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(54) COMPOSITIONS FOR ELECTRODEPOSITION COATING

(71) We, MITSUBISHI RAYON CO., LTD., a Corporation organised under the laws of Japan, of 8, Kyobashi-2-chome, Chuo-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a coating composition suitable for use in electrodeposition coating methods. More particularly, the invention pertains to a coating composition for electrodeposition coating which, according to an electrodeposition coating method and by one-coat finish, can form on the surface of a metal a film having excellent surface gloss and various prominent characteristics of a thermosetting resin.

For the purpose of imparting corrosion resistance and beautiful appearance to metal materials, water-type or organic solvent-type coating materials have heretofore been applied to the metal materials by spray-coating, roll-coating, curtain flow coating, dip-coating or the like method. Recently, however, attention has come to be paid to electrodeposition coating methods using water-type coating materials which have such advantages that the resulting films are uniform; even such metal materials as being complex in shape can be easily coated; no danger of fire is encountered in the coating steps; no sanitary problem is brought about; and the reduction in cost is possible due to central controlling of the coating steps. As processes for preparing coating

[Price 25p]

compositions usable in such electrodeposition coating methods, there have been known the processes disclosed in United States Patent No. 3,230,162 and British Patent Nos. 1,030,425, 1,027,813 and 1,115,130. However, these are chiefly employed merely for forming under coatings.

Conventional electrodeposition coating materials mostly contain, as the binder resin, highly water-soluble resins containing a large amount of dissociating functional groups for effecting electrophoresis and a large amount of hydrophilic functional groups, and hence are favorable in adhesion to materials to be coated. However, they have such drawbacks that bubbles are liable to be trapped in the resulting films; they are high in water-solubility so that the resulting films are low in heat flowability at elevated temperatures thus making it impossible to obtain excellent surface gloss; and they contain highly water-soluble resins and therefore the films obtained after baking are great in sensitivity to water and low in anti-corrosion property.

In an attempt to overcome the drawbacks of known coating materials, the inventors made various studies and found that in order to obtain, according to electrodeposition method and by one-coat finish, a film having, in combination, excellent surface gloss and various prominent characteristics owned by thermosetting coating materials, it is necessary that the amount of hydrophilic functional groups in the binder resin component of the coating material be made as small as possible so far



as the resin component can be stably dispersed in water to enhance the flow characteristics of the coating material at elevated temperatures, thereby improving the resulting film in surface gloss as well as in anti-corrosion properties.

In the practice of electrodeposition coating, a great factor to make the resulting film always uniform is that the composition of the electrodeposition coating bath should not vary with time. However, in the case of a conventional coating material using a highly water-soluble resin component as a binder, the dissolved state of the resin component in water varies with lapse of time, and thereby the stability of the electrodeposition coating bath deteriorates. Further, a polymerization solvent employed in preparing a resin solution differs, in general, from a solvent necessary for dispersing a resin in water, and therefore, in dispersing the resin in water, it is necessary to effect solvent substitution. If polymerization solvent is left behind depending on the procedure of said solvent substitution, or when the dissolved state of the resin undergoes variation due to said solvent substitution treatment, the stability of the electrodeposition coating bath is lowered in some cases. Further, in the case of a coating material containing a pigment, the stability of the dispersion is greatly affected not only by the properties of the resin employed but also by those of the pigment employed.

Based on such a detailed knowledge as mentioned above, the present inventors made studies to accomplish the present invention relating to a coating composition for electrodeposition coating which can give by one-coat finish a film having excellent surface gloss and prominent physical and chemical characteristics, in which is used as essential resin component a copolymer obtained from an N - alkoxyalkyl(meth)acrylamide monomer, itaconic or α -methyleneglutaric acid monomer and other copolymerizable vinyl monomer.

It is therefore a primary object of the present invention to provide a coating composition for electrodeposition coating which is favorable in stability of electrodeposition coating bath and which can form, according to electrodeposition coating method and by one-coat finish, a film having excellent surface gloss and physical and chemical characteristics, which coating composition comprises a coating material containing as essential resin component a water-soluble or water-dispersible resin, which is a copolymer obtained from an N - alkoxyalkyl(meth)acrylamide monomer, itaconic or α -methyleneglutaric acid monomer, and other copolymerizable vinyl monomer, said copolymer having an acidity represented by pKa of at least 8.0, a polymer chain extension represented by parameter n of from 0.5 to 1.5, a neutralization degree represented by α of from 30—80% (i.e. percentage of carb-

oxyl groups neutralized; the same shall apply hereinafter), a glass transition temperature of 60°C. or below, and a number average molecular weight of 20,000 or less.

A secondary object of the invention is to provide said coating composition for electrodeposition coating which is favorable in bath stability, characterized in that it contains a pigment capable of satisfying the equation

$$|pKp - pKa| \geq 0.1,$$

wherein pKp represents the acidity of the pigment; and pKa represents the acidity of the resin.

The characteristics of the resin which are for the achievement of the primary object of the present invention will be examined below.

As to the behaviour in water of acidic high polymers, it has been known, in general, that in the region where α is not excessively low or high, there is established the following equation:

$$pH = pKa + n \log \frac{\alpha}{1 - \alpha} \quad [I]$$

wherein pKa is a parameter which represents the acidity of the resin and is defined by the following equation:

$$pKa = -\log Ka,$$

wherein Ka is the dissociation constant of the resin; n is a parameter showing the extension of polymer chain; α represents the apparent neutralization degree of the resin component which is given by the ratio of the total equivalent of the added amine or ammonia base to the total equivalent of the carboxylic acid contained in the copolymer resin; and pH represents the pH of the aqueous solution or dispersion of the resin deposition coating bath.

The values of pKa and n are indexes representing the hydrophilic property of the resin, and vary depending on the composition of the resin. For example, in the case of a polymer containing acid groups, which groups are dissociating functional groups, or non-dissociating hydrophilic functional groups, the value of pKa decreases and the value of n increases in proportion to the content of said functional groups. On the other hand, when the content of acid groups is maintained constant and the content of non-dissociating hydrophilic functional groups is lowered, the value of pKa increases and the value of n is substantially maintained constant. Whether a resin is water-soluble or water-dispersible is decided according to the values of pKa, n and α , and a resin, which is great in pKa value or which is low in n value and α , becomes more water-dispersible.

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In order to obtain a film having excellent surface gloss and prominent physical and chemical characteristics, according to electrodeposition coating method and by one-coat finish, the present inventors studied, based on the above-mentioned knowledge, the usable ranges of pKa, n and α , to find the facts described below.

That is, when a resin component low in pKa value is used, the resulting electrodeposition coating bath becomes acidic even if the neutralization degree of resin is made high and, depending on the kind of metal, there are some cases where the generation of corrosion is observed on the metal surface during coating by electrodeposition. Further, a resin component low in pKa value is high in solubility in water, and the groups of the high polymer constituting the resin are entangled with each other and are electrodeposited in this state on the surface of metal to be coated. Accordingly, the resulting film is low in heat reflowability and has no smooth surface gloss. On the other hand, a resin component having a high pKa value is not dissolved in water even though the neutralization degree of the resin is made high, but is brought into a dispersed state. Since the dispersed particles tend to adhere to one another, the film-forming ability of the resin component during coating by electrodeposition is lowered and the dispersion stability of the resin in the electrodeposition coating bath is impaired. With increasing pKa value, however, the heat reflowability of the resin is improved and the surface gloss of the resulting film is increased. In the present invention, the value of pKa was measured when the bath concentration was 11% by weight and the temperature was 25°C.

An examination of the n value shows the following:

In water, the n value of a water-soluble high polymer tends to vary, in general, from a certain value to 1. Although no explanation for this phenomenon has been clarified yet, it is thought that the phenomenon is ascribable to the orientation, in the water phase, of the hydrophilic functional groups contained in the resin component, and to the process of dispersion into water of high polymer due to

a chemical force. In fact, an aqueous bath containing the high polymer having a value of n nearly equal to unity does not cause any variation due to lapse of time. Further, with the variation of n value due to lapse of time, the value of pKa tends to decrease due to lapse of time, whereby the electrodeposition coating bath is lowered in pH and in specific resistance. If such a resin is used as a coating material for electrodeposition coating, the electrodeposition coating bath formed by use thereof undesirably becomes unstable with lapse of time.

In an electrodeposition coating method in which one-coat finish is effected, it is, of course, necessary that the film obtained after baking should have practical properties. In order to obtain a film having excellent surface gloss, however, it is necessary that the film formed at the time of electrodeposition coating should have heat reflowability. As to the ability of forming an electrodeposited film, the glass transition temperature, represented by Tg, of the high molecular weight substance constituted by the resin component becomes an important factor. If a resin component high in Tg is used, the adhesion of dispersed particles of coating material takes place with difficulty, so that the film formed on the surface of a metal to be coated is not increased in electric resistance and is undesirably lowered in throwing power (i.e. the ability of a paint to coat completely the recessed areas and shielded portions of the object forming the anode). Further, the heat reflowability of film at the time of curing becomes inferior, and the gloss of the film obtained is poor.

The molecular weight of resin also is an important factor. If a resin high in molecular weight is used, there is observed the same phenomenon as in the case where a resin high in Tg is used. Further, not only the value of pKa is lowered but also the value of n is liable to increase. Accordingly, the use of a resin high in molecular weight is not desirable.

The glass transition temperature Tg referred to herein signifies the Tg of a copolymer comprising monomer units other than cross linking functional monomer units, and is calculated according to the equation

$$1/T_g = W_1/T_{g1} + W_2/T_{g2} + \dots + W_x/T_{gx}$$

[II]

where x is the number of different types of monomer units making up the copolymer and wherein $W_1, W_2, \dots$ up to W_x represent, in weight %, the proportions of individual types of monomers constituting the polymer component, assuming that the proportion of the polymer comprising monomers other than cross linking functional monomer is 100 weight %; and

$T_{g1}, T_{g2}, \dots$ up to T_{gx} , represent the glass transition temperatures of homopolymers of the individual monomer components.

Further, the molecular weight is a number average molecular weight calculated according to osmotic pressure method. The range of molecular weights suitable for one coat finish is from 5,000 to 20,000. If the molecular weight is less than 5,000, the polymer is un-

desirably lowered in water dispersibility, and if the molecular weight is more than 20,000, the polymer tends to be lowered in pKa value, and the electrodeposition characteristics thereof are undesirably lowered.

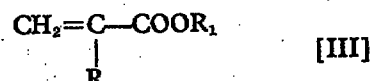
Accordingly, the required conditions for obtaining a film having excellent surface gloss and prominent film properties, according to electrodeposition coating method and by one-coat finish, are such that the resin component employed in the coating composition should have such characteristics as an acidity pKa of at least 8.0, a polymer chain extension parameter n of from 0.5 to 1.5, a neutralization degree α of from 0.3 to 0.8, a glass transition temperature T_g of 60°C. or below, and a number average molecular weight of 20,000 or less. Particularly when the bath stability is to be sufficiently secured, it is necessary that the electrodeposition coating bath should contain as an essential component 2—20% by weight of a resin having pKa of from 8.5 to 9.5; n parameter of from 0.8 to 1.3; T_g of 30°C. or below, preferably from -25° to 10°C.; and a number average molecular weight of 15,000 or less, and that, when the bath contains 11% by weight of solids, the specific electroconductivity of the bath should be controlled to 150—800 micro-mhos/cm (measured at 25°C.).

An electrodeposition coating material composed of a water-soluble or water dispersible resin capable of satisfying the above-mentioned conditions has an excellent one-coat finish property. For the purpose of obtaining a resin component, which satisfies such conditions, monomers constituting said resin will be examined below.

