

UNITED STATES PATENT OFFICE

2,346,658

CORROSION RESISTANT COATING

Joseph B. Brennan and Leona Marsh, Euclid,
Ohio; said Marsh assignor to said BrennanNo Drawing. Application December 2, 1938,
Serial No. 243,542

8 Claims. (Cl. 204—58)

Our invention relates to the forming of insulating and corrosion resistant oxide coatings of film forming metals such as aluminum, magnesium, tantalum, zinc, etc., and their alloys.

We have for an especial object of our invention the formation of a novel type of such film or coating which evinces great capillarity in that it is highly absorptive, flexibility in that it can be distorted without cracking excessively, stability in that it resists chemical and electrochemical disintegration, uniformity in that it is of equal thickness even on irregular shaped bodies.

Another object of this invention is the formation of a smooth although somewhat porous coating which is electrically burned onto the aluminum. Another object is the production of a tenacious corrosion resistant coating at higher voltages than have been used in past practice. A further object is the formation of a smooth, microscopically porous, adherent coating which is relatively and permanently, resistant to severe atmospheric conditions.

We have for a further object of our invention the simplification of methods in producing such oxide coating by methods heretofore not disclosed.

It is ordinary practice to secure contact with pieces to be anodized or electrolytically coated by attachment on a so-called rack used to exert positive pressure on each piece to be so anodized or coated individually. This ordinary practice requires the individual mounting of each piece on the so-called rack prior to the introduction thereof into the anodizing bath.

By our method such individual mounting is unnecessary since we obtain and retain piece to piece contact during film formation without individual mounting on a rack or otherwise. Furthermore even though piece to piece contact is very light and even after the pieces are filmed, we obtain conduction through their film to adjacent pieces because of our peculiar novel method of forming electrolytically. Thus anodic films can be formed by our method in a plating barrel having electrodes which will not disintegrate as of aluminum.

In forming this coating on metals such as aluminum we preferably use direct current, however, our work has shown that considerable alternating current ripple does not affect the formation nor the quality of the coating. The voltage is governed by the sparking voltage of the electrolyte used. Many of the electrolytes which we found to produce the quality of corrosion resistant coating desired have fairly definite spark-

ing voltages at a voltage higher than the usual electrolyte used for anodically forming a corrosion resistant coating on aluminum.

Apparently any metallic conductive material may be used as the cathode. We obtained good coatings using both aluminum anode and cathode, the aluminum cathode appearing bright as originally after a number of runs. We also found that copper and many other metals as the cathode could be used with an aluminum anode to produce excellent coatings.

Although the temperature does not affect the quality of the corrosion resistant coating of the aluminum when varied from twenty-five to about eighty degrees centigrade we prefer to use a moderately low temperature to reduce the evaporation of the electrolyte and its tendency to solidify. Temperature control may be affected by liquid conduction coils in the electrolyte thermostatically controlled.

In our electrolytes which produce satisfactory coatings at or above the sparking voltage of the respective electrolyte we include organic, inorganic, and mixed potential condensation products. We have found organic potential condensation products of the formaldehyde type to be particularly useful for our purpose in so much that the coating can be formed with little regard to temperature, or purity of the chemicals used. Since an urea-formaldehyde condensation product containing film forming salts is completely miscible with water or alcohol, we have found this condensation product particularly adaptable for the production of our corrosion resistant coatings.

Our investigation has shown that electrolytes of the artificial resin or condensation product type containing oxygen bearing or film forming salt and/or acid as disclosed in our U. S. Patent No. 2,095,966 are particularly useful for anodically forming corrosion resistant films on aluminum, the formation preferably being at or in excess of the sparking voltage.

The following formula is cited as an example of one of the urea-formaldehyde formulae used for anodically coating aluminum.

	Parts
Urea	200
Formaldehyde (40% solution by volume)	165
Boric acid	200
Ammonium hydroxide (sp. gr. 0.9)	112

Phenol-formaldehyde condensation products containing boric acid and ammonium hydroxide, boric acid and sodium hydroxide, etc. also form

- Ward, J. A., & Bickman, P. (1996). *Preschoolers' social interactions: A comparison of children with and without autism*. In J. A. Roberts, R. M. Young, & J. A. Bickman (Eds.), *Children's social interactions: A developmental perspective* (pp. 111-130). New York: Guilford Press.
- Watt, N. S., & Plomin, R. (1982). *Genetic influences on children's social behavior*. In J. A. Roberts, R. M. Young, & J. A. Bickman (Eds.), *Children's social interactions: A developmental perspective* (pp. 131-144). New York: Guilford Press.
- Watt, N. S., & Plomin, R. (1984). *Genetic influences on children's social behavior*. In J. A. Roberts, R. M. Young, & J. A. Bickman (Eds.), *Children's social interactions: A developmental perspective* (pp. 131-144). New York: Guilford Press.
- Watt, N. S., & Plomin, R. (1986). *Genetic influences on children's social behavior*. In J. A. Roberts, R. M. Young, & J. A. Bickman (Eds.), *Children's social interactions: A developmental perspective* (pp. 131-144). New York: Guilford Press.

by dipping or spraying or centrifuging or vacuum impregnating the article to be coated, form a coating after burning in with an arc light or similar light minutely thin but affording a tough, flexible continuous insoluble layer over the metal previously protected by the anodic treatment. Dyes may be dissolved in the sensitized solution for coating the metal, water soluble dyes being used in the albumen type of sensitized coatings.

