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3,493,483

ELECTRODEPOSITION METHOD AT HIGH VOLTAGE**Gerald R. Gacesa, Franklin, Wis., assignor to PPG Industries, Inc., Pittsburgh, Pa., a corporation of Pennsylvania****No Drawing. Continuation-in-part of application Ser. No. 581,166, Sept. 22, 1966. This application Jan. 28, 1969, Ser. No. 794,750****Int. Cl. C23b 13/00; B01k 5/02****U.S. Cl. 204—181****10 Claims****ABSTRACT OF THE DISCLOSURE**

This invention relates to a method of electrodeposition an organic coating on a conductive base. More particularly, this invention relates to a method of increasing the deposition of electrodepositable compositions at voltages above the normal rupture voltage of the system.

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of application Ser. No. 581,166, filed Sept. 22, 1966.

Electrodeposition is a relatively new coating technique which, although based on well-known principles, has only recently become technically feasible through the development of electrodepositable compositions which have the desired characteristics to meet the demands placed on a modern coating material. The coatings achieved have excellent properties for many applications and electrodeposition results in a coating which does not run or wash off during baking. Virtually any conductive substrate may be coated by electrodeposition. The most commonly employed substrates include the base metals such as iron, steel, aluminum, copper, zinc, brass, tin, nickel, and chromium, as well as other metals and pretreated metals, impregnated paper or other substrates rendered conductive under the conditions employed may also be coated.

The conditions under which electrodeposition is generally conducted are that an aqueous bath containing the coating composition is placed in contact with an electrically conductive anode and an electrically conductive cathode. The surface to be coated is employed as one of the electrodes. In the examples herein, the surface to be coated is employed as the anode. The voltage employed, as stated in the art is between 50 and 500 volts. In practice, however, since the prior art teachings make no effort to control time, the usual voltage employed is far below 500 volts since if normal film build is allowed, rupture occurs far below 500 volts.

While electrodeposition is in many respects advantageous compared to ordinary application methods, problems have arisen in the fact that for any given system at any given voltage there is a practical limitation as to the amount of film that can be built upon the substrate being coated and if the voltage is increased above a certain point to increase the rate of film build, which varies with the system, the "rupture voltage," i.e., that voltage at which the paint film ruptures and the voltage falls off noticeably more slowly, remains constant, or increases, is exceeded. This voltage is termed the normal rupture voltage hereinafter. It is noted that the rupture of each particular resin system displays varying but usually consistent characteristics. In some cases film rupture can be best observed by the uniformity of the cured electrocoated film. A ruptured film will usually have a rough or uneven film build. There may be areas of greater film thickness or there may be actual voids or pinholes in the film when cured, usually by baking.

It has now been found that voltages higher than the normal rupture voltage of the electrodeposition composition in question may be employed for controlled time intervals to achieve uniform non-ruptured films.

At least one theory advanced for this result is that, since electrodeposition is conducted in an aqueous media, during the electrodeposition at least some electrolysis of water occurs and gases are produced at the electrodes and that these gas bubbles are occluded to the article being coated, which serves as one of the electrodes. This layer of gas bubbles then interferes with the desired mechanisms which produces film build on the electrode.

It has been found that if relatively high voltages are employed for relatively short periods of time, as opposed to the normal voltages (below the rupture voltage) for the uncontrolled normal time periods, that film rupture can be avoided. One theory advanced for this result is that the film build occurs so rapidly that the gas evolution does not have an opportunity to form to the extent that occurs during normal deposition conditions. The coating time employed in the process of this invention is generally at one quarter of the time employed to obtain the same coating thickness at voltages below the normal rupture voltage and preferably is 10 seconds or less, more preferably, one second or less.

The voltages employed in the process of the invention are above the normal rupture voltage for the particular bath system involved and may be as high as 500, 1000 or even 2000 volts or higher. Many resin compositions employed in the electrodeposition art have rupture voltages below 300 volts or even 200 volts; thus, the process of the invention in some cases may be applicable at voltages of 300 volts or even 200 volts or lower, depending on the resin system, while still displaying the advantages described since the coating takes place above the normal rupture voltage.

