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METHOD FOR PRODUCING DEPOSITS OF METAL COMPOUNDS ON METAL

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The present invention relates to deposits of metal compounds and particularly to the formation of such deposits as films or the like, as well as their application to articles to be coated with them.

In the past, considerable difficulty has been experienced with the application of metal compound films such as oxides and carbonates on supports. These difficulties revolve around the fact that the oxides and other such compounds are not suitable for direct application in adherent form, from a separate body of such oxides. As a result, it has become necessary to go to considerable trouble to develop the proper adhesion as by resorting to electrophoretic deposition or the formation of the compound in situ from the metal surface of a support. However, electrophoretic deposition is awkward at best, and in situ formation has the disadvantage of being relatively non-adherent, particularly where the conversion of the metal to the metal compound is accompanied by an appreciable expansion in volume.

Among the objects of the present invention is the provision of a metal compound applying process which avoids the above and related disadvantages.

Additional objects of the present invention include the provision of a novel process for applying a film of metal compound in which the compound is readily formed in situ without regard to the composition of the surface on which the coating is formed.

The above as well as further objects of the present invention will be more clearly understood from the following description of several of its exemplifications.

According to the present invention, a film or coating of a metal compound is applied to a support by exposing the support to the gaseous decomposition of an organic hydroxy salt of such metal. Suitable organic hydroxy salts are alcoholates and phenolates. Such hydroxy salts are made in any suitable manner. As disclosed for example in the article by O. Dermer in Chemical Review, vol. 14, pages 385 to 410 (1934), some metals will directly react with alcohols to form alcoholates, the presence of a small amount of free iodine being usually helpful. The alcoholates can then be separated out from the reaction mixture as by distilling off the excess alcohol. The residue can, if desired, be purified by fractionally distilling the alcoholates, preferably under reduced pressure. The distillation temperature should be held down to a point where no appreciable decomposition will take place.

The alcoholate before or after purification is then used to apply the desired coating. For this purpose the support upon which the coating is to be applied is exposed to a stream of the alcoholate vapor maintained at a temperature slightly below, at, or above the temperature of decomposition. The surface of the support where the coating is desired can be kept at a temperature somewhat higher than the surroundings so that decomposition will take place there preferentially.

With some metals, such as aluminum, magnesium, and zinc, the decomposition results in the deposition of an adherent film of metal oxide. With other metals, such as

barium and strontium, the film is a carbonate of the metal. In either case, however, the film deposits quite rapidly and can be built up to an appreciable thickness without becoming brittle or loose, and makes a highly effective dielectric coating.

Phenolates are somewhat easier to form but behave in substantially the same manner as alcoholates, except that the deposits formed from the phenolates more frequently contain organic residues. If desired, such deposits can be baked at about 250–350° C. to drive off any organic content. Such baking can, if at a sufficiently high temperature, also convert any carbonate to oxide, but it is preferred that this type of conversion be effected simultaneously with the original decomposition, if the oxide is desired.

In general, the organic hydroxy salt of any metal can be used. However, aluminum, magnesium, zinc, barium, strontium, calcium, titanium, zirconium and lead are preferred inasmuch as they make particularly suitable deposits. Alcoholates that are suitable for the present invention include methylates, ethylates, n-propylates, isopropylates, n-butylates, isobutylates, sec-butylates, tert-butylates, any of the isomeric amylates, hexylates and higher alcoholates such as benzylates, as well as salts of unsaturated alcohols such as allyl alcohol and furfuryl alcohol, and substituted alcohols such as triethanolamine and 3-chloropropanol-1. Suitable phenolates are salts of phenol, o-cresol, m-cresol, p-cresol, any of the isomers of xylenol, ethyl-phenol, chlorophenol and aminophenol, alpha and beta naphthol, and other substituted phenols.

The decomposition temperatures of the organic hydroxy salts vary over a considerable range. Thus magnesium methylate deposits a very good coating at about 80° C. whereas aluminum isobutylate has to be heated to about 350° C. before a suitable deposit is formed. However, the decomposition of all the above-listed compounds is readily effected.

As one specific example of the present invention, aluminum ethylate is boiled under a pressure of 500 millimeters of mercury and the vapors led into a tube through which a copper wire is passed, using entrance and exit seals to minimize leakage into the tube from the surroundings. By means of fixed contacts engaging the moving wire, a sufficient electric current is passed through the wire to heat it to about 275–285° C. As the ethylate vapors reach the wire, a film of aluminum oxide deposits on it. A dwell of only a few seconds is sufficient to provide an adherent film of excellent dielectric characteristics that will withstand an electric potential of 600 volts.

Instead of direct electrical heating, the wire can be heated by an induction-type heater. Alternatively, the wire can be heated by the application of external heat to the surrounding tube as by means of an encircling oven, but the coating is less efficiently deposited by this method.

The coating need not be effected by a continuous process. Thus, a batch of wire or foil can be placed in a closed container with a quantity of aluminum propylate, and the container then heated to 210–220° C. and evacuated to 20 millimeters of mercury. After a few minutes, the wire or foil is coated and the container can be opened and cooled.

