

Oct. 10, 1972

J. P. HAUGHNEY

3,697,467

AQUEOUS DISPERSION OF POLYCARBOXYLIC ACID RESIN WITH SILICA

Filed Nov. 3, 1969

2 Sheets-Sheet 1



FIG. 1



FIG. 2

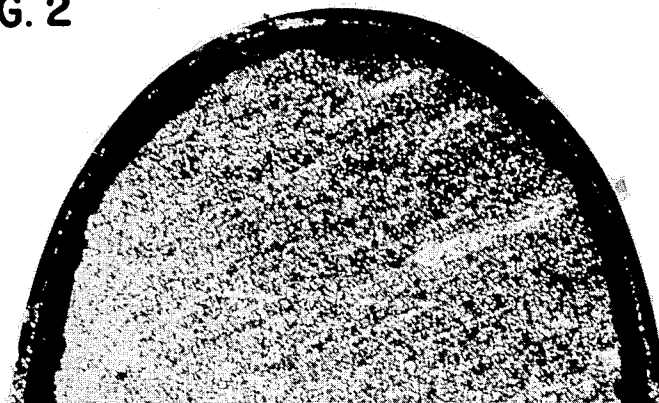


FIG. 3

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2 Sheets-Sheet 2

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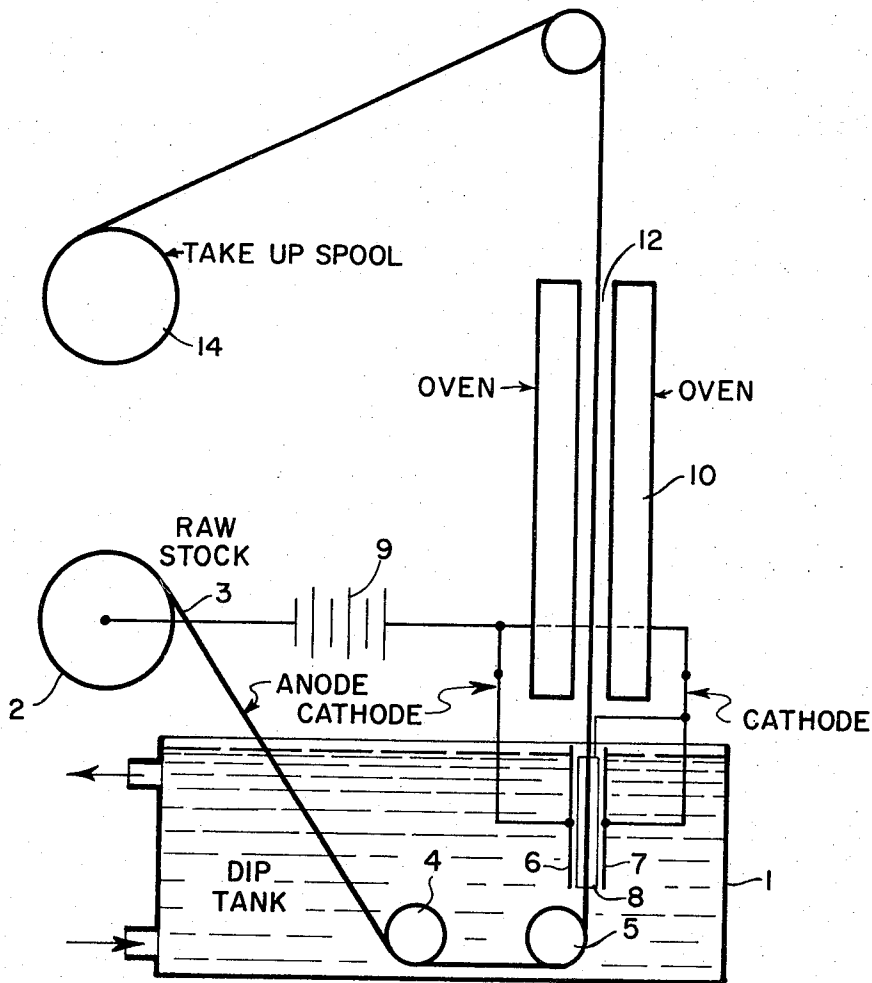