Normally, the time for optimum coating is first predetermined by routine testing and then the voltage is preset and the article coated at the preset voltage, the time being controlled either manually or automatically. Alternatively, the bath residence time may be controlled, as in strip coating, by controlling the speed of the strip being coated to give the desired bath residence time. The coating time required to achieve the desired film build becomes shorter as the voltage increases and very short residence times are possible.

A number of electrodepositable resins are known and can be employed to provide the electrodepositable composition of this invention. Virtually any water-soluble, water-dispersible or water-emulsifiable polycarboxylic resinous material can be electrodeposited and, if film-forming, provides a coating which may be suitable for certain purposes. Any such electrodepositable is inclined among those which can be employed in the present invention, even though the coating obtained may not be entirely satisfactory for certain specialized uses.

The preferred resins which may be employed in the process invention comprise a reaction product or adduct of the drying oil or semi-drying oil fatty acid ester with a dicarboxylic acid or anhydride. Preferably, the drying oil or semi-drying oil per se is employed. Generally, drying oils are those oils which have an iodine value of above about 130, and the semi-drying oils are those which have an iodine value of about 90 to 130, as determined by Method ASTM-D1467-57T. Examples of such esters include linseed oil, soya oil, safflower oil, perilla oil, tung oil, oiticica oil, poppyseed oil, sunflower oil, tall oil esters, walnut oil, dehydrated castor oil, herring oil, menhaden oil, sardine oil and the like.

Also included among such esters are those in which the esters themselves are modified with other acids, includ-

ing saturated, unsaturated or aromatic acids such as butyric acid, stearic acid, linoleic acid, phthalic acid, isophthalic acid, terephthalic acid or benzoic acid, or an anhydride of such an acid. One inexpensive acid material which has been found to produce good results in many instances is rosin, which is composed of chiefly abiotic acid and other rosin acids. The acid-modified esters are made by transesterification of the ester, as by forming a di- or monoglyceride by alcoholysis, followed by esterification with the acid; they may also be obtained by reacting oil acids with a polyol and reacting the acid with the partial ester. In addition to glycerol, alcoholysis can be carried out using other polyols such as trimethylolpropane, pentaerythritol, sorbitol and the like. If desired, the esters can also be modified with monomers such as cyclopentadiene or styrene and the modified esters produced thereby can be utilized herein. Similarly, other esters of unsaturated fatty acids, for example, those prepared by the esterification of tall oil fatty acids with polyols, are also useful.

Also included within the terms "drying oil fatty acid esters" and "semi-drying oil fatty acid esters," as set forth herein, are alkyd resins prepared utilizing semi-drying or drying oils; esters of epoxides with such fatty acids, including esters of diglycidyl ethers of polyhydric compounds as well as other mono-, di- and polyepoxides; semi-drying or drying oil fatty acid esters of polyols, such as butanediol, trimethylolethane, trimethylolpropane, trimethylolhexane, pentaerythritol, and the like; and semi-drying or drying fatty acid esters of resinous polyols such as homopolymers or copolymers of unsaturated aliphatic alcohols, e.g., allyl alcohol or methallyl alcohol, including copolymers of such alcohols with styrene or other ethylenically unsaturated monomers with non-oil modified alkyd resins containing free hydroxyl groups.

Any alpha, beta-ethylenically unsaturated dicarboxylic acid or anhydride can be employed to produce the reaction products described herein. These include such anhydrides as maleic anhydride, itaconic anhydride, and other similar anhydrides. Instead of the anhydride, there may also be used ethylenically unsaturated dicarboxylic acids which form anhydrides, for example, maleic acid or itaconic acid. These acids appear to function by first forming the anhydride. Fumaric acid, which does not form an anhydride, may also be utilized, although in many instances it requires more stringent conditions than the unsaturated dicarboxylic acid anhydrides or acids which form such anhydrides. Mixtures of any of the above acids or anhydrides may also be utilized. Generally speaking, the anhydride or acid employed contains from 4 to 12 carbon atoms, although longer chain compounds can be used if so desired.

While the exact nature of the reaction product of the acid or anhydride with the fatty acid ester is not known with certainty, it is believed that the reaction takes place by addition of the unsaturated linkage of the acid or anhydride to the carbon chain of the oil. In the case of non-conjugated double bonds, such as are present in linseed oil, the reaction may take place with the methylene group adjacent to the non-conjugated double bond. In the case of oils having conjugated double bonds, such as tung oil, the reaction is probably of the Diels-Alder type.

