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3,451,902

PROTECTIVE LOCALIZED AREA RESIN COATINGS FOR ELECTROPLATING

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No Drawing. Continuation-in-part of application Ser. No. 543,070, Apr. 18, 1966. This application July 5, 1966, Ser. No. 562,466

The portion of the term of the patent subsequent to June 25, 1985, has been disclaimed
Int. Cl. C23b 5/48

U.S. Cl. 204—15

4 Claims

The present application is a continuation-in-part of co-pending U.S. application Ser. No. 543,070, filed Apr. 18, 1966 and now Patent No. 3,390,061.

The present invention relates in general to protective coatings and more particularly to resin-based protective coatings advantageously adapted for use in connection with coating operations requiring the deposition of metal upon metal.

A wide variety of methods for effectuating metal to metal coating operations are, of course, well known in the art being extensively described in the literature both patent and otherwise. The state of the art in this regard is such as to require little in the way of explanatory comment. Thus, it is common knowledge that the deposition of metal upon metal can be carried out by implementation of a number of techniques including, for example, galvanic, i.e., electrodeposition, dip coating, etc. The particular method selected will, of course, depend upon a number of considerations with perhaps the paramount criteria relating to the nature of the coating desired. Otherwise stated, the feasibility of a given coating method will depend, inter alia, upon the type of metal serving as the base material, the type of coating to be deposited, the physical extent of the metallic film to be deposited, i.e., whether all or only certain pre-selected surfaces of the base material are to be coated. In those instances wherein the entire surface area of the metallic article is to be coated, i.e., wherein complete immersion of the metallic article in the plating bath is indicated, it is quite likely that any of the conventional coating techniques promulgated for such purposes is eminently applicable.

In contradistinction, the industrial applications are legion wherein metal on metal deposition is desirably effected upon only certain and pre-selected surfaces of the metallic article. Moreover, the particular application may require that only certain discrete areas of a given metal surface be so coated as would be the case for example when providing ornamental or decorative designs. As will be readily apparent, the utilization of coating techniques which require immersing the entire metallic article in the plating medium, e.g., electroplating, would not be feasible in the absence of some manipulative technique designed to locally immunize such metallic article against the effect of the plating medium. Heretofore, a wide variety of techniques have been evolved in the art by which such localized immersion can be accomplished. Paramount among the manipulative techniques thus far evolved in this regard are those based upon the use of protective coatings of a temporary nature, i.e., temporary in the sense of being unaffected by prolonged contact with the solution media employed in the coating operation but which are nevertheless easily removed by suitable post-coating treatment. Invariably, such protective coating compositions contain as the essential ingredient a film-forming, polymeric resinous material, either natural or synthetic, capable of forming a strong, adhesive bond with the metal article being coated.

Despite the relatively widespread commercial acceptance of methods based upon the employment of temporary

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protective resin coatings, considerable difficulty has nevertheless been encountered as regards the obtention of optimum results. In the main, the resinous materials thus far employed for such purposes are uniformly characterized in that they fail to provide the requisite measure of protection, i.e., metal surfaces coated therewith will usually exhibit some degree of metal deposition. As will be readily appreciated, it is of the utmost importance that the protective resin coating be substantially, if not completely, impermeable to the plating bath in order to exclude even the remotest possibility of spurious metal deposition. Moreover, in many cases, it has been ascertained that the degree of adhesion extant between the resin coating and the metal surface tends to diminish to an intolerable extent, such a tendency being particularly manifest with the use of even moderately severe conditions of operation, e.g., temperature, period of immersion, solution corrosivity, etc.

A further source of difficulty stems from the fact that many of the resin materials currently employed for the aforescribed purposes exhibit undesirable change in solubility characteristics as a result of prolonged immersion in the plating bath to the extent that complete removal of the protective resin coating from the metal surface is rendered extremely difficult. The latter phenomena often necessitates resort to mechanical, e.g., abrading as opposed to purely chemical, i.e., solubilization techniques to assure such removal. Such techniques are in most instances burdensome both from the standpoint of economics as well as ease of processing.