FIG. 4

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3,697,467

## AQUEOUS DISPERSION OF POLYCARBOXYLIC ACID RESIN WITH SILICA

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Filed Nov. 3, 1969, Ser. No. 873,531

Int. Cl. C08f 29/34, 29/38

U.S. Cl. 260—296 TA

11 Claims

### ABSTRACT OF THE DISCLOSURE

There are provided an improved electrocoating process, composition and article characterized by the inclusion in each of a polycarboxylic acid resin and a minor amount of extremely finely divided silica. Electrodeposition of a dielectric coating from a bath including an acidic polymer, a base, and a minor amount of such silica enables more nearly uniform electrocoating and when cured, as by thermal means, yields an improved product exhibiting higher dielectric breakdown voltages along edges and other contoured surfaces.

### BACKGROUND OF THE INVENTION AND PRIOR ART

It has long been a problem to coat contoured portions of anodes, e.g. the edges of metal objects having both broad surfaces and narrow edges. There is a tendency for coatings to drain from and pull away from the intersecting planes defined by the broad surface and narrow edges.

The problem is particularly acute and the fault critical in coating strips of metal used as electrical conductors, notably copper, aluminum, magnesium, silver, etc. Hereofore the marked differences in dielectric strength of coatings on such edges as compared with surfaces has seriously interfered with development of electrical windings for a variety of well established electrical end uses.

This invention relates to a new process, composition and article which when used as hereinafter disclosed give rise to a coated metal strip or foil having a high, relatively uniform dielectric coating on the broad surface, narrow edge and the surface defining the meeting of these edges, be it a line or the larger surface area available with some strip where it has been possible to provide a radius defining a larger connecting area.

To avoid confusion in the understanding between correlated areas of use, in the coatings industry generally an enamel is understood to mean a liquid vehicle capable of depositing a stet film containing sufficient pigment to provide the final film with opacity in an amount insufficient to materially impair the natural glass characteristic of the vehicle itself.

In the electrical insulation field enamel is used to define a vehicle standardly devoid of pigmentation in the paint sense, though the color of the vehicle itself may be, and often is, dark due to the presence of colloidal or smaller particles of light absorbing material. Insulating varnishes in the electrical wire, strip and foil field, then, though called "enamels" are not commensurate with "enamels" as are used to finish major appliance surfaces. Pigmentation in the latter sense seriously impairs the quality of insulating varnish or enamel in a number of respects.

It has been recently proposed to electrodeposit wire enamels on conductive elongated metal bodies in wire, strip and foil form; and there are known advantages in the electrodeposition process for accomplishing this end.

However, when electrocoating metallic ribbons, e.g. strip and foil stock, it is present experience that while the broad surfaces where coated can be made to withstand from 250–1500 volts before breakdown of the dielectric coat-

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ing, edges thereof may become conductive at from 0 to 200 volts, the higher end being improved to some extent by edge pretreatment to the order of 350 to 450 volts on the narrow edge.

Despite the known practical advantage of use of foil and strip metal for electrical end uses the low order of breakdown voltage across edges has materially retarded the progress and development of superior electrical equipment potential with use of foil and strip to replace the usual wire wound devices.

To the solution of these problems, there is provided an electrically conductive metal anode coated with an improved dielectric or insulating composition by the process of electrodeposition of the coating from an aqueous bath forming a part of an electrical circuit and containing a polyelectrolyte of an acidic polymer in water imparting a negative charge to inorganic particles originally dispersed in said polymer.

There is also provided in accordance with this invention a novel wire and strip or foil enamel comprising a synthetic polycarboxylic acid resin and containing dispersed therein an extremely finely divided form of silica in an amount sufficient to increase the dielectric breakdown point on interconnecting surfaces between the broad surface and the thin edge to a level such that the final insulated metallic conductive body can be used more widely in areas where dielectric breakdown between adjacent surfaces or convolutions has heretofore limited practical use.