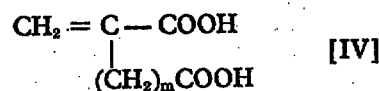
Generally, monomers having cross linking functional groups which display thermosetting properties are mostly high in polarity and great in degree of hydrophilic property. In order to obtain an electrodeposited film having desired solvent resistance, stain resistance and anti-corrosion property, the cross linking density of the film should be made high. For the achievement of the above purpose, therefore, cross linking functional monomers should be used in considerably large amounts. However, polymers obtained by using large amounts of said hydrophilic vinyl monomers are low in pKa value and high in n value, and hence are not desirable. In order to improve the above points, it is necessary that the vinyl monomers containing a more hydrophobic cross linking functional group be used to prepare polymers which have suitable values of pKa, n , T_g and an average molecular weight within the aforesaid range and which can attain suitable cross linking densities after curing. Generally, hydrophobic cross linking functional groups are relatively low in cross linking reactivity, but are advantageous in that in the heating step, they bring about heat reflow prior to cross linking

reaction to make it possible to form smooth coated surfaces.

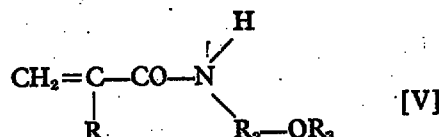
Based on the above-mentioned viewpoints, the inventors examined resins capable of meeting the objects of the present invention and found that the present invention can be achieved by using as the coating resin a copolymer composed of 93.5—35 mole % of a component (A), which is a monomer mixture comprising at least one monomer represented by the general formula



wherein R is a hydrogen atom or a methyl group, and R_1 is a branched or straight chain alkyl group having 1—18 carbon atoms, and at least one copolymerizable ethylenically unsaturated monomer; 1.5—15 mole % of a component (B), which is a compound represented by the general formula

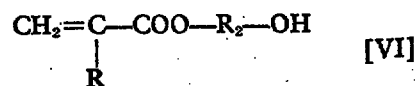


wherein m is 1 or 2; and 5—50 mole % of a component (C), which is at least one compound represented by the general formula



wherein R is as defined above, R_2 is a branched or straight chain alkylene group having 1—8 carbon atoms, and R_3 is a branched or straight chain alkyl group or cycloalkyl group having up to six carbon atoms.

The compound represented by the general formula [III], which is used in the present invention is an acrylate or methacrylate ester in which the alkyl group represented by R_1 is for example a methyl, ethyl, n-propyl, isopropyl, n-butyl, secondary butyl, tertiary butyl, pentyl, 2-ethylhexyl, nonyl, decyl, dodecyl or stearyl group. If the hardness of the resulting film and the stability of the coating bath employed are to be taken into consideration, it is desirable to use, in a suitable combination, a long chain alkyl acrylate or methacrylate and a short chain alkyl acrylate or methacrylate. The copolymerizable ethylenically unsaturated monomer may be styrene, an α -alkyl-substituted styrene derivative, acrylonitrile, or a hydroxyalkyl acrylate or methacrylate represented by the general formula



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wherein R and R₂ are as defined above. Specific examples of said hydroxyalkyl acrylates and methacrylates are those in which the hydroxyalkyl group is a 2-hydroxyethyl, 2-hydroxy - n - propyl, 2 - hydroxy - n - butyl, 2 - ethyl - 2 - hydroxyethyl or 1 - hexyl - 2-hydroxyethyl group.

The above mentioned component (A) is a monomer mixture constituting part of the copolymer, which is prepared by polymerising the component (A) with the other monomer components. A particularly good coating composition for electro-deposition coating can be obtained when the component (A) is selected such that the molar ratio of the monomer represented by the general formula (III) to said other copolymerisable unsaturated monomer is 99.9/0.1 to 40/60. If, instead of the component (B), which is a compound represented by the general formula (IV), as the carboxylic acid component, there is used acrylic, methacrylic, crotonic, fumaric or maleic acid or an anhydride of said acids, inferior copolymerizability results, and therefore the use of said acids is not desirable. Polymers to be used in the electrodeposition coating methods are required to be uniform in structure and the like, particularly in pKa value. If polymers having a wide pKa value distribution are used, polymers low in pKa value migrate or orient, with lapse of time, into the aqueous phase, whereby not only the stability of the coating bath is impaired but also the properties of the resulting films are degraded. It is therefore a required condition to use itaconic or α -methyleneglutaric acid, which is excellent in copolymerizability.

The latter acids not only play important roles to impart electrophoretic properties to the coating material component but also are elements indispensable for dispersing the coating material components into an aqueous medium. They are important also as cross linking reaction catalysts in the baking step of films. Further, in the case of pigmented coating materials using pigments in combination, they display effects of improving the affinity of the pigments for the resin components. However, these latter acids are hydrophilic compounds, so that when used in large amounts, they bring about the degradation in characteristics of the resin obtained and in physical properties of the resulting films. It is therefore necessary to use the acids in amounts of from 1.5 to 15 mole %.

An important characteristic of the invention resides in the use of the compounds represented by the general formula [V]. Typical as said compounds are acrylamides or methacrylamides in which, in the N-alkoxyalkyl group, the N-alkoxy group represented by R₃O— is a methoxy, ethoxy, butoxy, n-propoxy, pentoxy or cyclohexoxy group, and the alkylene group represented by —R₂— is a methylene, ethylene, propylene, hexylene or

2-ethylhexylene group. These compounds are more hydrophobic cross linking functional monomers than acrylamides, methacrylamides and N - methylol - acrylamides or -methacrylamides, and can be used in considerably large amounts without giving any detrimental effect to the pKa and n values of the resulting polymers. Further, they give films having not only a desired cross linking density but also heat reflowability, and therefore glossy coated surfaces can be obtained. Among these monomers, N - n - butoxymethyl acrylamide and N - n - butoxymethyl methacrylamide can be said to be particularly preferable comonomers in that not only are they easy to copolymerize with other monomers and the resulting polymers are favorable in storage stability, but also they also have high affinity for pigments, melamine resins and epoxy resins which are used in combination with the essential resin component. The amounts of these monomers employed are in the range of 5—50 mole %, preferably 10—30 mole %, when the pKa and n values of the resulting polymers are taken into consideration.

For the preparation of polymers usable in the present invention, the aforesaid monomers may be polymerized, in conventional manner, in a common organic solvent in the presence of a desired amount of a free radical polymerization catalyst and a molecular weight modifier. However, if the dispersion stability in water of the resulting polymer and the stability over a period of time of the aqueous bath are taken into consideration, the use of organic solvents miscible with water is particularly desirable. Examples of these organic solvents are alcohols such as methanol, ethanol, butanol, propanol, and isopropyl alcohol; glycols such as ethylene glycol, propylene glycol, hexylene glycol, and diethylene glycol; Cello-solves such as methyl Cello-solve, ethyl Cello-solve, and butyl Cello-solve; or aqueous mixtures thereof. Great advantages attained by use of the above-mentioned polymerization solvents are as mentioned below. ["Cello-solve" is a Registered Trade Mark.]

In the step of dispersing a polymer in water, it is not necessary to effect such solvent substitution as in the case where a water-insoluble polymerization solvent has been used. Further, by reason of the fact that the polymer, in general, is formed having a distribution of pKa values, if solvent substitution has been effected, in the resulting polymer solution and dispersion, a polymer having a low pKa value tends to migrate into the aqueous phase. Accordingly, the polymer is lowered in stability during storage as a resin solution. In contrast thereto, if a water-miscible organic solvent has been used, no such solvent substitution is necessary in the step of dispersing the polymer in water. Moreover, the polymer is stored in the organic solvent, and therefore the dissolved state of the polymer does not

vary thus making it possible to obtain an electrodeposition coating composition, which is markedly excellent instability.

5 As the polymerization initiator to be used in the preparation of the polymer, any of the ordinary free radical polymerization initiators may be used. Examples of such polymerization initiators are benzoyl peroxide, cumene hydroperoxide, ditertiary butyl peroxide, azobisisobutyronitrile, and azobisisovaleronitrile. As the molecular weight modifier, there may be used mercaptans such as tertiary dodecyl mercaptan, n-dodecyl mercaptan, n-butyl mercaptan, or 2-mercaptoethanol.

10 In order to disperse the resulting copolymer in water, it is necessary that the copolymer be neutralized. Neutralizing agents usable include ammonia, primary, secondary or tertiary amines, including hydroxyalkylamines or salts thereof. However, these neutralizing agents can give adverse effects, depending on their hydrophilic properties and on the pKa and n values of the polymers, and therefore care must be taken in using them.

15 The above-mentioned N-alkoxyalkylamide copolymer can be prepared by a polymerisation process using monomeric N-alkoxyalkyl-acrylamides or -methacrylamides. In addition thereto, there are, as disclosed in United States Patent No. 2,870,611 and British Patent No. 1,115,130, the so-called polymer-modifying processes in which interpolymers having amide groups or N-methylolamide groups are obtained using acrylamide, methacrylamide, N-methylolacrylamides or N-methylolmethacrylamides as comonomers, and then the said amide or methylolamide groups are N-alkoxyalkylated or alkylated by use of aldehydes and alcohols, or alcohols respectively. However, according to the above-mentioned polymer-modifying processes, hydrophilic groups are liable to remain. Further, the solvents employed are water-insoluble organic solvents, and therefore the resulting polymer solutions have to be subjected to solvent substitution thus bringing about detrimental effects on the pKa and n values of the polymers. Moreover, the polymers are deteriorated in heat flowability and the electrodeposition coating baths are lowered in bath stability. According to the aforesaid processes, therefore, it is impossible to obtain the present coating compositions for electrodeposition coating which are suitable for one-coat finish and which have excellent film-forming ability.

55 Further, when the above processes are employed, it is necessary to add acid catalysts in order to completely N-alkoxyalkylate the amide groups or alkylate the N-methylolamide groups contained in the polymers. These acid catalysts undesirably bring about detrimental effects at the time of electrodeposition coating, and therefore it is impossible to obtain, according to said processes, electrodeposition coating materials suitable for one-coat finish.

Accordingly, in order to obtain a suitable electrodeposition coating material, it becomes an essential condition to use an N-alkoxyalkyl-acrylamide or -methacrylamide as a comonomer in the preparation of the polymer. In this case, however, there arises a great problem in that isolated N-alkoxyalkyl-acrylamide or -methacrylamide monomer is expensive.

In view of the above, the present inventors examined processes for inexpensively preparing N-alkoxyalkyl acrylamides and methacrylamides which are used as comonomers. As the result, the inventors have accomplished the following two methods:

The first method uses an N-alkylol-acrylamide or -methacrylamide as a starting material; together with a mixture comprising an appropriate alcohol, as alkylating agent and an organic solvent azeotropic with water, or a vinyl monomer azeotropic with water, as a dehydrating agent; and the unsaturated acid (B), which is an essential component of the present composition is used as a catalyst for alkylation of the N-alkylol group.

The second method uses acrylamide or methacrylamide as a starting material; together with a mixture or addition product of formaldehyde and an appropriate alcohol as a modifying agent for the amide group; and the same dehydrating agent and acid catalyst as in the first method are used. According to said methods, a monomer mixture comprising the component (C) and the component (B) can be easily obtained by feeding to the monomers a given amount of an acid catalyst, which is an element indispensable in the present invention. Further, when a vinyl monomer azeotropic with water is used as the dehydrating agent, a monomer mixture comprising (A), (B) and (C) can be obtained with ease and at low cost. As the acid catalyst, α -methyleneglutaric acid or itaconic acid, which is useful also as a comonomer, is used. As the dehydration agent, an aromatic hydrocarbon solvent such as benzene or toluene, or a vinyl monomer such as acrylonitrile, displays prominent effects.