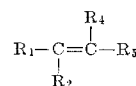
The reaction between the acid or acid anhydride and the drying oil or semi-drying oil fatty acid ester takes place readily without the use of a catalyst and at temperatures in the range of about 100° C. to about 300° C. or higher, with the reaction generally being carried out between about 200° C. and about 250° C.

While the reaction products can be comprised solely of adducts of the fatty acid ester and the dicarboxylic acid or anhydride, in many instances it is desirable to incorporate into the reaction product another ethylenically unsaturated monomer. The use of such monomer often produces films and coatings which are harder and more resistant to abrasion and which may have other similar

desirable characteristics. For this purpose, any ethylenically unsaturated monomer can be employed. Examples of such monomers include monoolefinic and diolefinic hydrocarbons such as styrene, alpha-methyl styrene, alpha-butyl styrene, vinyl toluene, butadiene-1,3, isoprene, and the like; halogenated monoolefinic and diolefinic hydrocarbons, such as alpha-chlorostyrene, alpha-bromostyrene, chlorobutadiene and similar compounds; esters of organic and inorganic acids, such as vinyl acetate, vinyl propionate, vinyl-2-chlorobenzoate, methyl acrylate, ethyl methacrylate, butyl methacrylate, heptyl acrylate, decyl methacrylate, methyl crotonate, isopropenyl acetate, vinyl alpha-bromopropionate, vinyl alpha-chlorovalerate, allyl chloride, allyl cyanide, allyl bromide, allyl acetate, dimethyl itaconate, dibutyl itaconate, ethyl alpha-chloroacrylate, isopropyl alpha-bromoacrylate, decyl alpha-chloroacrylate, dimethyl maleate, diethyl maleate, dimethyl fumarate, diethyl fumarate, and diethyl glutaconate; organic nitriles, such as acrylonitrile; and the like.

As is apparent from the above discussion and the examples set forth, which, of course, do not include all of the ethylenically unsaturated monomers which may be employed, any such monomer can be utilized. The preferred class of monomers can be described by the formula:

(I)



where R_1 and R_2 are hydrogen or alkyl, R_4 is hydrogen, alkyl carboxyalkyl and R_5 is cyano, aryl, alkyl, alkenyl, aralkyl alkaryl, alkoxycarbonyl or aryloxycarbonyl. The preferred compounds are styrene, substituted styrenes, alkyl acrylates, alkyl methacrylates, diolefins and acrylonitrile.

The reaction of the fatty acid ester, the acid or anhydride and any additional monomer or monomers can be carried out concurrently, that is, with each of the components of the reaction product being mixed together and heated to reaction temperature. However, because the monomer and the acid or anhydride are often quite reactive with each other, the oil or other fatty acid ester is preferably first reacted with the acid or acid anhydride, and then this product is subsequently reacted with any ethylenically unsaturated monomer or monomers employed. For example, a reaction product of linseed oil, maleic anhydride and styrene is made by first reacting maleic anhydride with linseed oil and then reacting the maleinized oil with styrene. When the process is carried out in this manner, the reaction of the additional monomer with the initial reaction product is usually carried out at somewhat lower temperatures, usually between about 25° C. and 200° C.

The proportions of each of the components going to make up the reaction product are ordinarily not critical. Generally speaking, between about 10 percent and about 45 percent by weight of the unsaturated acid or acid anhydride is reacted with from about 55 percent to about 90 percent by weight of fatty acid ester. In the presently preferred products, usually 15 percent to 30 percent of anhydride and 70 percent to 80 percent of oil ester are employed. If an ethylenically unsaturated monomer is incorporated in the reaction product, it is typically used in amounts between about 5 percent and about 35 percent by weight, based upon the total weight of acid or anhydride and ester, with between 10 percent and 25 percent being used in those products preferred at present. Thus, in most instances, the total composition of the reaction product may comprise from about 35 percent to about 90 percent by weight of the fatty acid ester and from about 10 percent to about 65 percent of the acid or anhydride and other monomer combined, with between about 6 percent and about 45 percent of the acid or anhydride always present.