Following the practice of the coating of metal ribbons by the combination of electrical deposition from an aqueous bath and the dispersion of the particular class of polycarboxylic acid polymers herein disclosed containing from about 0.5% to about 6% of finely divided silica based on the solids content of the acidic polymer, it has been found possible to produce coated anodes, including metallic foil and strip capable of withstanding up to about 3000 volts on the broad areas and up above 1500 volts across the areas intermediate thereof, e.g. edges, at 0.9 to 1.1 mils film thickness of the flat surface. Heretofore, 100 to 400 volts breakdown was standardly found at similar film thickness. In excess of 500 volts is essential to meet the minimum requirements for certain uses in the electrical industry.

The present invention is an improvement upon the electropainting process and paint binder concentrate composition therefor described in U.S. Pat. 3,230,162 and issued to A. E. Gilchrist on Jan. 18, 1966. In that patent, there is described a process for electrocoating an anode with a pigmented coating composition in an electrical circuit including a bath of an aqueous medium in electrical contact with an anode and a cathode. There is dispersed in the bath a paint containing as the predominant fraction of the film-forming material a synthetic polycarboxylic acid resin at least partially neutralized with a sufficient quantity of a water soluble amino compound to maintain the resin as a dispersion of anionic polyelectrolyte in said bath. The acidic resin has an electrical equivalent weight between about 1,000 and 20,000, an acid number between about 30 and about 300, and in the bath exhibits anionic polyelectrolyte behavior. A direct current is passed through a circuit at a potential between 50 and 500 volts thereby causing the coating composition film to electrodeposit on the anode, whereupon the anode is withdrawn from the bath.

It has been found that the process and compositions of the above Pat. 3,230,162 can be improved in respect of applying an insulating varnish to elongated metal anodes by the omission of a pigment as such and the inclusion in the aqueous bath of a minor amount of an extremely finely divided silica, preferably fumed silica, having an average particle diameter in the range of from 0.001

micron to 3 microns, desirably with less than about 0.05% retained upon a Standard 325 mesh screen. These silica materials are commercially available. By so improving the bath composition, and electrodepositing the improved bath composition, a substantial improvement in the dielectric strength of the coating and the uniformity of deposition over contoured surfaces is observed. The improvements of the present invention are obtained with all of the resinous compositions described in the Pat. 3,230,162, but excluding pigments and other solid particulate matter except as herein noted. In addition, it has been found that it is not necessary to limit the neutralizing composition to a water soluble amino compound. Any basic material which is water soluble may be used for the purposes indicated. Thus, the alkali metal bases, the water soluble amino and hydroxy amino compounds, and ammonia may be utilized to effect neutralization of the polycarboxylic acid resin to an extent sufficient to maintain the resin as a dispersion of anionic polyelectrolyte in the bath. The disclosure of Pat. 3,230,162 is included herein in its entirety by reference thereto with the modifications indicated herein.

#### BRIEF DESCRIPTION OF THE DRAWINGS

In the annexed drawings:

FIG. 1 is a photomicrograph of a cross-section of aluminum foil of the type used in making electrical coils, and showing the nature of a coating obtained from a pigment-free electrocoating bath including a polyacrylic acid resin but without silica present.

FIG. 2 is a photomicrograph of a cross-section of aluminum foil coated with the same electrocoating bath to which has been added about 3% by weight of the resin solids of fumed silica having an average particle diameter of 0.012 micron.

FIG. 3 is a photomicrograph of a cross-section of a contoured aluminum foil having an electrodeposited coating of the same composition as used in FIG. 2.

FIG. 4 is a diagrammatic and schematic illustration of an apparatus suitable for use in carrying out the process of the invention on metallic foil or strip.