The present coating compositions for electrodeposition coating are of the self-cross linking type and give films excellent in physical properties. However, in order to further improve the properties of the resulting films, such as hardness and corrosion resistance, it is desirable that melamine resins or epoxy resins also be included in the compositions. The improvement is carried out by blending 60 parts by weight or less of N-alkoxymethylmelamine and/or epoxy resins with 100 parts by weight of the resin component comprising 93.5 to 35 mole % of the component (A), 1.5 to 15 mole % of the component (B) and 5 to 50 mole % of the component (C). Usable as such melamine resins are N-alkoxymethyl melamines, preferably those in which the alkyl moiety of the alkoxymethyl group has 1—4

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 components can be used. These epoxy resins
 and compounds can include for example, con-
 densation products of polyethylene glycol or
 polypropylene glycol with epichlorohydrin; tri-
 glycidyl isocyanurate; epoxy resins obtained
 from epichlorohydrin and bisphenol A; epox-
 idized resins; vinyl cyclohexene dioxide; di-
 glycidyl phthalate ester; and glycerine tri-
 glycidyl ether. These epoxy resins display
 great effects particularly in that they can im-
 prove the corrosion resistance of the resulting
 films. Further, these compounds are ordinarily
 used in the form of solutions in suitable sol-
 vents, but may also be used in the form of
 powders.

In order to disperse the polymer, obtained
 in the above manner, in an aqueous medium
 and to use the dispersion as an electrodeposi-
 tion coating bath, the specific electroconductiv-
 ity of the bath at the time of preparation
 should be controlled to 150—800 micro-mhos/
 cm. (measured for 11% by weight of solids
 at a bath temperature of 25°C.). If the
 specific electroconductivity of the bath is more
 than 800 micro-mhos/cm., the electrodeposi-
 tion of the coating material components onto
 the surface of a metal to be coated becomes
 low in efficiency. When the specific electro-
 conductivity is less than 150 micro-mhos/cm.,
 the amount of coating material particles elec-
 trodeposited onto the surface of a metal to
 be coated increases, but, on the other hand,
 the degree of racking of coating material par-
 ticles on to the surface of material to be
 coated decreases to bring about such undesir-
 able phenomena that the adhesion between the
 resulting film and the material to be coated
 is lowered and the solvent is left in the film.
 It is even more desirable that the specific
 electroconductivity of the electrodeposition
 coating bath be adjusted to 200—600 micro-
 mhos/cm.

A polymer product obtained according to
 an ordinary polymerization process is a mix-
 ture of polymers having considerably wide dis-
 tributions of pKa, n and molecular weight
 values. Therefore, if a conventional electro-
 deposition coating material, which contains
 such a polymer as mentioned above, is used
 to form an electrodeposition bath, polymers
 low in pKa value migrate into the aqueous
 phase with lapse of time, whereby the whole
 system of the coating bath is lowered in
 apparent pH, and the specific electroconductiv-
 ity of the bath increases and, at the same
 time, becomes closer to a definite value. Fur-
 ther, in the above process, there occur such
 phenomena as variation in dissolved state of
 coating material particles, lack in the differ-

ence of electrophoretic migration of the par-
 ticles, and formation of precipitate. Owing to
 such variation of coating bath with lapse of
 time, the resulting film is undesirably de-
 graded in gloss and is deteriorated in physical
 properties due to increase in film thickness.

The electrodeposition coating material of
 the present invention that has been developed
 in order to overcome such undesirable pheno-
 mena as mentioned above. However, even in
 the case of an electrodeposition coating bath
 prepared by using the present coating mat-
 erial, which contains the polymer obtained
 under such strict conditions as above, there
 are observed such phenomena that the bath
 is lowered in pH and is increased in specific
 electroconductivity when allowed to stand for
 a long period of time after preparation, with
 the result that the resulting film is degraded
 in gloss and deteriorated in physical properties.
 Such phenomena are considered ascribable to
 the fact that water-soluble polymers low in
 pKa value orient and migrate into the aqueous
 phase, as mentioned previously. When said
 water-soluble polymers, which have migrated
 into the aqueous phase, are removed from
 the bath according to a dialysis process or a
 process using ion exchange compounds, e.g.
 ion exchange resins or membranes, the pH
 and specific electroconductivity of the bath
 can be brought back to substantially the same
 pH and specific electroconductivity values at
 the time of preparation of the bath, whereby
 the gloss and properties of the resulting bath
 can be maintained constant.

In addition to the above process for the
 stabilization of electrodeposition coating bath
 by use of the ion exchange compounds, there
 can be used a method in which an amphoteric
 electrolyte capable of acting as a base in the
 vicinity of the pole of a material to be coated
 is added to the electrodeposition coating bath,
 whereby the stability of the bath can be greatly
 improved. The phenomenon taking place in
 the above method has not been clarified in
 detail, but is considered accountable to the
 mild deposition of coating material particles in
 the vicinity of the pole. Preferable as such
 amphoteric electrolyte are those having an iso-
 electric point of 6.5—8.5, e.g. amino acids
 such as L-histidine and L-glycine. The bath
 stability can also be improved by preventing
 the coating material particles from agglomerat-
 ing in the aqueous medium, or by adding to
 the coating bath a nonionic surface active agent
 effective for preventing polymers low in pKa
 value from elution into the aqueous medium.
 As the nonionic surface active agent, there
 may be used, for example, a copolymer of
 ethylene oxide with propylene oxide. If a high
 anti-corrosion property is desired to be im-
 parted to the resulting film, an alkylamine,
 preferably a water-insoluble alkylamine, which
 can neutralize the acid groups contained in
 the polymer, may be added during the curing

of the film. The alkylamines include n-butylamine (which is water-soluble), n-hexylamine, n-octylamine and laurylamine (which are slightly soluble in water).

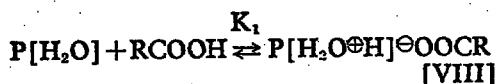
5. Electrodeposition coating materials containing pigment have heretofore been obtained by use of pigmented paste prepared by neutralizing a coating material to impart water dispersibility thereto, adding a pigment to the coating material, and then kneading the resulting mixture. However, the coating materials for electrodeposition coating, which are obtained according to such a process as above, differ widely in stability in aqueous bath.
- 10 Further, the development of coating materials excellent in dispersion stability has conventionally been effected in a mere trial and error manner, and processes for the analysis and solution of causes for said difference in bath stability have not yet been found.

- 15 In view of such actual state as mentioned above, the present inventors made studies, paying attention to the point that no matter how excellent resins for one-coat finish had been developed, the pigmented paste material having excellent characteristics and suitable for one-coat finish could not be obtained unless the characteristics of pigments employed should also be taken into consideration. As
- 20 the result, the inventors have found that a pigmented coating material for electrodeposition coating which has excellent characteristics and which is suitable for one-coat finish can be obtained by use of a resin which, after
- 25 neutralization, shows such characteristics in the formula [I] as $8.0 \leq pK_a$, $0.5 \leq n \leq 1.5$ and $0.3 \leq \alpha \leq 0.8$, and of a pigment which satisfies the relationship

$$|pK_p - pK_a| \geq 0.1 \quad [II]$$

- 40 wherein pK_p is the acidity of the pigment, and pK_a is the acidity of the resin.

- The dispersion stability of a coating material in an aqueous bath containing a pigment and a resin is greatly affected by the affinity
- 45 between the resin and the pigment. In the present invention, the step of coating the resin with the pigment is carried out in an organic solvent, and it is considered that the wetting phenomenon between resin and pigment progresses according to the equation



- 55 wherein $P[H_2O]$ represents a pigment having adsorption water, and $RCOOH$ represents a resin containing carboxylic acid groups. Thus, the dispersion stability in water of the pigment, which has once been coated, is greatly dominated by the characteristics of the resin employed. It is considered that K_1 in the process

of the formula [VIII] is proportional to the value of

$$|pK_p - pK_a|,$$

i.e. the difference between pK_a , which represents the proton releasability of the resin-containing carboxylic acid groups, and pK_p , which represents the proton-discharging force of $P[H_2O]$. The greater the value of

$$|pK_p - pK_a|,$$

the more firmly the pigment is coated with the resin, and the dispersibility of the resultant product is comparable to that of a resin containing no pigment, whereby the effect of using the resin suitable for one-coat finish and having excellent pK_a and n values can also be displayed.

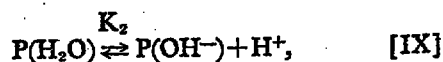
If a pigment and a resin in such a relationship as pK_p is approximately equal to pK_a are used, the wetting phenomenon according to the formula [VIII] between the pigment and the resin becomes a markedly small value, and the water-dispersibility of the pigment itself is also inhibited. It is therefore considered that the resulting aqueous bath is lowered in dispersion stability and, at the same time, the pigment and the resin tend to show different behavior in the electrodeposition coating step, with the result that the properties of the resulting film are also lowered. Accordingly, in order to obtain a pigmented coating material, which has excellent dispersion stability in water and which is suitable for one-coat finish, it becomes necessary that the condition

$$|pK_p - pK_a| \geq 0.1$$

be satisfied.

In the present invention, pK_a is a value measured under the conditions set forth below.

A water-insoluble pigment has an amphoteric property, and when the pigment is dispersed in an alkaline or acidic medium, it shows excellent dispersibility, whereas at about a neutral pH, the dispersibility thereof becomes markedly low. In a dispersion at an alkaline pH, the pigment is negatively charged, and the pH lowers with increasing pigment concentration. Accordingly, OH^- is adsorbed on the pigment surface, and the pigment disperses according to the equilibrium equation



wherein P is the pigment. Since the dispersibility of the pigment becomes higher with increasing $P(OH^-)$, there is established the equation

$$K_2 = [P(OH^-)] [H^+] / [P(H_2O)].$$

Accordingly,

$$\text{pH} = \text{pK}_2 + \log \frac{[\text{P}(\text{OH}^-)]}{[\text{P}(\text{H}_2\text{O})]}$$

When pK_2 is replaced by pKp , it is possible, in view of the relationship between the term

$$\log \frac{[\text{P}(\text{OH}^-)]}{[\text{P}(\text{H}_2\text{O})]}$$

which represents the dispersibility of the pigment, and the pH of aqueous bath, to define pKp by the pH at the time when the pigment begins to disperse at the alkaline side. When the pH at said time is measured, the value of pKp can be calculated.

Pigments usable in the present invention, include inorganic pigments such as titanium dioxide, red iron-oxide, carbon black, cobalt blue, ultramarine blue, ceruleum, manganese blue, mars violet, chromium oxide, cobalt chromium green, yellow iron oxide, cadmium yellow and barite; and organic pigments such as Permanent Red 4R, Hansa Yellow and Phthalocyanine Blue. Other pigments that are sparingly soluble in water may also be used. However, the pigments should be so selected as to necessarily satisfy the relationship

$$|\text{pKp} - \text{pKa}| \geq 0.1.$$

The present coating compositions for electrodeposition coating can give, both in respect of clear coatings and colored enamel coatings, not only films having excellent physical and chemical properties but also films having white and light clear colors and having excellent surface gloss.

In the present invention, the coating operations may be effected in such a manner that electrodeposition coating is carried out ordinarily at a voltage of 40—200 V, and the resulting film is washed with water, is dried, and is then baked at 140°—250°C. for about 30 minutes.

The coating compositions of the present invention are extremely significant in that even in the case of chemically treated cold rolled steel plates, on which it has heretofore been considered difficult to form films having excellent surface gloss and prominent properties according to electrodeposition coating method and by one-coat finish, the present coating compositions can form such excellent films on cold rolled steel plates.

The present invention is illustrated in further detail below with reference to examples, in which all parts and percentages are by weight.