The products produced in the above manner are comprised of polymeric chains of moderate length. The average molecular weight of the products to be used in electrodeposition should be low enough so that its flow characteristics at high solids are maintained, but high enough to provide adequate throwing power. The desirable molecular weight levels vary with the coating composition and conditions employed. Generally those products having molecular weights of up to 10,000 or somewhat higher have given the best results.

Neutralization of these products is accomplished by reaction of all or part of the dicarboxylic anhydride groups with a base. Usually up to about half of such groups are neutralized in unesterified adducts; the partially esterified products are often neutralized to a greater extent, based on unesterified acid groups remaining.

It is preferred in certain instances that the neutralization reaction be carried out in such a manner that amido groups are attached to part of the carbonyl carbon atoms derived from the dicarboxylic acid or anhydride. By amido groups are meant trivalent nitrogen atoms attached with one valence to the carbonyl carbon atom with the other two valences being linked to hydrogen or carbon atoms in the same or different organic radicals. Amido groups are formed, for example, when the reaction with the neutralizing base is carried out with a water solution of ammonia, a primary amine or a secondary amine, or when the product is reacted with such an amine in the absence of water.

Compositions within this general class are described in U.S. Patents Ser. Nos. 3,366,563 and 3,369,983.

Another type of electrodepositable coating composition which gives desirable results are the water-dispersible coating compositions comprising at least partially neutralized interpolymers of hydroxyalkyl esters of unsaturated carboxylic acids, unsaturated carboxylic acids and at least one other ethylenically unsaturated monomer. These are employed in the composition along with an amine-aldehyde condensation product or a polyepoxide, or both, with the interpolymers usually making from about 50 percent to about 95 percent by weight of the resinous composition.

The acid monomer of the interpolymers is usually acrylic acid or methacrylic acid, but other ethylenically unsaturated monocarboxylic and dicarboxylic acids, such as ethacrylic acid, crotonic acid, maleic acid, or other acids of up to about 6 carbon atoms can also be employed. The hydroxyalkyl ester is usually hydroxyethyl or hydroxypropyl acrylate or methacrylate, but also desirable are the various hydroxyalkyl esters of the above acids having, for example, up to about 5 carbon atoms in the hydroxyalkyl radical. Mono- or diesters of the dicarboxylic acids mentioned are included. Ordinarily, the acid and ester each comprise between about one percent and about 20 percent by weight of the interpolymers, with the remainder being made up of one or more other copolymerizable ethylenically unsaturated monomers. The most often used are the alkyl acrylates, such as ethyl acrylate; the alkyl methacrylates, such as methyl methacrylate; and the vinyl aromatic hydrocarbons, such as styrene; but others can be utilized.

The above interpolymers are at least partially neutralized by reaction with a base as described above; at least about 10 percent, and preferably 50 percent or more of the acidic groups are neutralized, and this can be carried out either before or after the incorporation of the interpolymers in the coating composition. The bases above can be used, with ammonia and amines being preferred; except when a polyepoxide is present, in which case there is preferably employed a hydroxide, such as sodium hydroxide, or if an amine, a tertiary amine. Other acrylic-type resins, such as those containing N-alkoxymethyl acrylamide and carboxylic acid groups may likewise be employed.

The amine-aldehyde condensation products included

in these compositions are, for example, condensation products of melamine, benzoguanamine, or urea with formaldehyde, although other amino-containing amines and amides, including triazines, diazines, triazoles, guanadines, guanamines and alkyl and aryl-substituted derivatives of such compounds can be employed, as can other aldehydes, such as acetaldehyde. The alkylol groups of the products can be etherified by reaction with an alcohol and the products utilized can be water-soluble or organic solvent-soluble.

Electrodepositable compositions comprising the above interpolymers and an amine-aldehyde resin are more fully described in U.S. Patent No. 3,403,088.

Still another electrodepositable composition of desirable properties comprises an alkyd-amine vehicle, that is, a vehicle containing an alkyd resin and an amine-aldehyde resin. A number of these are known in the art and may be employed. Preferred are water-dispersible alkyds such as those in which a conventional alkyd (such as glyceryl phthalate resin), which may be modified with drying oil fatty acids, is made with a high acid number (e.g., 50 to 70) and solubilized with ammonia or an amine, or those in which a surface active agent, such as a polyalkylene glycol (e.g., "Carbowax"), is incorporated. High acid number alkyds are also made by employing a tri-carboxylic acid, such as trimellitic acid or anhydride, along with a polyol in making the alkyd.