The foregoing situation has proved to be of special consequence in connection with the production of bimetallic plates contemplated for ultimate use in the photomechanical reproduction arts, i.e., the preparation of photomechanical printing plates. Conventionally, such printing plates comprise for example an aluminum base provided on one side with a surface coating of copper, chromium or the like, such surface coating serving as the support for a light-sensitive, resist-forming layer. An integral phase in the processing of such sensitized elements involves the etching out of the surface metal coating, this being accomplished pursuant to the provision of a final plate having grease-repellent and grease-receptive areas. However, as mentioned hereinbefore, the techniques heretofore provided for the preparation of such bimetallic base plates have left much to be desired.

Thus, a primary object of the present invention resides in the provision of improved, resin-containing protective coatings admirably suited for use in connection with metal to metal coating operations and wherein one or more of the surfaces of such metal is to be protected against the plating medium.

Another object of the present invention resides in the provision of improved resin-containing protective coatings of a temporary nature advantageously adapted for use in connection with the preparation of bimetallic plates and wherein such resin is completely unaffected by the metal plating medium, e.g., the electrolytic plate bath; forms an adhesion bond of exceptional strength with the metal being coated; and is capable of being easily and completely removed from the metal surface subsequent to the plating operation.

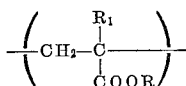
Other objects and advantages of the present invention will become apparent as the description proceeds.

The attainment of the foregoing and related objects is made possible in accordance with the present invention which in its broader aspects relates to the use of thermoplastic, film-forming, acrylic resins which are soluble in alkaline media, i.e., a pH ranging from approximately 7.5 to 8.0, as the protective coating material in metal to metal coating techniques.

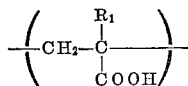
In accordance with the present invention, it has been ascertained that the use of such resins, and especially in coating operations involving the application of a metallic coating to one side of an aluminum base, leads to a considerable reduction in processing time as well as materials handling. For example, it has been found that resin materials of the aforescribed type are completely unaffected by the plating solutions conventionally employed in the copper coating of aluminum. As is well known, such plating solutions are usually one of four types viz. copper cyanide, copper sulfate, copper fluoborate or copper pyrophosphate. Not only do such resin materials serve as effective diffusion barrier layers, but in addition, retain a firmly adherent bonding with the aluminum surface throughout the entire plating operation. Perhaps the salient advantage attending the use of such resin materials relates to their ready solubility in alkaline media. Thus, immediately following completion of the plating operation, e.g., electrodeposition of copper on aluminum, the protective resin coating can be easily removed by treating same with an alkaline media, e.g., an ammonium hydroxy solution having a pH ranging from 7.5 to 8.0.

The film-forming alkaline soluble resin materials contemplated for use in accordance with the present invention are preferably derived from the polymerization of one or more monomers of the alpha, beta-monoethylenically unsaturated carboxylic acid series including their esters and salts. Suitable monomers include for example, acrylic acid, methacrylic acid, methylacrylate, ethylacrylate, butylacrylate, etc., methylmethacrylate, ethylmethacrylate, butylmethacrylate, and the like.

Resins of this type are readily available commercially such as the product Carboaset from the B. F. Goodrich Chemical Co., e.g., Carboaset 525. Although beneficial results may be obtained with the use of alkaline soluble resins of the general type encompassed by the aforesaid definition, it has nevertheless been determined that optimum realization of the improvements made possible by the present invention are obtained with those polymeric materials containing within their skeletal structure, on a mole basis, from about 80% to about 99% of units of the following structural formula:



wherein R represents hydrocarbon e.g., alkyl, aralkyl, aryl and alkaryl and preferably lower alkyl of 1 to 4 carbon atoms, e.g., methyl, ethyl, butyl, etc. and wherein R₁ represents lower alkyl; and from about 1% to about 20% of units of the following structural formula:



wherein R₁ has the above defined significance.