The following experimental results design-

ated A to E are included to assist in explaining the invention.

(A) Preparation of a monomer mixture comprising N-n-butoxymethyl acrylamide and itaconic acid:

The monomers and other components shown below were charged into a three-necked flask fitted with a stirrer, a decanter and a thermometer, and the mixture was dehydration-condensed at 70—97°C. for 6 hours.

Acrylamide	444 parts	
n-Butanol	760 "	
Benzene	700 "	
Itaconic acid	162.5 "	
40% n-butanol solution of formaldehyde	538 "	
Hydroquinone monomethyl-ether	3.5 "	

The decanter had previously been charged with benzene, and the time when the amount of effluent water had reached a given amount was deemed as the terminal point of the condensation reaction. The resulting product was analyzed according to gas chromatography to find that the conversion of acrylamide to N-n-butoxymethyl acrylamide was 96.5%. 2,500 parts of the said product was charged with 1055 parts of isopropanol, and 1055 parts was distilled off as an azeotropic mixture of benzene with isopropanol.

(B) The monomers and other components shown below were charged into the flask employed in (A), and a monomer mixture comprising N-n-butoxymethyl acrylamide and itaconic acid was obtained in the same manner as in (A).

N-methylol acrylamide	632 parts	
n-Butanol	1030 "	
Benzene	703 "	
Itaconic acid	162.5 "	
Hydroquinone monomethyl-ether	3.5 "	

The resulting product was analyzed according to gas chromatography to find that the conversion of N-methylol acrylamide to N-n-butoxymethyl acrylamide was 97.5%. 2,500 parts of the said product was charged with 1055 parts of isopropanol, and benzene was distilled off as an azeotropic mixture with isopropanol.

(C) In the same manner as in (A), a monomer mixture comprising N-n-butoxymethyl acrylamide, itaconic acid and acrylonitrile was obtained from the monomers and other components shown below.

	Acrylamide	444	parts
	40% n-butanol solution of formaldehyde	538	"
	Acrylonitrile	700	"
5	Itaconic acid	162.5	"
	Hydroquinone monomethyl-ether	3.5	"
	n-Butanol	760	"

The resulting product was analyzed according to gas chromatography to find that the conversion of acrylamide to N-n-butoxymethyl acrylamide was 96.0%.

(D) In the same manner as in (A), a monomer mixture comprising N-n-butoxymethyl acrylamide and methacrylic acid was obtained from the monomers and other components shown below.

	N-Methylol acrylamide	632	parts
20	n-Butanol	1030	"
	Benzene	703	"
	Methacrylic acid	120	"
	Hydroquinone monomethyl-ether	3.5	"

The resulting product was analyzed according to gas chromatography to find that the conversion of N-methylol acrylamide to N-n-butoxymethyl acrylamide was 96.3%. This product was carefully concentrated, and N-n-butoxymethyl acrylamide having a boiling point of 110°—115°C./1 mmHg was isolated, yield 85%.

(E) In the same manner as in (A), above, a monomer mixture comprising N-n-butoxymethyl acrylamide and α -methylene-glutaric acid was obtained from the monomers and other components shown below.

	Acrylamide	444	parts
40	40% n-butanol solution of formaldehyde	538	"
	n-Butanol	760	"
	Benzene	700	"
	α -Methyleneglutaric acid	180	"
45	Hydroquinone monomethyl-ether	3.5	"

The resulting product was analyzed according to gas chromatography to find that the conversion of acrylamide to N-n-butoxymethyl acrylamide was 95.5%.

EXAMPLE 1

The compounds shown below were charged into a four-necked flask fitted with a stirrer, a thermometer and a cooler, and the mixture was polymerized in a nitrogen atmosphere at 68°C. for 6 hours and then at 75°C. for additional 2 hours.

	Ethyl acrylate	271	parts
	Styrene	166	"
	N-n-Butoxymethyl acrylamide	100	"
	Itaconic acid	12.4	"
	2-Mercaptoethanol	5.8	"
	Azobisisobutyronitrile	24	"
	Isopropanol	427	"

The resulting copolymer solution was neutralized by addition of 6.65 parts of β -dimethylaminoethanol to obtain a resinous solution having a solids content of 57.2 wt. %, an acid number of 9.8, Tg. of 15°C., pKa of 8.7, n value of 0.9 average molecular weight of 8.5×10^3 and α value of 0.45. To 100 parts of this resin solution, 75 parts of titanium oxide having pKp of 9.53 was added, and the mixture was ground in a ball mill for 24 hours. The mixture was further charged with 200 parts of the resin solution and was ground for additional 24 hours to obtain a white pigmented paste. This enamel was used to prepare an electrodeposition coating bath having a solids concentration of 12.8 wt. %, a pH of 8.42, a specific electroconductivity of 1.75×10^2 micro-mhos/cm. (measured at 25°C. when the solid content was 11%; the same shall apply hereinafter. Using the thus prepared coating bath, a cold rolled steel plate, a zinc phosphate-treated steel plate, and a ferric phosphate-treated steel plate were individually subjected to electrodeposition coating as the anode at a bath temperature of 25°C. for 3 minutes at 60 V (distance between electrodes=40 mm; cathode area/anode area=5/7). After water-washing and air-drying, the resulting films were baked at 180°C. for 30 minutes. The efficiencies of the thus formed films were as shown in Table 1.

TABLE 1

Item	Substrate	colled rolled steel plate	ferric phosphate-treated plate	zinc phosphate-treated plate
Gloss value (60°)		90.5	89.1	86.9
Thickness (μ)		28	26	29
Pencil hardness		2H	2H	2H
Cross cut		100/100	100/100	100/100
Solvent	{ Xylene Isopropanol Acetone	4	4	4
resis-		4-5	4	4
tance		5	5	5
Alkali resistance		5	5	5
Acid resistance		5	5	5

In the above table:

Gloss value was measured according to 60° mirror surface reflection method.

Cross cut value was measured in such a manner that squares of 1 mm in side were drawn with a needle on the surface of the film and were peeled off by use of an adhesive tape, and the number of the remaining squares was represented by percentage.

Solvent resistant was measured in such a manner that the film surface of the coated plate was rubbed 20 times with a gauze impregnated with the organic solvent, and the damaged degree of the film surface was evaluated according to a 1 to 5-grading system. The best resistance value was represented by 5, and the worst value by 1.

Alkali resistance was measured in such a manner that a spot of a 5% aqueous caustic soda solution was placed on the film surface of the coated plate for 24 hours and the damaged degree of the film was evaluated according to a 1 to 5-grading system.

Acid resistance was measured in such a manner that spot of a 5% aqueous hydrochloric acid solution was placed on the film surface of the coated plate and the damaged degree of the film was evaluated according to a 1 to 5-grading system.

Substrate was a colled rolled steel plate of 70 mm × 15 mm × 0.8 mm, which was used either as such or after treatment with an anti-rust surface treating agent.

From the results shown in Table 1, it is evident that the films formed by use of the present coating composition are excellent not only in gloss but also in other properties and that the coating composition of the present invention is suitable for one-coat finish.

EXAMPLE 2

The compounds shown below were charged into the same device as in Example 1, and the mixture was polymerized for 12 hours in the same manner as in Example 1 to obtain a resin solution.

2-Ethylhexyl acrylate	806	parts
Styrene	520	"
N - n - Butoxymethyl acrylamide-itaconic acid mixture obtained in Example 1 (B)	965	"
Itaconic acid	16.5	"
Azobisisobutyronitrile	59.0	"
2-Mercaptoethanol	22.5	"
Isopropanol	763	"

To the thus obtained resin solution, 44.4 parts of β-dimethylaminoethanol was added to prepare a resin having Tg of -9°C., pKa of 9.20, n value of 1.17 average molecular weight of 9.6×10^3 , and α value of 0.40, 100 parts of this resin solution was charged with 75 parts of titanium dioxide having pKp of 9.6, and the mixture was ground in a ball mill for 24 hours. The mixture was further charged with 200 parts of the resin solution and was ground to obtain a white pigmented paste.

- This enamel paste was used to prepare an electrodeposition coating bath having a solids concentration of 13%, a pH of 9.02 and a specific electroconductivity of 2.24×10^2 micro-mhos/cm (at the time when the solid content was 11%). Using the thus prepared coating bath, a colled rolled steel plate, a zinc phosphate-treated steel plate and a ferric phosphate-treated steel plate were individually subjected to electrodeposition coating at a bath temperature of 25°C. for 3 minutes at 80 V under the same electrode conditions as in Example 1. After water-washing and air-drying, the resulting films were baked at 180°C. for 30 minutes. The efficiencies of the thus formed films were as shown in Table 2.

TABLE 2

Item \ Substrate	colled rolled steel plate	ferric phosphate-treated plate	zinc phosphate-treated plate
Gloss value	86.3	86.5	84.3
Thickness (μ)	38/0	41.0	34.6
Pencil hardness	F—H	F—H	F—H
Cross cut	100/100	100/100	100/100
Solvent	Xylene	5—4	5—4
resis-	Isopropanol	5	5
tance	Acetone	5	5
Alkali resistance	5	5	5
Acid resistance	5—4	5—4	5—4
Erichsen value (mm)	9.0	8.1	7.7
Impact resistance (cm)	>50	>50	>50
Bending test	2 mm	—	—
Salt spray test	12.5 mm	12.5 mm	3.5 mm

- In Table 2, tests other than impact resistance, bending test and salt spray test are the same as in Table 1.

- Impact resistance was measured in such a manner that onto the film surface, an iron hammer having a diameter of $\frac{1}{4}$ inch and a weight of 500 g. was vertically dropped from a certain height, and the impact resistance of the film was represented by the height of the iron core at the time when the film surface had been damaged.

- Bending test was carried out in such a manner that a core of steel rod was disposed on the back side of the coated steel sheet and the steel plate was bent to an angle of 360°. The result of the bending test was represented by the diameter of a

core of steel rod measured in millimetres at the time when the film surface had been damaged by said test.

Salt spray test was carried out in such a manner that the film was linearly cut to form a linearly cut portion on the film surface and was sprayed with a 5% aqueous sodium chloride solution at 40°C. for 48 hours, and then the cut portion was peeled off by use of an adhesive tape. The result of the salt spray test was represented by the width of peeled film at the time when the film had been peeled.

The variations with lapse of time of coating baths obtained in the above manner were observed on the basis of gloss values of the resulting films. The results were as shown in Table 3.

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TABLE 3

Substrate \ Elapsed days	0	13	17	17(Exc)	25
Colled rolled steel plate	84.1	76.5	59.4	81.6	81.3
Ferric phosphate treated plate	81.8	70.3	68.4	75.9	79.5
Zinc phosphate treated plate	73.5	69.1	70.5	69.1	76.3
Specific conductivity of bath (micro mhos/cm)	2.24×10^2	5.39×10^2	5.63×10^2	4.83×10^2	5.90×10^2
pH of bath	9.02	8.77	8.76	8.90	8.70

5 As is clear from the results set forth in Table 3, the coating compositions of the present invention are favorable in bath stability, and the baths prepared by use of the present coating compositions can give, even when allowed to stand for a considerably long period of time, films having excellent properties. In Table 3, (Exc) in the column 17th day shows that an ion exchange method was applied on the 17th day. When an electrodeposition coating bath is allowed to stand for a considerably long period of time, the elution of water-soluble polymers takes place to lower the pH of the bath and to increase the specific electroconductivity thereof, whereby the resulting film is deteriorated in efficiencies. If, in this case, the water-soluble polymers eluted into the bath are removed by means of an ion exchange resin, the bath can be restored to a bath which is high in stability and which can give a film excellent in properties, as is clear from Table 3.