The above alkyds are combined with an amine-aldehyde resin, such as those described hereinabove. Preferred are water-soluble condensation products of melamine or a similar triazine with formaldehyde with subsequent reaction with an alkanol. An example of such a product is hexakis(methoxymethyl)-melamine.

The alkyd-amine compositions are dispersed in water and they ordinarily contain from about 10 percent to about 50 percent by weight of amine resin based on the total resinous components.

Examples of compositions of this class are described in U.S. Patents Nos. 2,852,475; 2,852,476; and 2,853,459.

Yet another electrodepositable composition comprises a mixed ester resin vehicle obtained from a resinous polyol having a molecular weight of about 700 or higher and especially copolymers of styrene and allyl alcohol or an epoxy resin which serves as a polyol or the polyol derived therefrom, such as the condensation products of epichlorohydrin and diphenyl propane, which is partially esterified with a fatty acid and a maleinized drying oil fatty acid. Resins of this type are described in Belgian Patent 641,642.

The neutralization and solubilization of all the above vehicles is accomplished by the use of a base. Inorganic bases such as metal hydroxides or, more desirably, ammonia can be used for this purpose, as can organic bases, particularly amines. Among the preferred class of neutralizing bases are ammonia and any basic amine. Examples of such amine are primary and secondary amines including alkyl amines, such as methylamine, ethylamine, propylamine, butylamine, amylamine, and N-methylbutylamine; cycloalkyl amines, such as cyclohexylamine; unsaturated amines, such as allylamine, 1,2-dimethylpentenylamine and pyrrole; aryl amines, such as aniline; aralkyl amines such as benzylamine and phenethylamine; alkaryl amines, such as m-toluidine; cyclic amines, such as morpholine, pyrrolidine and piperidine; diamines, such as hydrazine, methylhydrazine, 2,3-toluenediamine, ethylenediamine, 1,2-naphthalenediamine and piperazine; and substituted amines, such as histamine, dihydroxylamine, ethanolamine, and diethanolamine, as well as tertiary amines such as trimethylamine, triethylamine, dimethyl ethanolamine, N-methyl morpholine, triethanolamine and the like.

It has been found advantageous in many instances to effect part of the neutralization with certain solid amines, notably amino-alkyl-alkenediols, such as, for example, 2-methyl-2-amino-1,3-propanediol; 2-ethyl-2-amino-1,3-propanediol or 2-methyl-2-amino-1,4-butanediol. The films

produced when a small amount of such amines are employed are considerably harder and often have improved water resistance. However, preferably not more than about 4 percent by weight of the resinous components of these solid amines are utilized, since they are relatively expensive and greater amounts do not further improve the film's properties and may even slightly decrease its water resistance.

The electrodepositable coating compositions of the instant invention comprise the above vehicles, containing a strontium chromate-containing pigment composition. The pigment composition, in addition to strontium chromate, may be of any conventional type, comprising, for example, iron oxides, lead oxides, carbon black, titanium dioxide, talc, barium sulfate and the like, as well as combinations of these and similar pigments. Color pigments such as cadmium yellow, cadmium red, phthalocyanine blue, chromic yellow, toluidine red, hydrated iron oxide and the like may be included if desired. Better results with pigmented compositions are attained if the weight ratio of pigment solids to vehicle solids is not higher than about 1.5 to 1, and preferably not higher than about 1 to 1.

There may also be included in the coating composition, if desired, additives such as antioxidants, for example, orthoamyl phenol or cresol (the commercial mixture of isomeric cresols is satisfactory). It is found especially advantageous to include such antioxidants in coating compositions which are used in baths which may be exposed to atmospheric oxygen at elevated temperatures and with violent agitation over extended periods of time.

In formulating the coating composition, ordinary tap water may be employed. However, such water may contain a relatively high level of metals and cations; while not rendering the process inoperative, the use of water containing these cations may result in variations in the properties of the bath when used for electrodeposition. Thus, it is often desirable to utilize deionized water, i.e., water from which free ions have been removed as by passage through an ion exchange resin, in making up the coating compositions of the invention.