#### DETAILED DESCRIPTION AND EXAMPLES

The polycarboxylic acid resins of the present invention are of a wide variety seemingly unlimited by anything but their ability to be put into aqueous solution, or apparent solution, or in ultrafine aqueous dispersion in a bath by at least partial neutralization with a basic material in which condition they can be typified as polyelectrolytes in aqueous dispersion. The dispersed or solubilized resins show migration in the bath with respect to the electric current characteristic of current-carrying anions in an aqueous solution and other solution properties. Accordingly, in the same manner as disclosed in Patent 3,230,162, these are considered as solutes with respect to their critical operative action, which solutes co-precipitate on the anode with dispersed silica particles as hereinafter described. The especially useful polycarboxylic acid resins useful as insulative film forming materials in the present compositions have an electrical equivalent weight between about 1000 and about 20,000 and preferably between about 1,000 and about 2,000 for ease of dispersion and efficiency of operation. These resins disperse effectively in the electrocoating bath when partially to fully neutralized with respect to acid number with water soluble basic compounds including water soluble amino compounds and convert from a fluent material to a highly adherent, comparatively immobile film when deposited on a metallic anodic surface by the electrocoating process and thermally cured. The resin solids content of the electrocoating bath is generally between 5% and 20% by weight of the bath. The term "electrical equivalent weight" resin is defined in Pat. 3,230,162 and is used herein in the same sense.

The broad class of polycarboxylic acid resins described

and exemplified in U.S. Pat. 3,230,162 are improved in respect of their electrocoatability by the inclusion therein of from 0.5% to about 6% by weight of the resin solids of extremely finely divided silica in the aqueous bath and, when deposited under the electrocoating conditions set forth in Pat. 3,230,162, show an improvement in dielectric strength of the coating, particularly in the region of intersecting planes or surfaces and about contoured edges of thin metal sections, such as aluminum foil or aluminum strip commonly used for electrical purposes, e.g. in the fabrication of electrical components.

In addition to the specific examples of polycarboxylic acid resins set forth in the aforesaid Pat. 3,230,162, the following specific examples will also illustrate the broad applicability of my discovery.

#### EXAMPLE 1

An acidic acrylic resin which has performed satisfactorily is formed from the following materials:

|                                | P.b.w. <sup>1</sup> |
|--------------------------------|---------------------|
| Butyl Cellosolve -----         | 203                 |
| Butyl acrylate -----           | 305                 |
| Acrylic acid -----             | 51                  |
| Styrene -----                  | 101                 |
| 2-hydroxypropyl acrylate ----- | 51                  |

<sup>1</sup> Parts by weight.

The resin is made in a typical resin reactor. The butyl Cellosolve is added to the reactor and heated to 250° F. All the ethylenically unsaturated monomers, i.e. butyl acrylate, acrylic acid, styrene, and 2-hydroxypropyl acrylate are added together with a suitable catalyst to form an interpolymerizable monomer mix. The ratio of catalyst to the monomer mix is in the range of from 10 to 13 parts of the catalyst to each 100 parts of the monomer mix. The polymerizable monomers and solvents are heated at 250° F. for about 5 to 7 hours at which time the acid value of the acrylic acid resin or polymer is between about 70 and 75. The resin is completed and cooled to room temperature. A suitable catalyst is azo-bis-isobutyro-nitrile. Near the end of the cook, cumene hydroperoxide or other free radical polymerization catalyst is added at about 1% to 3% by weight of the resin solids. The ethylenically unsaturated monomers useful herein generally have a molecular weight below about 150 and contain less than 10 carbon atoms. They may be hydrocarbons, halogen-containing hydrocarbons or acids or esters, or hydroxyl-containing materials. Thus, acrylic acid and its homologues, acrylic acid esters and their homologues, acrylonitrile, vinyl alcohol, vinyl chloride, vinylidene chloride, vinyl benzene (styrene), etc., may be used in addition to acrylic acid as secondary, tertiary and quaternary monomers to yield the acidic polymers hereof. The monomer mix may contain 2, 3, 4 or more monomers to form the acidic interpolymers.

The resin of this example is then solubilized for electrocoating. However, before solubilizing, 20 parts per 1000 parts of resin solution as produced above of fumed silica having an average particle diameter of 0.012 micron with no more than 0.05% retained on a Standard 325 mesh screen is added to the resin. Thereafter, 213 parts of a 10% solution of lithium hydroxide monohydrate in water and 1237 parts of deionized water are added, and the dispersion thoroughly mixed, e.g. in a Cowles unit.