EXAMPLE 3

25 A mixture comprising the compounds shown below was polymerized under the same conditions as in Example 2, and was neutralized with 17.8 parts of β -dimethylaminoethanol to obtain a resin solution having a solids content

of 57.2%, an acid number of 19.6, and a viscosity of U (Gardner). 30

2-Ethylhexyl acrylate	276 parts	
Styrene	207 "	
2-Hydroxyethyl methacrylate	31.3 "	
N-n-Butoxymethyl acrylamide-itaconic acid mixture obtained in Example 1 (B)	389 "	35
Itaconic acid	6.5 "	
Isopropanol	312 "	
Azobisisobutyronitrile	22.4 "	40
2-Mercaptoethanol	6 "	

The thus obtained resin had Tg of -1.5°C ., pKa of 8.73, n value of 1.15 average molecular weight of 9.2×10^3 , and α value of 0.4. The resin solution was treated in the same manner as in Example 2 to obtain a white pigmented paste. This paste was used to prepare a coating bath having a solids concentration of 13%, a pH of 8.6, and a specific electroconductivity of 3.57×10^2 micro-mhos/cm (at the time when the solids content was 11%). Subsequently, electrodeposition coating and baking were effected under the some conditions as in Example 2. The properties of the resulting films were as shown in Table 4. 55

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TABLE 4

Item	Substrate	colled rolled steel plate	ferric phosphate- treated sheet	zinc phosphate- treated sheet
Gloss value		85.2	83.2	82.2
Thickness (μ)		28	28	26
Pencil hardness		F	F	H
Cross cut		100/100	100/100	100/100
Solvent resis- tance	Xylene	4-5	4-5	4-5
	Isopropanol	4-5	4-5	4-5
	Acetone	4	4-5	4-5
Alkali resistance		5	5	5
Acid resistance		4	4	4

EXAMPLE 4

A mixture comprising the compounds shown below was polymerized under the same conditions as in Example 2, and was neutralized with 17.8 parts of β -dimethylaminoethanol to obtain a resin solution having a solids content of 57.5%, a viscosity of Q (Gardner), and an acid number of 19.9.

2-Ethylhexyl acrylate	234	parts
Ethyl acrylate	100	"
Styrene	156	"
N-n-Butoxymethyl acrylamide		
distilled and isolated from		
the mixture obtained in Ex-		
ample 1 (D)	157	"
Itaconic acid	32.5	"
Azobisisobutyronitrile	22.5	"
2-Mercaptoethanol	9	"
Isopropanol	539	"

The resin obtained had Tg of -23.5°C , pKa of 8.79, n value of 1.11, average mole-

cular weight of 9.0×10^3 and α value of 0.4. The resin solution was treated in the same manner as in Example 2 to form a white pigmented paste. This paste was used to prepare an electrodeposition coating bath having a solids concentration of 13%, a pH of 8.70, and a specific electroconductivity of 2.53×10^2 micro-mhos/cm (at the time when the solids content was 11%). Subsequently, electrodeposition coating and baking were effected under the same conditions as in Example 2.

On the other hand, an aqueous solution containing 0.01 mol/l. of L-histidine was prepared and was adjusted to the same pH as that of the aforesaid electrodeposition coating bath. 50 g. of said aqueous solution was incorporated into 500 g. of the aforesaid coating bath to prepare another coating bath. The thus prepared two baths were individually subjected to tests with continuous stirring in open at 25°C . The results are shown in Table 5 by way of variations in gloss value and thickness of the resulting films.

TABLE 5

Test days	No incorporation of L-Histidine		L-Histidine Initially incorporated		L-Histidine Incorporated after 20 days	
	Gloss	Thickness	Gloss	Thickness	Gloss	Thickness
0	86.3	43	85.6	38	86.3	43
20	20.0	100	81.1	34	82.5	37

(Note: Test plate employed was a zinc phosphate-treated plate.)

As is clear from the above table, the bath which has not been incorporated with the L-histidine solution is greatly lowered in stability as compared with the bath incorporated therewith. Further, the stability of a bath lowered in stability is improved by incorporation of the L-histidine solution in an amount equal to that of the bath.

Ethyl acrylate	447	parts
Lauryl methacrylate	359	"
Styrene	520	"
N-n-Butoxymethyl acrylamide-itaconic acid mixture obtained in Example 1 (B)	965	"
Itaconic acid	16.5	"
Azobisisobutyronitrile	59.0	"
2-Mercaptoethanol	22.5	"
Isopropanol	763	"

10

EXAMPLE 5

This example shows the case where a long chain acrylate was used in combination with a short chain acrylate in order to impart heat flowability to the resulting film.

15

A mixture comprising the compounds shown below was polymerized under the same conditions as in Example 2, and was neutralized with 44.4 parts of β -dimethylaminoethanol to obtain a resin solution having a solids content of 57.7%, a viscosity of U (Gardner), and an acid number of 19.3.

20

The thus obtained resin had Tg of 20°C., pKa of 9.15, n value of 1.18, average molecular weight of 12.0×10^3 and α value of 0.4. The resin was treated in the same manner as in Example 2 to form a white pigmented paste. This paste was used to prepare an electrodeposition coating bath having a solids content of 13%, a pH of 8.90, and a specific electroconductivity of 2.35×10^3 micro-mhos/cm (at the time when the solids content was 11%). Subsequently, electrodeposition coating and baking were effected under the same conditions as in Example 2. The properties of the resulting films were as shown in Table 6.

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TABLE 6

Item \ Substrate	colled rolled steel plate	ferric phosphate-treated plate	zinc phosphate-treated plate
Gloss value	85.3	85.5	84.1
Thickness (μ)	37	39	35
Pencil hardness	F—H	F—H	F—H
Cross cut	100/100	100/100	100/100
Solvent	Xylene	5	5
resis-	Isopropanol	5	5
tance	Acetone	5	5
Alkali resistance	5	5	5
Acid resistance	5	5	5

EXAMPLE 6

This example shows the fact that even when a monomer mixture synthesized by use of acrylonitrile as an azotropic dehydrating agent is used, films excellent in properties are obtainable.

A mixture comprising the compounds shown

below was polymerized in the same manner as in Example 2 and was neutralized with 8.9 parts of β -diethylaminoethanol to obtain a resin solution having a solids content of 59.6%, a viscosity of Y (Gardner), and an acid number of 10.5.

15	2-Ethylhexyl acrylate	340 parts
	Styrene	234 "
	N-n-Butoxymethyl acrylamide-itaconic acid - acrylonitrile mixture obtained in Example 1 (C)	200 "
20	Itaconic acid	3.25 "
	Azobisisobutyronitrile	22.5 "
	2-Mercaptoethanol	6 "
	Isopropanol	332.3 "

The resulting resin had Tg of -1.5°C ., pKa of 8.7, n value of 1.19, average molecular weight of 11.0×10^3 and α value of 0.4. The resin solution was treated in the same manner as in Example 2 to obtain a white pigmented paste. This paste was used to prepare an electrodeposition coating bath having a solid content of 13%, a pH of 8.5, and a

specific electroconductivity of 3.13×10^3 micro-mhos/cm (at the time when the solids content was 11%). Subsequently, electrodeposition coating and baking were effected under the same conditions as in Example 2. The efficiencies of the resulting films were as shown in Table 7.

TABLE 7

Item	Substrate		
	colled	rolled	
	steel	plate	
Gloss value	83	82	80
Thickness (μ)	28	30	32
Pencil hardness	F	F	F
Cross cut	100/100	100/100	100/100
Solvent resis- tance	Xylene	5	5
	Isopropanol	5	5
	Acetone	5	5
Alkali resistance	5	5	5
Acid resistance	5	5	5

EXAMPLE 7

This example shows the fact that even when a monomer mixture is synthesized from an acrylamide or N-butoxymethyl acrylamide, a favorable resin for electrodeposition coating can be obtained.

Into the same device as in Example 1 were charged 50 parts of azobisisobutyronitrile, 10 parts of 2-mercaptoethanol, and a mixture comprising the compounds shown below.

Ethyl acrylate	693	parts
Styrene	426	"
N-n-Butoxymethyl acrylamide-itaconic acid mixture obtained in Example 1 (A)	486	"
Isopropanol	800	"

The resulting mixture was elevated in temperature in 2 hours. In this case, 5 parts of 2-mercaptoethanol and 3 parts of azobisisobutyronitrile were added, and the mixture was maintained at 68°C. After 2 hours, 3 parts

of azobisisobutyronitrile was added, and the heating was continued for additional 2 hours. At the 6th hour from the beginning, the temperature was elevated to 75°C. and polymerization was effected for additional 2 hours. The resulting solution was neutralized by addition of 17.8 parts of β -dimethylaminoethanol to obtain a resin solution having a solids content of 54.3%, a viscosity of R (Gardner), and an acid number of 9.8. This resin had Tg of 17.5°C., pKa of 9.0, n value of 0.88, average molecular weight of 9.8×10^3 and α value of 0.4. The resin solution was treated in the same manner as in Example 2 to obtain a white pigmented paste. This paste was used to prepare an electrodeposition coating bath having a solids concentration of 13%, a pH of 8.55, and a specific electroconductivity of 2.50×10^2 micro-mhos/cm (at the time when the solids content was 11%). Subsequently, electrodeposition and baking were effected under the same conditions as in Example 2. The properties of the resulting films were as shown in Table 8.

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TABLE 8

Item \ Substrate	colled rolled steel plate	ferric phosphate-treated plate	zinc phosphate-treated plate
Gloss value	84.5	85.6	83.5
Thickness (μ)	22	26	26
Pencil hardness	H	H	H
Cross cut	100/100	100/100	100/100
Solvent	Xylene	4	4
resis-	Isopropanol	4	5
tance	Acetone	5	5
Alkali resistance	5	5	5
Acid resistance	5-4	5-4	5-4

COMPARATIVE EXAMPLE 8

5 This comparative example shows the fact that if the resin employed is excessively high in Tg (glass transition temperature), no excellent film is obtainable.

10 A mixture comprising the compounds shown below was polymerized according to the process of Example 2 and was neutralized with 14.2 parts of β -dimethylaminoethanol to obtain a resin solution having a solids content of 56.5%, a viscosity of Z (Gardner), and an acid number of 19.3.

15	Ethyl acrylate	50	parts
	Methyl methacrylate	50	"
	Styrene	395	"
	N-n-Butoxymethyl acrylamide	78.5	"
	Itaconic acid	26	"
	Azobisisobutyronitrile	22.4	"
20	2-Mercaptoethanol	6	"
	Isopropanol	372	"

This resin had Tg of 84°C., pKa of 8.60, n value of 0.95, average molecular weight of 14×10^3 and α value of 0.4. The resin solution was treated in the same manner as in Example 2 to obtain a white pigmented paste. This paste was used to prepare an electro-deposition coating bath having a solids concentration of 13%, a pH of 8.8, and a specific electroconductivity of 4.9×10^2 micro-mhos/cm (at the time when the solids content was 11%). Subsequently, electrodeposition coating (with the metal to be coated as the anode) and baking were effected under the same conditions as in Example 2. The properties of the resulting films were as shown in Table 9, but the films had no smoothness and were low in throwing power.

TABLE 9

Item \ Substrate	colled rolled steel plate	ferric phosphate- treated plate	zinc phosphate- treated plate
Gloss value	30	28	29
Thickness (μ)	70	75	56
Pencil hardness	6H	6H	6H
Solvent	Xylene	4	4
resis-	Isopropanol	4	4
tance	Acetone	4	4
Alkali resistance	1	1	1
Acid resistance	1	1	1

EXAMPLE 9

A mixture comprising the compounds shown below was polymerized according to the process of Example 2 and was neutralized with 44.4 parts of β -dimethylaminoethanol to obtain a resin solution having a solids content of 56.8% and an acid number of 19.5.