Metal foil coated in the above manner makes very good capacitors for high voltage-high temperature use when laminated or wound with other coated or uncoated foils. The coated foils need not be of film-forming metal but can be copper, zinc, lead or the like. However, film-forming foils such as aluminum can be used with coating of a compound of the same or different metal deposited in accordance with the present invention.

In addition to the above so-called "electrostatic" type of capacitor, electrolytic capacitors can also be made with the above dielectrics either by themselves or in combina-

tion with the prior art dielectric films of film-forming metal. Thus a porous oxide coating can be electrolytically formed on aluminum using a standard sulfuric or oxalic acid electrolyte, and instead of using a subsequent oxidation to form dense oxide to complete the dielectric coating, the porous oxide can be very effectively covered with a layer of an oxide or carbonate deposited in accordance with the present invention. Furthermore, since the deposit does not work its way into points of contact between different objects, even a mass of metal wool can be coated with it to provide a suitable anode construction for an electrolytic capacitor. The wool portions are well interconnected electrically and make a very low resistance anode. Such an anode is then combined with a cooperating electrode and an electrolyte to complete the electrolytic capacitor.

Both polarized (D. C.) and unpolarized or symmetrical (A. C.) electrolytic capacitors can be made with the electrodes coated by organic hydroxy salt decomposition.

The wire foils or wool coated as above are highly suited for use where the dielectric coating is subjected to high temperatures, as in high temperature capacitors and wire-wound electrical resistors or heating coils, using wires of suitable composition such as nickel-chromium alloys or the like.

According to a further phase of the present invention, the organic hydroxy salts can be decomposed to give self-supporting particles of oxides or other dielectric material. To this end these salts are decomposed under conditions in which they do not vaporize significantly and the solid decomposition products are particulate in form. By starting with salt masses of specific sizes, as by spray drying solutions of the salt under standard conditions, and then screening the dried products, the resulting masses after decomposition are stable dielectric particles of predetermined and reproducible sizes. Such particles are suitable for incorporation into resinous binders and subsequent fabrication into thin dielectric films, sealing structures and composition resistance units. These particles are used in wire coating processes to form refractory coatings which can then be coated with an exterior film of resinous material when desired. Resinous materials which can be used in connection with these particles are natural and synthetic resins such as the acrylic acid derivatives represented by polymerized methyl methacrylate, polyvinyl alcohol derivatives represented by polyvinyl carbazole and the resin sold under the trade name "Formvar," glyptal resins, silicones, rubber latex, synthetic rubbers generally, halogenated rubbers, melamine-formaldehyde resins, polyvinyl resins, such as polypentachlorostyrene and polystyrene, polyesters, such as the linear type obtained by the condensation of terephthalic acid and ethylene glycol, polytetrahaloethylene resins, phenol-formaldehyde resins, polyparaxylene, polyamides, polyacrylonitrile alkyd resins, including the styrene and long chain types, urea resins, the sulfone resins, and the epoxy resins such as the condensation products of epichlorohydrin with di-hydroxy compounds of aromatic and aliphatic nature.

According to another phase of the present invention,

the organic hydroxy salts are decomposed upon supporting structures primarily by hydrolysis rather than thermally. As the carbon chain length of the organic component of the salt increases the more stable the salt is against hydrolysis.

As an example of this phase of my invention, an aluminum foil having a porous oxide film such as formed by electrolytic oxidation in oxalic acid was impregnated by molten aluminum isopropoxide. After completing the impregnation in a water-free atmosphere, steam was introduced to hydrolyze the compound, leaving aluminum hydroxide in the pores. The coated foil was then heated at 600° C. to form a unitary dielectric of α aluminum oxide.

A further means of procuring a high voltage oxide film for aluminum is to form the foil in an electrolytic solution containing colloidal particles of aluminum isopropoxide. It was found that maximum formation in a boric acid electrolyte containing the colloidal aluminum salt was in excess of 1000 volts as contrasted to a maximum formation of 500 to 600 volts in an electrolyte not containing the colloidal aluminum salt. The methoxy and ethoxy salts of aluminum were found not as satisfactory because of their case of hydrolysis. It is to be realized that the other valve forming metals are equally suitable for use. Furthermore, the oxide film does not have to be that of the conductor but is useful in depositing a thin dielectric film e. g. aluminum oxide, upon a metal as zirconium, which is not readily susceptible to formation or does not have an oxide with such desirable electrical characteristics.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is understood that the invention is not limited to the above specific embodiments except as defined in the appended claims.

What is claimed is:

1. A process for applying to a surface a dielectric film of a metal compound, said process including the steps of directing onto the surface a stream of the vapors of an organic hydroxy salt of said metal, and heating the surface to a temperature that causes the impinging vapors to decompose into a solid compound of said metal that adheres to and covers the surface.

2. The process of claim 1 in which the metal is selected from the class consisting of aluminum, magnesium, zinc, barium, strontium, calcium, titanium, zirconium and lead.

3. The process of claim 1 in which the organic hydroxy salt is an alcoholate.

4. The process of claim 1 in which the organic hydroxy salt is a phenolate.

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