As indicated above, other metal hydroxides including sodium hydroxide, potassium hydroxide, ammonium hydroxide, triethanolamine, diethanolamine, monoethanolamine, morpholine, and the like may be used as the solubilizing agent. The material resulting has a solids content of about 30%, and for electrocoating purposes, it is further reduced with deionized water to a solids content of from 10% to 12%.

Instead of styrene, other vinyl aromatic hydrocarbons may be used including vinyl toluene,  $\alpha$ -chloro styrene,  $\alpha$ -methyl styrene, etc.

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The extremely finely divided silica additions are also useful in improving the electrocoatability of epoxy ester carboxylic acid resins. A typical example of such a resin is produced as follows:

## EXAMPLE 2

|                                                                                 | P.b.w. |
|---------------------------------------------------------------------------------|--------|
| Bisphenol A/epichlorohydrin epoxy resin (epoxy equivalent weight 130-145) ----- | 457    |
| Linseed oil fatty acid -----                                                    | 439    |
| Succinic acid anhydride -----                                                   | 104    |

These ingredients are cooked in an alkyd kettle equipped with a condenser, and heating or cooling coils. The epoxy resin and the linseed oil fatty acid are heated with a few percentages (4-6%) of xylene for solvent cooking process and a conventional catalyst, e.g. 250-500 p.p.m. of sodium carbonate based on the weight of the epoxy resin. The temperature of the cook is raised slowly to about 450° F. over 3 to 4 hours time. Foaming from the interaction of the materials occurs at a temperature in the range of from 300° to 400° F. The input of heat to the kettle will control the foaming. The reaction is continued at 450° F. for 1 to 2 hours. At this point, the acid value is about 10 to 15. The material is then cooled to 300-325° F. and the succinic acid anhydride is added. The resin is cooked at 300° F. for an additional 2 to 4 hours at which time the acid value is in the range of from 60 to 66. This resin is then cooled, thinned, and filtered.

The foregoing polycarboxylic acid resin is solubilized in the following manner:

|                                                             | P.b.w. |
|-------------------------------------------------------------|--------|
| Polycarboxylic acid epoxy linseed oil ester -----           | 1000   |
| Fumed silica (0.012 micron average particle diameter) ----- | 20     |
| 10% aqueous solution of lithium hydroxide monohydrate ----- | 310    |
| Deionized water -----                                       | 2370   |

This produces a solution of 30% total solids which is further reduced to 10% to 12% total solids with deionized water for electrocoating purposes.

The epoxy resin may vary widely in epoxy content from 130 grams per epoxide group to 1100 grams per epoxide group. The fatty acid used to modify the epoxy resin can be any of those drying oil acids or semidrying oil acids typically used in alkyd resin formulations, such as soya fatty acid, tall oil fatty acid, safflower fatty acids, castor oil fatty acids, and the like. The amount of fatty acid used is based upon the amount of epoxy resin used. Considering the total weight of epoxy resins and fatty acid as 100 parts, the amount of fatty acid utilized may vary from about 35% to about 65% while the amount of the epoxy resin varies from 65% to 35%. Many of these resins are available in the trade. Many different anhydrides may be used to carboxylate the epoxy resin esters including maleic anhydride, succinic anhydride, phthalic anhydride, trimellitic anhydride, pyromellitic anhydride, and the like.