5	2-Ethylhexyl acrylate	806	parts
10	Styrene	520	"
	N-n-Butoxymethyl acrylamide	400	"
	α -Methyleneglutaric acid	90	"
	Azobisisobutyronitrile	59	"
	2-Mercaptoethanol	22.5	"
15	Isopropanol	753	"

The resin obtained had Tg of $-8.0^{\circ}\text{C}.$, pKa of 9.25, n value of 1.15, average molecular weight of 10.5×10^3 and α value of 0.4. This resin was treated in the same manner as in Example 2 to obtain a white pigmented paste. This paste was used to prepare an electrodeposition coating bath having a solids content of 13%, a pH of 9.0, and a specific electroconductivity of 2.13×10^2 micro-mhos/cm (at the time when the solids content was 11%). Subsequently, electrodeposition coating and baking were effected under the same conditions as in Example 2. The properties of the resulting films were as shown in Table 10. As is clear from the results set forth in the table, the use of α -methyleneglutaric acid also results in films substantially the same in properties as in the case where itaconic acid is used.

TABLE 10

Item \ Substrate	colled rolled steel plate	ferric phosphate-treated plate	zinc phosphate-treated plate
Gloss value	85.5	84.7	83.8
Thickness (μ)	40	39	39
Pencil hardness	F—H	F—H	F—H
Cross cut	100/100	100/100	100/100
Solvent	Xylene	5	5
resis-	Isopropanol	5	5
tance	Acetone	5	5
Alkali resistance	5	5	5
Acid resistance	5	5	5

EXAMPLE 10

To 375 parts of the white pigmented paste obtained in Example 2 was added 30 parts of an epoxy resin having a melting point of 64—74°C., an epoxy equivalent of 450—500, and a molecular weight of about 900 (which resin was a condensation product of bisphenol A with polyethylene glycol and was used in the form of a 50% butyl Cellosolve solution). After being ground, the mixture was used to prepare an electrodeposition coating bath having a solids concentration of 13.2%, a pH of

8.66, and a specific electroconductivity of 3.02×10^2 micro-mhos/cm (at the time when the solids content was 11%). Using the thus prepared electrodeposition coating bath, a ferric phosphate-treated steel plate and a zinc phosphate-treated steel plate were connected as the anode and subjected to electrodeposition coating at 80 V for 3 minutes. Subsequently, the resulting films were baked at 180°C. for 30 minutes. The efficiencies of the films were as shown in Table 11.

TABLE 11

Item \ Substrate	ferric phosphate-treated plate	zinc phosphate-treated plate
Gloss value	80.0	76.8
Thickness (μ)	34	36
Pencil hardness	F	F
Cross cut	100/100	100/100
Solvent	Xylene	5
resis-	Isopropanol	5
tance	Acetone	5
Alkali resistance	5	5
Acid resistance	5	5
Salt spray test	4.5 mm	1.5 mm

By comparison with the salt spray test results set forth hereinbefore in Table 2, it is evident that with the acrylic coating materials the addition of an epoxy resin increases the corrosion resistance of the resulting films.

EXAMPLE 11

To 100 parts of the resinous solution obtained in Example 3 was added 10 parts of a water-soluble melamine-resin. This mixed resinous solution was treated in the same man-

ner as in Example 2 to obtain a white pigmented paste. This paste was used to prepare a coating bath having a solid concentration of 13 weight %, a pH of 8.9, and a specific electroconductivity of 3.15×10^2 micro-mhos/cm (at the time when the solid content was 11 weight %).

Subsequently, electrodeposition coating and baking were effected under the same conditions as in Example 2. The efficiencies of the resulting films were as shown in Table 12.

TABLE 12

Item \ Substrate	colled rolled steel plate	ferric phosphate-treated plate	zinc phosphate treated plate
Gloss value	84.5	84.7	83.3
Thickness (μ)	32	32	28
Pencil hardness	H-2H	H-2H	H-2H
Cross cut	100/100	100/100	100/100
Solvent	Xylene	5	5
resis-	Isopropanol	5	5
tance	Acetone	5	5
Alkali resistance	5	5	5
Acid resistance	5	5	5

EXAMPLE 12

Electrodeposition coating baths were prepared in the same manner as in Example 2, except that the amount of the 2-mercaptoethanol, which had been used as a molecular weight modifier, was varied as shown in Table 13. Using the thus prepared coating baths,

colled rolled steel plates were connected as the anode and subjected to electrodeposition coating at 80 V for 3 minutes. Subsequently, the resulting films were baked at 180°C. for 30 minutes. The properties of the films were as shown in Table 13.

TABLE 13

Amount of 2-mercaptoethanol added (based on the monomer mixture)	1.25%	0.83%	0.42%
pKa Value of resin	9.20	9.13	9.05
n	1.17	1.08	1.92
α	40	40	40
Gloss { [I] of film	81.7	79.1	63.3
{ [II] " " "	68.9	75.3	49.5
Molecular weight of resin	9,910	9,800	14,730

In the table, Gloss [I] is the gloss value of the film formed by effecting the electrodeposition coating immediately after preparation of the bath, and Gloss [II] is the gloss value of the film obtained by effecting the electrodeposition coating after continuously stirring the bath at 40°C. for 7 days after preparation.

From the results set forth in Table 13, it is evident that, depending on the difference in molecular weight, the polymers differ in pKa and n values, though the monomers constituting the polymers are same, and the stability of electrodeposition coating baths prepared therefrom and the gloss of the resulting films

are greatly affected. It is also understood that particularly when a polymer high in molecular weight is used, no film excellent in gloss can be obtained because the resin is decreased in pKa value, is increased in n value and is made inferior in bath stability, and the resulting film is degraded in heat reflowability.

EXAMPLE 13

2 g. of each of the pigments set forth in Table 14 were individually dispersed in 100 g. of water. The dispersions were adjusted to the pH values as shown in Table 14. After 3 hours, the precipitated volumes of the pigments were measured, and the pKp values of the pigments were calculated as above.

TABLE 14

pH of dispersion	Pigment		
	TiO ₂ (R-505)	Carbon Black (#100)	Red iron oxide
2.0	98	10	95
3.0	98	10	95
4.0	98	10	95
5.0	10	10	95
6.0	10	10	15
7.0	10	10	15
8.0	10	97	15
9.0	95	97	15
10.0	96	97	95
11.0	98	97	97
12.0	98	97	97
pKp	8.6	7.8	9.6

Of the pigments shown in Table 14, TiO₂ (R-550) is a product of Ishihara Sangyo K.K., and Carbon Black is a product of Mitsubishi Kasei K.K.

The precipitated volume referred to in the above is the volume, represented by %, of a pigment or enamel which has precipitated after dispersing it in water at a certain pH and allowing the dispersion to stand for a definite period of time. The greater the said value,

the more favorable the water dispersibility.

Pigmented pastes were obtained by treating resins having pKa values of 8.33 and 9.06 and pigments having the pKp values shown in Table 15, in the same manner as in Example 2. These pastes were used to prepare coating baths. The thus prepared pigmented baths were measured in respect of dispersion stability to obtain the results shown in Table 15.

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TABLE 15

pKa of resin	pKp of pigment	Precipitated volume		pKa of tesin	pKp of pigment	Precipitated volume
		After 1.5 hours	After 3 hours			
8.33	9.70	72.5	55.5	9.06	9.70	96
"	9.05	71.5	50.5	"	9.53	73
"	8.60	22.0	11.0	"	9.45	61
"	8.30	10.0	10.0	"	8.95	52
"	7.75	33.0	11.0	"	8.60	52
"	6.73	99.0	99.0	"	77.5	54
"				"	6.73	84

From the results shown in Table 15, it is clear that a coating bath obtained by combining a pigment and a resin which satisfy the condition

$$|pKp - pKa| \geq 0.1$$

is excellent in water dispersibility of paint particles and is prominent in dispersion stability thereof, as well. The resins having pKa values of 8.33 and 9.06 were prepared according to the process of Example 2 and neutralized to 45% of the apparent neutralisation degree with β -dimethyl aminoethanol.

The resin having pKa value of 8.33 has an n value of 0.9, Tg of 16°C and an average molecular weight of 9,000, and the resin having a pKa value of 9.06 has an n value of 1.4, Tg of 20°C and an average molecular weight of 12,000.

EXAMPLE 14

The resin having pKa of 9.20, which was obtained in Example 2, titanium oxide having pKp of 9.53, and carbon black having pKp of at least 10 were used to prepare colored coating baths in the following manner:

Grey pigmented bath:

To 100 parts of the resin solution, 55 parts of TiO_2 and 1.5 parts of carbon black were added. The mixture was ground in a ball mill for 24 hours and was then charged with additional 200 parts of the resin solution to obtain a grey pigmented paste. This paste was used to prepare a coating bath having a concentration of 13% and a pH of 8.75.

Black pigmented bath:

To 100 parts of the resin solution, 5.1 parts of the carbon black was added. The mixture was ground in a ball mill for 24 hours and was then charged with additional 200 parts of the resin solution to obtain a black pigmented paste. This paste was used to prepare a coating bath having a concentration of 11.8% and a pH of 8.8.

By the use of the above-mentioned baths, rolled steel plates and zinc phosphate-treated plates were connected as the anode and electrodeposition-coated at 8 V for 2 minutes, and the resulting films were baked at 180°C. for 30 minutes. The efficiencies of the films were as shown in Table 16.

TABLE 16

Colored enamel		Grey bath		Black bath	
Item	Substrate	colled rolled steel plate	zinc phosphate- treated plate	colled rolled steel plate	zinc phosphate- treated plate
Gloss value		75.1	71.8	87.2	86.6
Thickness (μ)		36	32	49	36
Pencil hardness		HB	HB	3B	2B
Cross cut		100/100	100/100	100/100	100/100
Solvent resis- tance	Xylene	4-5	4-5	5	4-5
	Isopropanol	5	4-5	4-5	4-5
	Acetone	5	5	4-5	4-5
Alkali resistance		5	5	5	5
Acid resistance		5	5	5	5

From the results set forth in Table 16, it is obvious that even formed into colored coatings, the coating compositions of the present invention give excellent films by one-coat finish.

The stabilities of the above coating baths are shown in Table 17 with reference to the gloss values of the films.

TABLE 17

Colored enamel		Grey		Black	
Elapsed days	Substrate	colled rolled steel plate	zinc phosphate- treated plate	colled rolled steel plate	zinc phosphate- treated plate
0		75.1	71.8	87.2	86.6
10		76.1	73.1	91.1	83.5
22		76.5	71.0	88.4	83.6

From the results set forth in Table 17, it is evident that the colored enamel coating baths in accordance with the present invention are markedly excellent in stability and always give uniform films.

COMPARISON EXAMPLE 1

A mixture comprising the compounds shown below was polymerized in the same manner as in Example 1 to obtain a resin solution.

