogen furnace at a suitable temperature where the silicates bond the particles of the aluminum oxide together, and in the case of a coated filament, a suitable temperature for this purpose may be 1600° C. If desired, the firing may be effected in a vacuum furnace at a temperature for example of about 500° C. In any event the article is preferably heated to such a temperature that the heating of the binder results in a residue of aluminum oxide and the temperature is preferably such that the bonding agent such as silicon dioxide bonds the particles of the aluminum oxide together without requiring actual fusion of the aluminum oxide itself. It will be understood of course that the above procedure may be cyclically repeated so as to increase the thickness of the insulating coating.

Where the finished article for example a filament is required to have an electron-emissive coating, the binder solution instead of having incorporated therein an insulating material will have incorporated one or more materials which when properly processed result in a coating having pronounced electron-emissive properties. Thus the above described binder solution may have added thereto appropriate quantities of a carbonate or carbonates or other compounds of the alkaline earth metals which upon subsequent heat treatment break down to form the emissive oxides. In certain specific cases it may be desirable to add to the solution a suitable quantity of a bonding agent, e. g., silicon dioxide, so that when the material is applied to the usual filament or tubular cathode sleeve, the emissive oxides are firmly bonded thereto, although the addition of such insulating bonds very decidedly reduces the emission from its normal value.

In certain cases it is desirable to provide insulator members such as mica sheets or discs with a coating of refractory insulation for example aluminum oxide, and the binder prepared as described above may be used for this purpose. Thus, a suitable quantity of the dry powder resulting from the action of nitric acid and aluminum, is dissolved in a suitable quantity of alcohol such as a methyl alcohol and the mixture stirred until the solution is complete, as indicated by its completely clear character. This solution may be subsequently diluted to the desired concentration by adding methyl alcohol, the concentration of the solution depending to a large degree upon the size of the mica part to be coated, and the thickness of the coating desired. The mica parts having been previously freed from oil, grease and dirt by any wellknown process are then placed in a suitable foraminous container,

e. g., an aluminum mesh cage or any similar cage which is not attacked by the alcohol or nitric acid. The cage containing the parts is then completely immersed in the above described solution which is preferably contained in an earthenware container or any similar container which is resistant to nitric acid and alcohol.

The foraminous container having the coated parts therein, is then removed from the solution and allowed to drain thoroughly. When completely drained the mica parts are then loaded into a suitable container such as a glass bulb which is mounted for rotation or tumbling, and into which hot air may be forced at for example a pressure of three pounds per square inch. The bulb and its contents are rotated or tumbled for approximately thirty minutes and until the coated micas no longer cling to gether or to the walls of the bulb.

The coated micas are then removed from the bulb and heated for several hours in a suitable oven preferably, although not necessarily, an electric oven open to the air. The duration of this heating is largely determined by the thickness of the coating, and may last until substantially all the volatile material has been removed. It will be understood of course that instead of relying upon the residue to provide the insulator coating, insulating powdered materials may be added to the binder solution as described above in connection with the coating of filamentary members. It will be understood of course that mica parts have been chosen merely as an illustrative, and that the above method may be employed for the coating of any similar material or articles.

While the above described methods specify that the binder is prepared preferably by the action of nitric acid on aluminum powder, it is understood that the binder may be prepared by employing beryllium, magnesium, titanium, zirconium and similar metals. Furthermore, while metallic aluminum has been described, it will be understood that any combination of aluminum with any one or more of metals such as beryllium, magnesium, titanium or the like, may be employed.

Various changes and modifications may be made herein without departing from the spirit and scope of the invention. Thus if it is desired to produce a binder which upon being ignited produces a residue of a refractory metallic oxide, a normal salt of the metal, e. g., aluminum nitrate, beryllium nitrate, etc., may be hydrolized by suitable means for example by heating with water, to a composition suitable for use as a binder, that is one having appreciable tackiness or stickiness. The powdered material resulting from the continued heating of this hydrolized normal salt may then be used in the same manner as the powder described above resulting from the action of nitric acid on the various metals set forth.

A product possessing the desired binder qualities may also be made by treating an aqueous solution a metallic nitrate such as aluminum nitrate, that is, the normal or neutral metallic salt e. g., $\text{Al}(\text{NO}_3)_3$ with a quantity of the powdered metal e. g., aluminum equal to approximately twice the weight of the metal in the quantity of metallic nitrate used. Upon digesting this mixture, a viscous aqueous solution is obtained which possesses substantially identical properties with the product described above obtained by dissolving powdered aluminum in nitric

acid. While the proportions of material given herein show that the final product should contain a ratio of aluminum to nitrogen of approximately one atomic weight of aluminum to one atomic weight of nitrogen, products which depart somewhat from this ratio may be used as binders and coating material although the desired viscosity of the solution is obtained when the ratios are approximately those as specified.

10 While it is preferred in accordance with the invention to employ a nitrate of aluminum, beryllium, magnesium, titanium, zirconium or similar metals to produce a binder liquid having a pH range such as set forth above, it will be understood that any inorganic salt or inorganic compound of these metals may be employed so long as the salt or compound is capable of reacting with the corresponding metal to produce a salt having characteristics similar to those described above in connection with the use of aluminum nitrate. For example, one of these metals such as aluminum may be mixed with aluminum chloride or aluminum sulphate in the proportions above set forth and the mixture subjected to the treatment described to produce a substance in which the respective molar proportions are in excess of those necessary to produce a normal or neutral salt of the acid and metal which may then be dissolved in water or alcohol to produce a binder liquid having the desired pH range.