## EXAMPLE 3

A typical polyester polycarboxylic acid resin may be produced as follows:

|                                        | P.b.w. |
|----------------------------------------|--------|
| 2,2,4-trimethyl-1,3-pentane diol ----- | 313    |
| Trimethylol ethane -----               | 106    |
| Isophthalic acid (95%) -----           | 100    |
| Trimellitic anhydride -----            | 116    |
| Azelaic acid -----                     | 228    |

These ingredients are cooked in the typical alkyd kettle equipped with condensers and heating and cooling jackets. The trimethyl pentane diol and the trimethylol ethane are mixed and heated together at 300° F. At this point the isophthalic acid is added and the temperature raised to 400° F. where it is held for about one hour and cooled

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to 350° F. The trimellitic anhydride and the azelaic acid are then added and the temperature held at 335° F. for a period of from 8 to 10 hours. At this point, the acid value is about 50 to 60. The resin is then cooled, thinned with a material, such as butyl Cellosolve, to 85% solids and filtered. The resin is then solubilized as follows:

|                                                              | P.b.w. |
|--------------------------------------------------------------|--------|
| Polyester polycarboxylic acid resin as above prepared -----  | 1000   |
| Fumed silica (0.012 micron average particles diameter) ----- | 20     |
| 10% aqueous solution of sodium hydroxide -----               | 264    |
| Deionized water -----                                        | 2330   |

This produces a 30% total solids solution which is then reduced to 10% to 12% total solids with deionized water for electrocoating purposes.

In stead of the polyols recited in the foregoing Example 3, there may be used ethylene glycol, propylene glycol, neopentyl glycol, glycerol, pentaerythritol and the like. Dibasic acids may be phthalic acid, tetrahydrophthalic acid, adipic acid, succinic acid, fumeric acid, maleic acid, and the like.

## EXAMPLE 4

Another example of a polyester is as follows:

|                                        | P.b.w. |
|----------------------------------------|--------|
| 2,2,4-trimethyl-1,3-pentane diol ----- | 570    |
| Trimethylol ethane -----               | 210    |
| Adipic acid -----                      | 500    |
| Trimellitic anhydride -----            | 225    |

The foregoing ingredients are cooked in a typical alkyd kettle equipped with a condenser and heating and cooling jackets. The trimethyl pentane diol and trimethylol ethane and adipic acid are heated to 400° F. for a period of two hours and then cooled to 325° F. The trimellitic anhydride is added and the temperature held at 325° F. until an acid value of 55-65 is obtained in about 7-10 hours. The resin is then cooled, thinned and filtered.

The foregoing resin is solubilized in the following manner:

|                                                             | P.b.w. |
|-------------------------------------------------------------|--------|
| Polyester polycarboxylic acid resin -----                   | 1000   |
| Melamine-formaldehyde resin -----                           | 120    |
| Fumed silica (0.012 micron av. particle diameter) --        | 20     |
| 10% aqueous solution of lithium hydroxide monohydrate ----- | 300    |
| Deionized water -----                                       | 1800   |

This yields a composition of 30% total solids which is then reduced to 10% to 12% total solids for electrocoating purposes.

## EXAMPLE 5

This example illustrates a preferred polycarboxylic acrylic acid resin and the best mode of carrying out the invention:

|                                   | P.b.w. |
|-----------------------------------|--------|
| Butyl acrylate -----              | 60     |
| 2-ethylhexyl acrylate -----       | 5      |
| Styrene -----                     | 15     |
| Acrylic acid -----                | 10     |
| Beta-hydroxypropyl acrylate ----- | 10     |

The foregoing ethylenically unsaturated polymerizable monomers are interpolymerized in the presence of a coupling solvent, e.g. butyl Cellosolve by refluxing for a period of 2-6 hours using p-tertiary butyl benzoate as a catalyst. The refluxing is continued until the product has an acid value above 70 but less than about 130. The vehicle is recovered as a 70% solids solution.

Prior to neutralization and formation of the polyelectrolyte containing electrocoating bath, 423 parts of the above polymer are combined with eight parts of fumed silica having a particle size between 3 and 100 millimicrons average particle diameter. The silica is blended by high-

speed agitation (for example in a Cowles unit). Thereafter 572 parts of deionized water are incorporated along with sufficient base (lithium hydroxide monohydrate) to increase the pH of the system above 7 but not in excess of about 8.5. These pH limits are preferred for the compositions of the present invention to yield best results although deviations therefrom may be followed with decreased efficiency of operation.