Ethyl acrylate	155	parts
2-Ethylhexyl acrylate	157	"
Styrene	146	"
N-n-Butoxymethyl acrylamide	118	"
Acrylic acid	22	"
Azobisisobutyronitrile	22.4	"
2-Mercaptoethanol	6	"
Isopropanol	474	"

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5 The resin solution was neutralized with 16 parts of β -dimethylaminoethanol to form a resin having pKa of 8.57, n value of 1.10, α value of 0.6 and Tg of -3.0°C . The resin solution had a solids content of 54.0%, an acid number of 11.8, and a viscosity of T (Gardner). From the said resin solution, a white pigmented paste was obtained in the same manner as in Example 2. This enamel 10 paste was used to prepare an electrodeposition coating bath having a solids concentration of 13%, a pH of 8.4 and a specific electroconductivity of 4.85×10^2 micro-mhos/cm (at the time when the solids content was 11%). Subsequently, electrodeposition coating was effected under the same conditions as in Example 2, and the resulting films were baked at 180°C . for 30 minutes. The properties of the thus formed films were as shown in Table 18. 15 20

TABLE 18

Item	Substrate		
	colled rolled steel plate	ferric phosphate-treated plate	zinc phosphate-treated plate
Gloss value	78.0	77.6	67.3
Thickness (μ)	28	27	27
Pencil hardness	H	H	H
Cross cut	100/100	100/100	100/100
Solvent resistance	Xylene	3	3
	Isopropanol	4	5
	Acetone	4-5	4
Alkali resistance	5	5	4
Acid resistance	5	4	4
Bath stability test	Gloss value at the 2nd day	18.7	13.2
	Gloss value at the 7th day	14.3	7.0
			32.0

5 In the table, tests other than the bath stability test are the same as in the case of Example 2. The bath stability test is represented by the gloss value of a film formed by subjecting the bath to continuous stirring in open at 25°C . and electrodeposition-coating the film during said stirring. From the results set forth in Table 18, it is clear that when acrylic acid is used as the acid monomer, the resulting resin is favorable in pKa and n values, but a coating bath made by use of said resin is marked in degradation in stability due to elapse time. This indicates the fact that the polymer obtained by the use of acrylic acid as the acid component is a mixture of polymers having various pKa values, so that the 10 15 20 25

polymers low in pKa value have gradually migrated into the aqueous phase.

COMPARISON EXAMPLE 2

40 An electrodeposition coating material was prepared by use of a polymer obtained in such a manner that an amide polymer was first formed using acrylic acid as acid monomer component and then the amide groups are N-butoxymethylated with formaldehyde and butanol. The results of examination of the properties of the electrodeposition coating material are shown in Table 19. 45

50 One half of a mixture comprising the compound shown below was charged into the same device as in Example 1, and polymer-

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155 parts
157 "
146 "
118 "
22 "
22.4 "
6 "
474 "

ization was initiated at the boiling point of the mixture. The remaining mixture was added dropwise in 3 hours and was polymerized.

	Acrylic acid	64	parts
5	Acrylamide	120	"
	Styrene	200	"
	Ethyl acrylate	216	"
	n-Butyl acrylate	200	"
	N-Butanol	560	"
10	di-, tert-Butyl peroxide	8	"
	tert-Dodecyl mercaptan	40	"

To the resulting polymer solution, 121.5 parts of paraformaldehyde was added, and the mixture was dehydrated, with reflux, until water had been completely removed. The amount of water removed was 59.4 ml.

The thus obtained resin solution was charged with TiO_2 and was treated in the same manner as in Example 2 to prepare an electrodeposition coating bath having a solids concentration of about 10%, a pH of 8.58, a specific electroconductivity of 6.17×10^2 micro-mhos/cm, pKa resin value of 8.53, n resin value of 0.74 and α resin value of 0.4.

The resin of the present invention, formed by using itaconic acid as the acid component

(the resin obtained in Example 2), had pKa of 9.20 and n value of 1.17, and gave a coating bath having a specific electroconductivity of 2.24×10^2 micro-mhos/cm. In view of the above, it is anticipated that the bath stability of a coating bath, which has been prepared by use of a polymer obtained by using acrylic acid as the acid component, would be such that the resulting films are inferior in properties. This is considered ascribable to the fact that acrylic acid, when used as the acid component, is low in copolymerizability with other monomers and gives a mixture of polymers having various pKa and n values, so that polymers low in pKa value elute into the aqueous medium to degrade the stability of the coating bath.

Using the thus prepared coating bath, a colled rolled steel plate (abbreviated as Fe), a zinc phosphate-treated plate (abbreviated as P—Zn), and a ferric phosphate-treated plate (abbreviated as P—Fe) were individually subjected to (A) coating at 60 V for 3 minutes and curing at 160°C. for 30 minutes, (B) coating at 80 V for 3 minutes and curing at 180°C. for 30 minutes, and (C) coating at 100 V for 3 minutes and curing at 180°C. for 30 minutes. The properties of the resulting films were as shown in Table 19.

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TABLE 19

Coating and curing conditions		(A)			(B)			(C)		
Item	Substrate	Fe	P-Fe	P-Zn	Fe	P-Fe	P-Zn	Fe	P-Fe	P-Zn
Gloss value		67.7	70.7	60.9	50.5	55.5	55.0	36.9	49.4	49.7
Thickness (μ)		37	34	33	44.5	45	36	65	53.5	45
Pencil hardness		2H	2H	2H	—	—	—	2H	2H	2H
Cross cut		100/100	100/100	100/100	—	—	—	100/100	100/100	100/100
Solvent	{ Xylene Isopropanol Acetone }	4-5	4-5	5	—	—	—	4-5	4-5	4-5
resis-		4-5	4-5	4-5	—	—	—	4-5	4-5	4-5
tance		5	5	4-5	—	—	—	4	4	4
Alkali resistance		2	2	2	—	—	—	2	2	2
Acid resistance		4	4	4	—	—	—	5-4	4	5-4
Erichsen value		—	—	—	15	6	7	—	—	—
Impact resistance		—	—	—	20	20	30	—	—	—

From the results set forth in Table 19, it is evident that films formed by use of the coating material of this referential example are not so excellent in gloss and are also low in Erichsen value and impact resistance as compared with films formed by use of the

present coating compositions.

Further, the stability of the above coating bath is shown in Table 20 with reference to the gloss values of films formed by effecting the coating at 60 V for 3 minutes and the curing at 180°C. for 30 minutes.

TABLE 20

Elapsed days \ Substrate	colled rolled steel plate	ferric phosphate treated plate	zinc phosphate treated plate	pH	Specific electro - conductivity micro-mhos/cm)
0	67.7	70.7	60.9	8.58	6.17×10^2
1	17.9	21.6	19.3	8.80	6.630×10^2
3	21.0	28.0	22.0	8.62	7.695×10^2

From the results set forth in Table 20, it is evident that a coating material obtained by use of acrylic acid as the acid component is markedly low in bath stability, and is not usable as an electrodeposition coating material, which is suitable for one-coat finish and which has practical efficiencies.

COMPARISON EXAMPLE 3

A mixture comprising the compounds shown below was treated in the same manner as in Example 2 to obtain a resin solution.

Acrylamide	25	parts
Methacrylic acid	25	"
n-Butyl acrylate	125	"
Styrene	75	"
n-Butanol	270	"
di-tert-Butyl peroxide	3.8	"
tert-Dodecyl mercaptan	2.5	"

450 parts of the resin solution was charged with 22.5 parts of paraformaldehyde and 2.25 parts of triethylamine, and was refluxed to introduce N-n-butoxymethyl groups into the amide copolymer. The resin solution is then treated in the same manner as in Example 2 to obtain a pigmented paste. This paste was used to prepare an electrodeposition coating bath having pKa resin value of 8.61, n resin value of 0.42, α resin value of 0.4, a pH of 9.1, and a specific electroconductivity of 7.43×10^2 micro-mhos/cm. Using the thus prepared bath, a colled rolled steel plate, a zinc phosphate-treated plate, and a ferric phosphate-treated plate were individually electrodeposition-coated at 66 V for 3 minutes, and the resulting films were baked at 175°C. for 30 minutes. The efficiencies of the films thus formed were as shown in Table 21.

TABLE 21

Item \ Substrate	colled rolled steel plate	ferric phosphate-treated plate	zinc phosphate-treated plate
Gross value	1.0	1.4	1.0
Thickness (μ)	60	60	50
Pencil hardness	H	F	H
Gross cut	20/100	100/100	100/100
Solvent	Xylene	5	2
resis-	Isopropanol	5	2
tance	Acetone	3	1
Alkali resistance	3	3	3
Acid resistance	3	3	3

From the results set forth in Table 21, it is evident that the electrodeposition coating material of this comparison example using methacrylic acid as the acid component has no entirely suitable properties, and is not suitable as a coating material for one-coat finish.

COMPARISON EXAMPLE 4

A mixture comprising the compounds shown below was treated in the same manner as in Example 3 to prepare an electrodeposition coating bath having pKa resin value of 6.84, n resin value of 2.21, α resin value of 0.4, a pH of 6.52, and a specific electroconductivity of 1.28×10^3 micro-mhos/cm.

15	Ethyl acrylate	425	parts
	Acryl amide	25	"
	Itaconic acid	50	"
	Azobisisobutyronitrile	22.4	"
	2-Mercapto ethanol	6	"
20	Isopropanol	472	"

Using the thus prepared bath, a colled rolled steel plate, a zinc phosphate-treated plate, and a ferric phosphate-treated plate were individually electrodeposition-coated to form films having, respectively, gloss values of 86.5, 28.0 and 83.5 and thicknesses of 47, 34.5 and 47. However, no film having other suitable properties could be obtained at all, since the resin in the bath was a thermoplastic resin.

COMPARISON EXAMPLE 5

Mixtures D—1 and D—2 comprising, respectively, the compounds shown below were treated in the same manner as in Example 2 to obtain resin solutions.

D—1

Ethyl acrylate	250	parts	
Styrene	143	"	
N-n-Butoxymethyl acrylamide	286	"	
Itaconic acid	29.3	"	
Isopropanol	269	"	40
Azobisisobutyronitrile	22.4	"	
2-Mercaptoethanol	6.0	"	

D—2

Ethyl acrylate	693	parts	
Styrene	426	"	45
N-n-Butoxymethyl acrylamide-itaconic acid mixture in Example 1 (A)	486	"	
Isopropanol	800	"	
Azobisisobutyronitrile	56	"	50
2-Mercaptoethanol	15	"	

The resin solutions were used to prepare electrodeposition coating baths in the same manner as in Example 2. Physical constants of the the resins and the coating baths were as shown in Table 22.

TABLE 22

Resin	D—1	D—2
pKa	7.75	9.06
n value	1.67	0.82
α value	0.35	0.40
Acid number	72.5	19.0
Electrochemical equivalent	1260	6750
Specific electroconductivity of bath	9.34×10^3 micro-mhos/cm	1.96×10^3 micro-mhos/cm
pH of bath	7.39	8.80
Tg	22°C.	15°C.

Using the said coating baths, colled rolled steel plates, ferric phosphate-treated plates, and zinc phosphate-treated plates were individually electrodeposition-coated to form films. The properties of the films were as shown in Table 23.

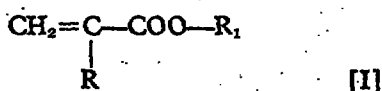
TABLE 23

Item	Resin Substrate	D-1				D-2		
		colled rolled steel plate	zinc phosphate- treated plate	ferric phosphate- treated plate	colled rolled steel plate	zinc phosphate- treated plate	ferric phosphate- treated plate	
Gloss value		48.2	10.3	13.2	92.8	91.3	90.8	
Thickness (μ)		75	30	71	36	35	38	
Pencil hardness		F	F	F	H	H	H	
Cross cut		100/100	100/100	100/100	100/100	100/100	100/100	
Solvent	Xylene Isopropanol Acetone	3	3	3	3	3	3	
resis- tance		4	4	4	4	3	4	
		2	2	2	4-5	4	5	
Alkali resistance		4	4	4	5	5	5	
Acid resistance		5	5	5	5	4	4	
Film surface		Coarse	Coarse	Coarse	Smooth	Smooth	Smooth	

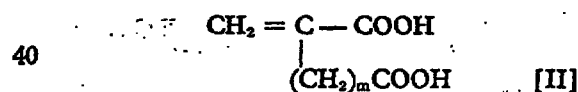
In this comparison example, the resin D—1, in which the copolymerization proportion of acid had been made large to increase the acid number of the polymer, and the resin D—2 of the present invention, in which the copolymerization proportion of acid had been made small, were used to examine the characteristics of the resins and the effects of said resins on films obtained by electrodeposition coating. As is clear from Tables 22 and 23, the increase in acid number of the resin results in the decrease in pKa value and the increase in n value of the resin, and results in the increase in specific electroconductivity of the coating bath made therefrom, with the result that the film obtained by electrodeposition coating is increased in thickness and is degraded in smoothness and gloss. It is thus evident that the increase in acid number of the resin employed makes it impossible to obtain an electrodeposition coating material suitable for one-coat finish.