As will be recognized, the presence of the carboxyl pendent groups may result from the fact that a corresponding proportion of acrylic acid type monomers was present in the initial polymerizable monomer mixture or alternatively, such carboxy groups may be introduced into the polymer skeletal chain by subjecting an acrylate polymer, i.e., one containing no free acid group, to a suitable hydrolysis after treatment. The manner in which the polymer is prepared is not a particularly critical factor in the practice of the present invention so long as the relative proportions of carboxy solubilizing substituents in the polymer chain are maintained within the above defined limitations. Furthermore, the acrylate monomers may be employed in admixtures of 2, 3 or more. Thus, methyl acrylate; ethyl acrylate; butyl acrylate monomer systems have been found to provide polymers eminently suited to the purposes of the present invention. The resin is applied in the form of an 0.5 to 1% solution in isopropyl alcohol, although other solvents such as methanol,

ethanol, acetone, diacetone alcohol, methyl Cellosolve, dioxane, cyclohexanol, ethyl acetate, and the like may be used. The addition of a small quantity of oleic acid and a surface-active agent such as Alkaterge A (Commercial Solvents Corporation) is advantageous in promoting uniform wetting when the resin is applied to the metal surface. The molecular weight of the resinous material is likewise not of critical import so long as it be capable of depositing continuous films from solvent media. Thus, the molecular weight may range from 5,000 to 10,000 up to several million. As a general proposition, however, resin materials having a molecular weight of from about 500,000 to 1,000,000 are preferred.

Although the protective resin coating compositions of the present invention may be advantageously employed in any metal to metal coating operation requiring complete immersion of the metal to be coated in the plating medium, they have particularly advantageous applicability to electroplating operations involving the deposition of copper or chromium upon aluminum.

The present invention will be further illustrated by the following examples but it is to be understood that the invention is not restricted thereto.

EXAMPLE I

This example illustrates the application of the present invention to the production of a copper-coated aluminum plate. An aluminum plate, the surfaces of which have been rendered oxide-free by dipping in sodium hydroxide solution, is flow-coated on one side with a protective coating comprising the following compositions:

	Parts
Carboaset 525 ¹ (0.75% in isopropyl alcohol) -----	98.0
Alkaterge A (1% in isopropyl alcohol) -----	1.0
Oleic acid (2% in isopropyl alcohol) -----	1.0

¹ Molecular weight approximately 800,000 as determined by light scattering.

Approximately 5 cc. of the above composition is employed per sq. ft. of area to be coated. The coating is then allowed to dry for a period of about 15 to 20 minutes. The aluminum plate thus coated is immersed in a plating bath of the copper sulfate type, the aluminum serving as the cathode, the anode being an oxide-free, high-purity copper, with the uncoated aluminum surface facing the anode.

The conditions and parameters of the electroplating operation are summarized as follows:

Copper sulfate .5H ₂ O -----	gms. 200
Sulfuric acid -----	gms. 70
Cathode current density -----	amps./per sq. ft. 30
Anode current density -----	amps./per sq. ft. 30
Water to make 1 liter.	
Bath temperature 85/90° F.	

The plating operation is carried out for a period of approximately 3 minutes. The aluminum cathode is removed from the plating bath and given a water rinse. Visual examination of the copper coated aluminum sheet revealed that the protective resin layer had remained intact throughout the entire electroplating treatment being totally unaffected by the plating solution.

Furthermore, the adhesion of the resin coating to the aluminum surface is in no way deleteriously affected. Despite the strong adhesive bond, the protective resin coating is easily and completely removed from the aluminum surface by swabbing with a pad which has previously been dipped in an ammonium hydroxide solution having a pH of about 7.8. Resin removal is complete by the solvent-swabbing treatment to the extent that a polished aluminum surface is obtained merely by wiping with a cotton cloth. Thus, it is readily apparent that the alkaline solubility of the resin material remains unchanged despite subjection to the plating medium. The total time consumed in removing the protective resin coating is approximately 45 seconds.