Cross-linking agents in amounts ranging from 0 to 15% by weight of the resin solids may also be included at the time the silica is added. Such cross-linking agents include melamine formaldehyde, hexamethylol melamine formaldehyde, epoxy and epoxy ester resins, etc., for control of the hardness of the cured film. While these materials have not been found to be essential, such further modification is often advantageous.

To exemplify the electrodeposition of the dielectric resins of the present invention and particularly the dielectric resin of the last example onto the surface of an elongated metal anode, the aqueous acrylic acid polymer is further reduced in total solids to from about 6% to about 12% to provide a solution having an electrical resistance of the order of from 500 to 1500 ohm centimeters.

Referring to FIG. 4, the dip tank 1 is filled with the electrocoating bath prepared in accordance with Example 5 above, and ribbon stock 3 is fed from the spool 2 downward into the tank 1 under immersed idler rolls 4 and 5, and upward between confronting flat surface cathode plates 6 and 7 and end cathode plates such as end cathode plate 8, the opposing end cathode plate not being shown in FIG. 4. Suitable means such as direct current battery 9 are provided and arranged to render the raw stock strip material 3 positive with respect to the cathode plates 6, 7 and 8. The bath in the dip tank 1 is water thin.

The metal ribbon, e.g. an aluminum foil, is advanced from the reel 2 downward through the bath, and as it is drawn between the cathode plates, the acid form of the dispersed resin plus the silica particles, which may be either mechanically entrained with the resin or may possibly carry a negative charge, are deposited out uniformly over the surfaces of the ribbon 3. A voltage of from 125 to 150 volts DC and a coating time of about 30 seconds at a current rate of from 0.9 to 2.0 amperes yield film deposits of the order of from 1 to 1.5 mils after drying.

Following the deposition, the metal ribbon is passed into a slit oven 10 where the temperature interiorly thereof is maintained on the order of 500 to 510° F., heating the stock at a rate of about 1 foot per minute to a stock temperature of from 125° F. to 500° F. at the exit and during a residence time in the heated zone 12 of about 5 minutes.

The completed cured coated ribbon is rewound on take-up reel 14 which serves to supply tension to the stock 3 as it traverses through the electrocoating steps.

The electrocoating characteristics, for example the near uniformity of deposition even on edges and contoured surfaces as well as the flat surfaces, available with the electrocoating bath compositions hereof are greatly improved and yield a product having improved dielectric properties.

As indicated above, the composition and processes of the present invention are particularly useful with respect to the coating of aluminum foils and strips, and wire useful in forming electrical components such as condensers or coils, and in the production of wire enamels for coating wire. Conventional electrocoating apparatus utilizing a circular cathode may be used for wire coating.

Compositions produced in accordance with the specific examples above set forth have been tested for dielectric breakdown voltages when coated upon both metallic ribbons and upon wire. The dielectric breakdown voltage of the coated film varies from 1000 to 3000 volts per mil of thickness on flat surfaces, and from 400 to 2000 volts on the edges. Tests are run in accordance with ASTM D-149-61, "Tests for Dielectric Breakdown Voltage and Dielectric Strength of Electrical Insulating Mate-

rials at Commercial Power Frequencies." The aluminum industry designates the metal ribbon as "strip" when its thickness is 10 mils or greater, and as foil when its thickness is less than 10 mils. These compositions have also been found to be successful as wire enamels on both copper and aluminum wire. The dielectric breakdown voltages for these coated films on wire varies from 1000 to 2000 volts per mil of thickness.

The following table gives comparative values for dielectric breakdown voltages for various polycarboxylic acid resins for both the edges and flat surfaces of aluminum foil with extremely finely divided silica and without extremely finely divided silica.