WHAT WE CLAIM IS:—

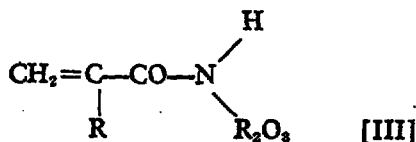
1. An aqueous coating composition for a one-coat electrodeposition process, comprising as an essential component a water-soluble or water-dispersible partial ammonium or amine salt of a copolymer resin comprising 93.5 to 35 mole % of a component (A) which is a monomer mixture of at least one compound represented by the general formula:



wherein R is a hydrogen atom or a methyl group, and R₁ is a branched or straight chain alkyl group having 1—8 carbon atoms, with at least one copolymerizable ethylenically unsaturated monomer, 1.5—15 mole % of a component (B), which is a compound represented by the general formula



wherein m is 1 or 2, and 5—50 mole % of a component (C), which is at least one compound represented by the general formula



wherein R is as defined above, R₂ is a branched or straight chain alkylene group having 1—8 carbon atoms, and R₃ is a branched or straight chain alkyl group having 1—6 carbon atoms, or a cycloalkyl group having up to 6 carbon

atoms, the characteristics of said resin after neutralization being such that, (1) in the equation defined by

$$\text{pH} = \text{pKa} + n \log \frac{\alpha}{1-\alpha} \quad \text{[IV]}$$

which is experimentally obtained in general as a relationship between pH and the degree of neutralization of a water-soluble dispersible resin, wherein pH represents the pH value if the aqueous resin solution or dispersion, pKa is a parameter which represents an acidity of the resin component and is defined by the equation: $\text{pKa} = -\log \text{Ka}$, wherein Ka is the dissociation constant of the resin, n is a parameter showing the extension of the polymer chain and α represents the apparent neutralization degree of the resin component which is given by the ratio of the total equivalent of the added amine or ammonia base to the total equivalent of the carboxylic acid contained in the copolymer resin, the resin satisfies the condition that $8.0 \leq \text{pKa}$; $0.5 \leq n \leq 1.5$; and $.3 \leq \alpha \leq .8$,

(2) the resin has a glass transition temperature Tg (as hereinbefore defined) of 60°C or below, and

(3) the resin has a number average molecular weight of 5,000 to 20,000.

2. A composition according to claim 1, wherein the characteristics of the resin after neutralization are such that the resin satisfies, in the equation [IV], the conditions of $8.5 \leq \text{pKa} \leq 9.5$, $0.8 \leq n \leq 1.3$, and $0.3 \leq \alpha \leq 0.8$, and the resin has a glass transition temperature Tg of 30°C or below, and has an average molecular weight of 5000 to 15,000.

3. A composition according to claim 1 or claim 2 which contains a pigment satisfying the relationship

$$|\text{pKp} - \text{pKa}| \geq 0.1 \quad \text{[V]}$$

wherein pKa is as defined in Claim 1, and pKp represents the acidity of the pigment, which is defined by the following equation: $\text{pKp} = -\log \text{Kp}$ wherein Kp is the dissociation constant of pigment P[H₂O] having water of absorption (as hereinbefore defined).

4. A composition according to any of Claims 1—3 which comprises up to 60 parts by weight of an N-alkoxymethylmelamine and/or an epoxy resin and 100 parts by weight of said resin component.

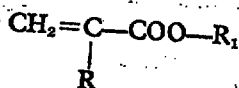
5. A composition according to any of Claims 1—3, which contains 2—20% by weight of the water-soluble or water dispersible resin and has a specific electroconductivity at 25°C of 150—800 micro-mhos/cm (measured with a composition having a solids content of 11% by weight).



In this comparison example, the resin D-1, in which the copolymerization proportion of acid had been made large to increase the acid number of the polymer, and the resin D-2 of the present invention, in which the copolymerization proportion of acid had been made small, were used to examine the characteristics of the resins and the effects of said resins on films obtained by electrodeposition coating. As is clear from Tables 22 and 23, the increase in acid number of the resin results in the decrease in pKa value and the increase in n value of the resin, and results in the increase in specific electroconductivity of the coating bath made therefrom, with the result that the film obtained by electrodeposition coating is increased in thickness and is degraded in smoothness and gloss. It is thus evident that the increase in acid number of the resin employed makes it impossible to obtain an electrodeposition coating material suitable for one-coat finish.

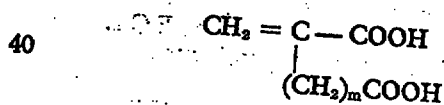
WHAT WE CLAIM IS:—

1. An aqueous coating composition for a one-coat electrodeposition process, comprising as an essential component a water-soluble or water-dispersible partial ammonium or amine salt of a copolymer resin comprising 93.5 to 35 mole % of a component (A) which is a monomer mixture of at least one compound represented by the general formula:



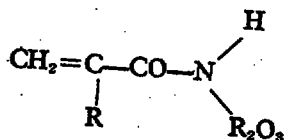
[I]

wherein R is a hydrogen atom or a methyl group, and R₁ is a branched or straight chain alkyl group having 1—8 carbon atoms, with at least one copolymerizable ethylenically unsaturated monomer, 1.5—15 mole % of a component (B), which is a compound represented by the general formula



[II]

wherein m is 1 or 2, and 5—50 mole % of a component (C), which is at least one compound represented by the general formula



[III]

wherein R is as defined above, R₂ is a branched or straight chain alkylene group having 1—8 carbon atoms, and R₃ is a branched or straight chain alkyl group having 1—6 carbon atoms, or a cycloalkyl group having up to 6 carbon

atoms, the characteristics of said resin after neutralization being such that, (1) in the equation defined by

$$\text{pH}=\text{pKa}+n \log \frac{\alpha}{1-\alpha} \quad \text{[IV]}$$

which is experimentally obtained in general as a relationship between pH and the degree of neutralization of a water-soluble dispersible resin, wherein pH represents the pH value if the aqueous resin solution or dispersion, pKa is a parameter which represents an acidity of the resin component and is defined by the equation: $\text{pKa} = -\log \text{Ka}$, wherein Ka is the dissociation constant of the resin, n is a parameter showing the extension of the polymer chain and α represents the apparent neutralization degree of the resin component which is given by the ratio of the total equivalent of the added amine or ammonia base to the total equivalent of the carboxylic acid contained in the copolymer resin, the resin satisfies the condition that $8.0 \leq \text{pKa}$; $0.5 \leq n \leq 1.5$; and $.3 \leq \alpha \leq .8$,

(2) the resin has a glass transition temperature Tg (as hereinbefore defined) of 60°C or below, and

(3) the resin has a number average molecular weight of 5,000 to 20,000.

2. A composition according to claim 1, wherein the characteristics of the resin after neutralization are such that the resin satisfies, in the equation [IV], the conditions of $8.5 \leq \text{pKa} \leq 9.5$, $0.8 \leq n \leq 1.3$, and $0.3 \leq \alpha \leq 0.8$, and the resin has a glass transition temperature Tg of 30°C or below, and has an average molecular weight of 5000 to 15,000.

3. A composition according to claim 1 or claim 2 which contains a pigment satisfying the relationship

$$|\text{pKp} - \text{pKa}| \geq 0.1 \quad \text{[V]}$$

wherein pKa is as defined in Claim 1, and pKp represents the acidity of the pigment, which is defined by the following equation: $\text{pKp} = -\log \text{Kp}$ wherein Kp is the dissociation constant of pigment P[H₂O] having water of absorption (as hereinbefore defined).

4. A composition according to any of Claims 1—3 which comprises up to 60 parts by weight of an N-alkoxymethylmelamine and/or an epoxy resin and 100 parts by weight of said resin component.

5. A composition according to any of Claims 1—3, which contains 2—20% by weight of the water-soluble or water dispersible resin and has a specific electroconductivity at 25°C of 150—800 micro-mhos/cm (measured with a composition having a solids content of 11% by weight).



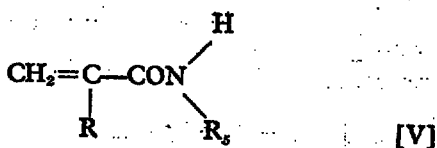
6. A composition according to any of Claims 1—5 wherein the water-soluble or water-dispersible resin has been prepared by polymerisation of the corresponding monomers in a water-miscible organic solvent as a polymerization medium.

7. A composition according to any of Claims 3—6, wherein the water-soluble or water-dispersible resin employed contains 10 to 30 mole % of the component (C).

8. A composition according to any of Claims 1—7 wherein the component (C) comprising the compound represented by the general formula [III] is N-n-butoxymethyl acrylamide or N-n-butoxymethyl methacrylamide.

9. A composition according to any of Claims 1—3 which comprises an epoxy resin and/or an N-alkoxymethyl melamine resin in which the alkyl moiety has 1—4 carbon atoms, and also comprises an acrylic resin copolymerised from the component (A), a monomer mixture formed by mixing in a molar ratio of from 99.9/0.1 to 40/60 at least one compound represented by the general formula [I] with at least one copolymerizable α,β -ethylenically unsaturated monomer; as the component (B), itaconic acid or α -methylene-glutaric acid; and as the component (C), N-n-butoxymethyl acrylamide or N-n-butoxymethylmethacrylamide.

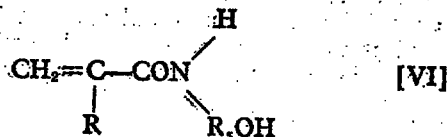
10. A composition according to any of Claims 1—9, wherein the water-soluble or water-dispersible resin has been prepared by use of the monomer mixture containing an N-alkoxyalkyl acrylamide or methacrylamide obtained by mixing, in a molar ratio of 99.9/0.1—20/80, a compound represented by the general formula



wherein R is a hydrogen atom or a methyl

group, and R_s is a hydrogen atom or an alkyl group having 1—12 carbon atoms, with itaconic acid or α -methylene glutaric acid or an anhydride thereof, and subjecting the mixture to dehydration condensation with alcohol and aldehyde in the presence of an organic solvent azeotropic with water or a copolymerizable vinyl monomer azeotropic with water.

11. A composition according to any of Claims 1—9, wherein the water-soluble or water-dispersible resin has been prepared by using the monomer mixture containing an N-alkoxyalkyl acrylamide or methacrylamide obtained by mixing in a molar ratio of 99.9/0.1—20/80 a compound represented by the general formula



wherein R is a hydrogen atom or a methyl group, and R_s is a branched or straight chain alkylene group having 1—3 carbon atoms, with itaconic acid or α -methylene glutaric acid or an anhydride thereof, and subjecting the mixture to dehydration condensation with alcohol in the presence of an organic solvent azeotropic with water or a copolymerizable vinyl monomer azeotropic with water.

12. A composition according to any of Claims 1—11, which additionally includes an amphoteric electrolyte having an isoelectric point of 6.5—8.5.

13. A composition according to Claim 12, wherein the amphoteric electrolyte is an amino acid.

14. A composition substantially as herein-described with reference to the non-comparative examples 1 to 7 and 9 to 14.

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