The expression hydrolized nitrate as employed in the specification and claims means a material having upon analysis the chemical and physical properties of a metallic nitrate peptized by the nitrate ion and in which the nitrogen is present with the metal in substantially equal atomic proportions. In this respect therefore the material has the apparent composition of a partially hydrolized nitrate wherein the oxyacid of nitrogen is present with the metal in substantially equal atomic proportions. Likewise the expression refractory metal oxide means oxides of the metals in the group including aluminum, beryllium, magnesium, titanium and zirconium.

What I claim is:

1. A binder material for coating articles with a refractory insulator comprising partially hydrolized aluminum nitrate in powder form, said material being soluble in water to produce a tacky liquid when heated.

2. The method of making an inorganic binder which includes the step of adding powdered metallic aluminum to a normal aqueous solution of aluminum nitrate, the quantity of aluminum being approximately twice the quantity of the combined aluminum in the nitrate.

3. The method of preparing a liquid suitable for use as a binder which includes mixing nitric acid and powdered metallic aluminum in the proportion of not less than one and not more than two and one-half parts of nitric acid to one part of aluminum.

4. The method of preparing a liquid suitable for use as a binder which includes mixing nitric acid and metallic aluminum in the proportion of approximately one molecular part of aluminum to approximately two molecular parts of nitric acid, heating the mixture to reduce the solute to a solid form, and dissolving said solute in water in the ratio of approximately 32 grams of said solid to approximately 250 cc. of water.

5. The method of providing a body with an electron-emissive coating which comprises subjecting a metal whose oxide is refractory to the

action of nitric acid the quantity of metal being in excess of that required to produce a normal nitrate, reducing the solute to solid form having the apparent composition of a hydrolized nitrate, dissolving the solute, mixing a carbonate of an alkaline earth metal with the latter solution, applying the mixture to the body, and baking said body to solidify said coating thereon.

6. A binder material for use in the manufacture of parts for electron-discharge tubes and containing a metal of the group aluminum, beryllium, titanium, zirconium, together with nitrogen in substantially equivalent proportions, said material being free from organic constituents and possessing substantial tackiness when dried and dissolved in water and leaving a residue of high electric insulating properties when ignited.

7. An insulating material for use in the manufacture of parts for electron-discharge tubes and containing a metal of the group consisting of aluminum, beryllium, titanium and zirconium, together with nitrogen in the form of an oxyacid, the metal and nitrogen being present in substantially equivalent atomic proportions to impart a tackiness to the material, and a quantity of a comminuted oxide of a metal of said group in uncombined form.

8. A binder material for use in the manufacture of parts for electron-discharge tubes and containing nitrogen and a metal of the group aluminum, beryllium, titanium, zirconium, the nitrogen and metal being present in approximately equal atomic proportions, said material being soluble in alcohol and possessing appreciable tackiness, and when ignited leaving a residue consisting substantially entirely of an oxide of the metal which oxide has high electric insulating properties.

9. A viscous binder liquid containing a metal of the group aluminum, beryllium, titanium, zirconium, with nitrogen present as an oxyacid, the metal and nitrogen being present in approximately equal atomic proportions, and dissolved in water to form a viscous tacky material having a pH range between 3.9 and 5.1.

10. The method of preparing a binder material free from organic constituents suitable for use in the manufacture of parts for electron-discharge tubes which includes the steps of dissolving in nitric acid a quantity of a metal of the group aluminum, beryllium, titanium, zirconium, the metal being added in excess of that required to produce normal $\text{Al}(\text{NO}_3)_3$ but not in excess of equal molecular parts of aluminum and nitric acid, and heating the solution until it acquires appreciable tackiness without gelling.

11. The method of preparing an inorganic binder material for providing articles with an electric insulating coating which includes hydrolyzing a solution of a normal nitrate of a metal of the group aluminum, beryllium, titanium, zirconium, until the nitrogen and metal are present in substantially equal atomic proportions, and then heating the solution at approximately 100°C . until a brittle water soluble material is produced.

12. The method according to claim 11 in which the brittle material is dissolved in water to produce a viscous tacky liquid.

13. The method according to claim 11 in which the brittle material is dissolved in water to produce a pH in the range between 3.9 and 5.1.

14. The method of preparing a tacky binder for use in providing articles with a coating of high electric insulation, which includes the steps

of hydrolyzing a solution of a nitrate of a metal of the group aluminum, beryllium, titanium, zirconium, until the nitrogen and metal are present in substantially equal atomic proportions, heating the solution to produce a brittle material, dissolving said brittle material, and heating the latter solution to produce a viscous tacky liquid substantially entirely free from organic constituents and which leaves when ignited a residue of an oxide of the metal which oxide has high electric insulating properties.

15. The method according to claim 14 in which a quantity of at least one refractory oxide of a metal of said group is added to said solution in uncombined form prior to heating.

16. An electron-emissive coating preparation containing a viscous tacky binder of a metal of

the group aluminum, beryllium, titanium, zirconium, with nitrogen in oxyacid form and with the nitrogen and metal present in substantially equal atomic proportions, and a quantity of alkaline earth metal carbonate mixed with said binder.

17. A binder material suitable for use in coating parts to be used within an electron-discharge tube, said material containing a reaction product of a powdered metal of the group aluminum, beryllium, titanium, zirconium, with nitric acid wherein the nitrogen is present as an oxyacid and in substantially equal atomic proportions with the metal, said material being water soluble and leaving a residue of the powdered meal oxide when baked.

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