Other additives which may be included in the coating composition if desired include, for example, wetting agents such as petroleum sulfonates, sulfated fatty amides, esters of sodium isothionates, or alkylphenoxypolyoxyethylene alkanols, as well as driers such as the linoleates, the naphthenates, the octanates and the tallates of such metals as lead, cobalt, manganese, iron, copper and zirconium. Other additives which may be employed include anti-foaming agents, suspending agents, bactericides and the like.

EXAMPLE I

A vehicle resin (Resin A) was prepared by heating a 4-to-1 weight mixture of linseed oil and maleic anhydride over a two-hour period up to a temperature of about 250° C.

A solubilized resin (Resin A solubilized) was prepared by mixing Resin A above with deionized water and diethylamine to give a solution with a pH of about 7.2 and a solids content of 40 percent.

A pigment paste (Paste B) was made by grinding the following in a steel ball mill:

	Parts by wt.
Resin A solubilized (above)	22.6
Dispersing agent (combination oil-soluble sulfonate and non-ionic surfactant—Witco 912)	.6
Barium sulfate	45.5
Strontium chromate	2.5
Carbon black (30 percent aqueous dispersion) ..	15.0
Diethylamine	.6

The above mixture was ground for 15 minutes and the pH checked. The pH should be approximately 9.0. The mixture was ground to a No. 7 reading on the Hegman

Grind Gauge. There was then added to the mill and mixed for 30 minutes:

	Parts by wt.
Resin A solubilized (above)	11.4
Diethylamine	1.8

This mixture is Paste B.

The electrodeposition composition was prepared as follows:

	Parts by wt.
To a mixture of:	
Resin A (above)	233.3
Diethylamine	23.4

was added while stirring:

Cresylic acid	2.3
Deionized water	233.3

After thorough mixing, there was added:

Deionized water	144.6
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The milliequivalents of amine was adjusted to 95–100 with diethylamine and there was then added:

Paste B (above)	196.4
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and after thorough mixing the composition was let down to 8 percent solids with deionized water. This was the bath composition.

The normal rupture voltage of this composition is between about 130 volts and about 150 volts. That is to say, at above this voltage before maximum build is obtained, the film will become broken, discontinuous or uneven. Thus, when untreated steel strapping 1" wide by 12" long were in an electrodeposition bath at 200 volts for 60 seconds, the film build was about 2 mils, however, the amperage fluctuated and the film was rough and ruptured. Surprisingly, however, when the similar pieces of steel strapping were coated for only 10 seconds at 200 volts, the amperage remained fairly constant at 7 amps and a film of very good appearance, with a thickness of 0.6 mils was obtained.

A voltage time ladder was run, increasing the voltage while decreasing the time of current flow.

Voltage	Time (seconds)	Film thickness (in mils)	Film appearance
200.....	10.0	1.2	Heavy film.
300.....	10.0	1.4	Do.
300.....	5.0	0.9	Do.
400.....	5.0	1.3	Do.
400.....	2.5	0.9	Do.
400.....	1.0	0.7–0.8	Smooth film.
500.....	1.0	0.7	Do.
600.....	1.0	0.8	Slight orange peel.
700.....	1.0	0.8	Do.
800.....	0.5	0.65	Do.
1,000.....	0.5	0.65	Do.

EXAMPLE II

Films were electrodeposited upon black plate (tin can stock before tinning) at voltages as high as 300 volts and at times as low as 0.5 seconds. Films as thin as 0.05 mils were deposited at 300 volts that were shown to be continuous and unruptured, even on the deges, by placing the plate in a copper sulfate bath without noticeable effect.

EXAMPLE III

A vehicle resin was prepared as follows:

A mixture of washed monomers was prepared by mixing 600 parts of N-butoxymethylacrylamide, 120 parts of acrylonitrile and 4050 parts of ethyl acrylate and washing this mixture first with 6000 parts of 5 percent sodium hydroxide and then 6000 parts of water.

To 5575 parts of the washed monomer mixture was added 425 parts of methacrylic acid, 180 parts of tertiary dodecyl mercaptan and 60 parts of azobisisobutyronitrile. This mixture was designated Mixture R.