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EXAMPLE II

A resin pre-coated aluminum sheet is prepared in the manner described in Example I. Copper plating of the coated aluminum surface is carried out with the following plating solution utilizing the parameters indicated.

Copper fluoborate -----gms--	224
Fluoboric acid -----gms--	15
Boric acid -----gms--	15
Cathode current density -----amps. per sq. ft--	35
Anode current density -----amps. per sq. ft--	30
Water to make 1 liter.	

The pH of the above solution is approximately 1.4. After electrodeposition of the copper film on the unprotected aluminum surface is complete, i.e., after a period of approximately 3 minutes, the aluminum cathode is removed from the bath and given a water rinse. Removal of the protective resin coating is accomplished in the manner described in Example I. Similar results are obtained in terms of ease of resin removal as well as resistance of the protective resin to the effects of the plating medium.

EXAMPLES III AND IV

Examples I and II are repeated utilizing a protective coating composition containing as the resin component a polymer containing, on a mole basis, 90.4% of a mixture of methyl acrylate, ethyl acrylate and butyl acrylate polymer units and 9.6% acrylic acid polymer units. Following the electroplating operation, resin removal is readily accomplished by swabbing with a cotton cloth which has been previously saturated with an ammonium hydroxide solution having a pH of about 7.5.

Results similar to those described in the above examples are obtained when utilizing a chromium plating bath maintained under an acid pH. It will be understood that the nature of the alkali employed in the resin-removal step is not particularly critical and accordingly, may be selected from a wide variety of materials, e.g., alkali metal hydroxides such as sodium hydroxide, potassium hydroxide, etc., trisodium phosphate, and the like. The important consideration in this regard is that the resin-removal bath be maintained at an alkaline pH and preferably within a pH ranging from 7.5 to 8.

Moreover, the nature of the plating bath is likewise not a critical factor in the practice of the present invention, the sole requirement being that such bath be maintained under an acid pH and preferably below 6.5.

The subject invention may be applied to production of metal surfaces containing ornamental or decorative designs thereon. The metal to be coated need not be planar but may be of arcuate or otherwise irregular configuration. In such instances, the resin may be suitably applied by the use of a suitable stencil, pattern, etc. The process

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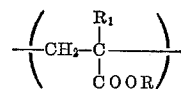
employed would be similar to that described in the above examples both as regards the electroplating operation and the protective resin removal operation.

The present invention has been disclosed with respect to certain preferred embodiments thereof, and there will become obvious to persons skilled in the art various modifications, equivalents or variations thereof which are intended to be included within the spirit and scope of this invention.

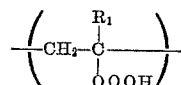
What is claimed is:

1. In a process of electroplating an aluminum sheet with a metal selected from the group consisting of copper and chromium, said electroplating being carried out at an acid pH, the improvement which comprises employing as the cathode an oxide-free aluminum sheet having coated thereon a protective layer comprising a film-forming, alkaline-soluble acrylic resin containing on a mole basis from about 80% to about 99% of acrylate units and from about 1 to about 20% of acrylic acid units, said resin being capable of forming a strong, adhesive bond with the aluminum surface and wherein said resin is capable of being completely removed from the aluminum surface subsequent to the electroplating operation by subjecting same to an alkaline medium maintained at a pH of at least 7.5.

2. A process according to claim 1 wherein said acrylate units corresponds to the following structural formula:



wherein R represents hydrocarbon and R₁ represents lower alkyl and said acrylic acid units correspond to the following structural formula:



3. A process according to claim 2 wherein said acrylate units comprise a mixture of methyl acrylate, ethyl acrylate, and butyl acrylate.

4. A process according to claim 1 wherein said electroplating is carried out at elevated temperatures.

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Disclaimer

3,451,902.—*Steven Levinos*, Vestal, N.Y. PROTECTIVE LOCALIZED AREA RESIN COATINGS FOR ELECTROPLATING. Patent dated June 24, 1969. Disclaimer filed Sept. 30, 1982, by the assignee, *Eastman Kodak Co.*

Hereby enters this disclaimer to all claims of said patent.

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