TABLE I.—DIELECTRIC BREAKDOWN VOLTAGES

|                          | With<br>silica, volts | Without<br>silica, volts |
|--------------------------|-----------------------|--------------------------|
| Epoxy ester (Example 2): |                       |                          |
| Edge.....                | 400-1,000             | 200-700                  |
| Flat.....                | 1,000-2,500           | 1,000-2,500              |
| Polyester (Example 3):   |                       |                          |
| Edge.....                | 400-700               | 200-600                  |
| Flat.....                | 1,000-2,000           | 1,000-2,000              |
| Acrylic (Example 5):     |                       |                          |
| Edge.....                | 500-1,500             | 100-500                  |
| Flat.....                | 1,000-2,500           | 1,000-2,500              |

In general, 500 volts breakdown voltage on an edge is acceptable. Higher breakdown voltages are, of course, desired.

There has thus been provided an improved electrocoating bath having improved electrocoatability characteristics and an improved electrocoated product, as well as a method for obtaining a more nearly uniform coating on an anode, particularly an elongated or continuous metallic anode which is characterized by edges defined by intersecting planes or surfaces. Such portions of metallic anodes are difficult to coat uniformly by conventional electrodeposition means with conventional electrocoating baths and as shown above, the inclusion of a small amount of an extremely finely divided silica in the electrocoating bath greatly improves the character of the deposition and the nature of the product obtained thereby.

What is claimed is:

1. A bath composition for electrodepositing on an anode for forming an organic insulative coating film thereon, said bath consisting essentially of an aqueous dispersion of:

(a) a synthetic preformed polycarboxylic acid resin having an electrical equivalent weight between about 1000 and about 20,000 and an acid number between about 30 and about 300, the concentration of said resin in said aqueous dispersion being between about 5% and about 20% by weight, said polycarboxylic acid being maintained in said aqueous dispersion with

(b) a sufficient quantity of a water-soluble base selected from the group consisting of water-soluble alkali metal bases, water-soluble amino compounds, water-soluble hydroxy amino compounds, and ammonia to maintain said polycarboxylic acid resin as anionic polyelectrolyte;

(c) extremely finely divided silica having an average particle diameter in the range of from 0.001 micron to 3 microns, and being present in said aqueous dispersion in an amount between about 0.5% to about 6% by weight of the polycarboxylic acid resin.

2. A bath composition in accordance with claim 1 in which the silica is fumed silica.

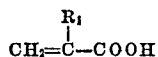
3. A bath composition in accordance with claim 1 in which the base is an alkali metal hydroxide.

4. A bath composition in accordance with claim 1 in which the base is lithium hydroxide monohydrate.

5. A bath composition in accordance with claim 1 in which the polycarboxylic acid resin is a polymerization

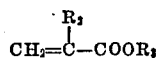
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product formed from at least two monomers, the first of which monomers has the general formula:



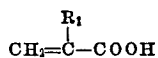
wherein  $R_1$  is hydrogen or a  $C_1-C_3$  alkyl group, and the second monomer is ethylenically unsaturated.

6. A bath composition in accordance with claim 5 wherein the second monomer has the general formula:

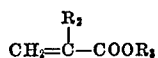


wherein  $R_2$  is hydrogen or a  $C_1-C_3$  alkyl group and  $R_3$  is a  $C_1-C_4$  alkyl group.

7. A bath composition in accordance with claim 1 wherein the polycarboxylic acid resin is formed from at least three monomers, the first of which has the general formula:



wherein  $R_1$  is hydrogen or a  $C_1-C_3$  alkyl group, the second monomer has the general formula:



wherein  $R_2$  is hydrogen or a  $C_1-C_3$  alkyl group and  $R_3$  is a  $C_1-C_4$  alkyl group, and the third monomer is a vinyl monomer.

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8. A bath composition in accordance with claim 7 in which the vinyl monomer is a vinyl aromatic hydrocarbon.

9. A bath composition in accordance with claim 8 in which the vinyl aromatic hydrocarbon is styrene.

10. A bath composition in accordance with claim 7 in which the first monomer is acrylic acid, the second monomer is butyl acrylate, and the third monomer is styrene.

11. A bath composition in accordance with claim 10 wherein the silica is fumed silica, and the base is lithium hydroxide.

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U.S. Cl. X.R.

117—229; 204—181; 252—229; 260—29.6 MM RB, 41 A, 831, 861