A catalyst mixture was prepared by mixing 30 parts of azobisisobutyronitrile, 500 parts of toluene and 250 parts of butanol. This mixture was designated Mixture S.

Into a reactor equipped with a reflux condenser, stirrer and thermometer was charged 750 parts of butanol and 500 parts of an aromatic hydrocarbon fraction having a boiling range of 370° F. to 710° F. and a K.B. of 93. The reactor was heated to reflux the contents (117° C.). Mixture R above was then added continuously over a period of three hours during which time the reflux temperature varied between 100° C. and 103° C. Then the reaction mixture was heated an additional hour at 103° C. and Mixture S was added continuously over a period of 3 hours, during which time the temperature was held between 104° C. and 105° C. The reaction was then heated for one hour at 105° C. To the reaction mixture was then added 100 parts of butanol and 100 parts of toluene.

200 parts of the reaction mixture was then distilled. The reaction mixture was cooled to room temperature and the vehicle resin thus produced (Resin T) had a 73 percent solids content and an acid value of 31.5.

A clear, electrodepositable composition was prepared as follows:

To 466 parts of Resin T were added 15.4 parts of triethylamine and the mixture thoroughly stirred, then 356 parts of deionized water was added and the mixture stirred again. The mixture was then filtered through a 10 micron maximum filter. 15.4 parts of triethylamine was added and after complete mixing the composition was let down with 1530 parts of deionized water.

having a Gardner viscosity at 25° C. of Q to U, measured in 40 percent butyl carbitol (Epon 1004), 1425 parts of tall oil fatty acid, 75 parts xylene were charged into a reactor equipped with stirrer, thermometer, inert gas inlet, reflux condensor and water trap. The reaction was heated with stirring in a slow inert gas sparge to 250° C. and held to an acid value of 5.0. This takes approximately 4.5 hours after reaching 200° C. The mixture is then sparged for one-half hour with inert gas to remove xylene and cooled to 150° C.

Reaction 3

To the above adduct (Reaction 2) was added the Reaction 1 adduct and the mixture was reheated to 145° C. and held for an hour. The resulting mixture was then thinned with 420 grams of 4-methoxy-4-methylpentanone-2, the final product having the viscosity of 300,000 centipoises and an acid value measured in alcoholic KOH of 25.0.

The electrodepositable composition was prepared by admixing 2000 parts of the product of Reaction 3 and 252 parts of 4-methoxy-4-methylpentanone-2, then 153 parts of triethylamine. The mixture was then slowly let down with deionized water to a solids content of 6.5 with a pH of 9.9.

The above composition was electrocoated as follows on phosphatized steel panels:

Panel	Amperes	Voltage	Time (seconds)	Temp. (° F.)	Film thickness (mils)	Comments
B-1-----	0.5-.06	150	60	78	0.4	Smooth film.
B-2-----	3.3-1.1	200	60	78	-----	Rough, ruptured, heavy film.
B-3-----	6.0-3.0	200	10	79	2.0	Smooth film.
B-4-----	6.0-4.0	250	5	79	2.0	Do.
B-5-----	6.0 5.0	250	1	80	0.2	Do.
B-6-----	6.0-5.0	300	1	80	0.7	Do.

The electrodeposition bath had a pH of 8.4.

The composition was electrocoated on a phosphate treated steel panel as follows:

Panel	Amperes	Voltage	Time (seconds)	Temp. (° F.)	Film thickness (mils)	Comments
A-1-----	.9-.16	50	60	77	.5	Smooth film.
A-2-----	1.3-.30	100	60	77	1.0	Do.
A-3-----	1.9-1.0	150	60	78	-----	Rough, ruptured film.
A-4-----	6.0-2.0	150	10	79	.9	Smooth film.
A-5-----	6.0-3.0	200	5	78	.7	Roughness at edges of smooth film.
A-6-----	6.0-4.0	250	1	78	.5	Smooth film.

EXAMPLE IV

An electrodepositable resin was prepared as follows:

Reaction 1

784 parts maleic anhydride and 2280 parts of tall oil fatty acid were charged to a reactor equipped with agitator, thermometer, inert gas inlet and reflux condenser. The air in the reactor was displaced by an inert gas blanket and the reaction mixture was heated slowly to 225° C. in about 2 hours and to 260° C. in another hour. The reaction was held at 260° C. for 3 hours and then cooled. Reaction mixture had a viscosity of 5,000 centipoises and an acid value of 255 measured in alcoholic KOH.

Reaction 2

1850 parts of an epoxy resin which is the reaction product of epichlorohydrin and para,para'-isopropylidene-diphenyl having a Durans melting point of between 95° C. and 105° C., an epoxy equivalent between 870 and 1025, having an average molecular weight of 1400 and

EXAMPLE V

The resin employed in this example was an acrylic resin comprising 5.0 percent hydroxyethyl methacrylate,

15.0 percent methacrylic acid, 80.0 percent styrene as a 72 percent solids solution in butyl Cellosolve. This resin solution had a viscosity of above 2,000,000 centipoises and an acid value of 70.9.

An electrodepositable composition was prepared having the following composition:

	Parts by wt.
Resin solution above	208.2
Amine resin (ethoxymethoxy melamine XM 1116)	38.0
Triethylamine	10.4
Deionized water	3544.0

The 6 percent solids composition had a pH of 9.4. The rupture voltage of this composition was approximately 100 volts.

The composition was coated on tin free can stock steel at 200 volts for 6 seconds to produce a 0.9 mil smooth unruptured film. Similar results were achieved at 300 volts for 3 seconds (0.6 mils) and at 300 volts for one second. The value of the foregoing technique is obvious. Under the conditions presently employed, i. e., operating below the normal rupture voltage of the electrodeposition com-

position, any attempt to continuously coat a coil or strip of material requires a long tank and a slow coil speed to achieve the required residence time in the bath to achieve the proper film thickness. By operating at voltages above the normal rupture system but at shorter, controlled times, the bath length may be decreased and/or the speed of the stock being coated may be increased while obtaining suitable films of substantially the same thickness as may be applied by the conventional methods. The savings in capital, investment, labor, and the increased productivity of any given unit are significant advantages.

What is claimed is:

1. In a method of electrodepositing an electrodepositable composition comprising a solubilized polycarboxylic acid resin on a surface serving as an anode, the improvement which comprises coating the surface at a voltage above the normal rupture voltage of said electrodepositable composition for a time which is 25 percent or less of the time required to obtain the maximum film build at the highest possible voltage below the normal rupture voltage of the electrodepositable composition.

2. A method as in claim 1 where the polycarboxylic acid resin comprises a reaction product of a drying oil fatty acid ester with a member of the group consisting of alpha,beta-ethylenically unsaturated dicarboxylic acids and anhydrides.

3. A method as in claim 1 where the polycarboxylic acid resin comprises a copolymer containing hydroxyl alkyl groups derived from a hydroxyalkyl ester of an ethylenically unsaturated mono- or dicarboxylic acid and carboxylic acid groups derived from an ethylenically unsaturated mono- or dicarboxylic acid.

4. A method as in claim 1 where the polycarboxylic acid resin is a mixed ester resin obtained from partially esterifying a resinous polyol having a molecular weight of about 700 or higher with a fatty acid, and then esterifying with a maleinized drying oil fatty acid.

5. A method as in claim 1 where the surface is coated at a voltage above about 200 volts for less than 10 seconds.

6. A method as in claim 1 where the surface is coated at a voltage above about 500 volts for less than 10 seconds.

7. A method as in claim 1 where the surface is coated at a voltage above about 1000 volts for less than one second.

8. A method as in claim 7 where the polycarboxylic acid resin comprises a reaction product of a drying oil fatty acid ester with a member of the group consisting of alpha,beta-ethylenically unsaturated dicarboxylic acids and anhydrides.

9. A method as in claim 5 where the polycarboxylic acid resin comprises a copolymer containing hydroxyl alkyl groups derived from a hydroxyalkyl ester of an ethylenically unsaturated mono- or dicarboxylic acid and carboxylic acid groups derived from an ethylenically unsaturated mono- or dicarboxylic acid.

10. A method as in claim 7 where the polycarboxylic acid resin is a mixed ester resin obtained from partially esterifying a resinous polyol having a molecular weight of about 700 or higher with a fatty acid, and then esterifying with a maleinized drying oil fatty acid.

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