We have also applied the dyes directly to the anodized metal and obtained a uniform pleasing color. The dyes can be applied after light exposing the sensitized coating, however, we prefer to dissolve the dyes in the sensitized solution before sealing the oxidized metal surface with this solution. Dilute solutions of greasy inks have been applied to the light exposed sensitized coating, resulting in a coated metal which wears exceedingly well under excessive corrosion conditions. A dilute solution of latex containing a small percentage of sensitizing compound as a chromate after being light exposed results in a tenacious flexible film not attacked by many corrosive materials.

Various aluminum alloys have been anodically treated at or in excess of the sparking voltage simultaneously by our method. We have found that aluminum of greater than 99.9% purity as (2S) and the aluminum alloys 17S, Al 7S, and 24S were equally well coated in the same bath for the same length of time. This simultaneously anodizing of different alloys in the same bath has not been successful heretofore to our knowledge.

Another indication of stability, uniformity and continuity of our oxide film is characterized in that metal pieces so coated may be brought into physical contact with one another without breakdown or sparking over or shorting when voltage is applied thereto. If these oxide coatings are impregnated as in a vacuum with a dielectric such as a wax or varnish then such oxide coatings so impregnated withstand many thousand volts. The above indicates the complete conversion of surface metal to film or oxide form with no points of high conduction of the surface and distinguishes the results of our process.

Heating and or vacuum drying of our films prior to applying seals is desirable in that it extends corrosion resistance characteristics. Drying prior to centrifugal impregnation also adds life to articles so coated because of increased penetration. There are certain cases where centrifugal impregnation may be combined with drying in vacuo or otherwise to advantage.

Furthermore formation in motion or with agitation of electrolyte or a combination thereof may in certain applications be particularly advantageous.

Baking in of impregnating compounds to complete resinification as for instance where a Glyptol cement or Bakelite cement is used as impregnation media it may be advantageous to harden and set same by application of heat thereto.

Other aids to penetration of impregnating compounds as by rolling in mechanically are contemplated.

Tumbling of articles in groups during formation and impregnation is also contemplated.

A corrosion resistant coating may also be obtained by forming slightly above the breakdown voltage of the film in a solution of boric acid and a borate salt.

Where formation electrolytes such as potential resins are used articles may be removed therefrom after formation and heat and pressure applied

thereto thereafter resulting in that the potential resin clinging thereto is converted over by said heat and pressure to a stable resin coating and seal.

Where objects of irregular shape are to be cured after having been removed from potential resin formation electrolyte the pressure may be applied with heat in a sealed pressure chamber filled with gas or other non-setting liquid under pressure. This system of applying heat and pressure to irregularly shaped resinous coated articles may be used to advantage extensively and is novel. The articles when removed from said pressure chamber are impregnated thoroughly and the resin is set.

One outstanding advantage to sealing methods disclosed by us herein is that we seal with compounds which after sealing are rendered insoluble as for instance in water. This is not true of heretofore used chromate seals.

By our formation method whereby piece to piece conduction can be had due to current leakage at high voltages continuous feeding and formation of strip material can be achieved through a bath to form a corrosion resistant coating thereon. Also by our formation method parts to be anodized may be fed on a screw or perforated belt or other conveying device through pre-cleaning bath, anodizing bath and sealing bath current being applied in the anodizing bath by grounding it and in the other baths if desired similarly or if desired they or their containers may be insulated from ground.

As an explanation of the peculiar results secured by us in our formation whereby we secure an extremely uniform coating both as to color and corrosion resistant properties we believe that these results are due to the fact that the electrolytes used by us are of extremely uniform resistance characteristics where they are in contact with the surfaces being anodized giving an extremely uniform field effect adjacent the gas layers deposited on the surfaces.

The higher voltages used by us are probably of extreme importance because of the fact that since the field effect gained therefrom in the vicinity of the formed gas layer is more intense it overcomes the variables existent due to minute metallic impurities present in the surface of the metal being anodized resulting in that our film builds over these minute areas of metallic impurity at least partially sealing these over with the inert oxide layer. In any case by our method the film layer seems to be one of perfect continuity and of completely uniform whiteness and of lower dielectric leakage than ordinary films. Our film is also more absorptive than any others known and tested.

We prefer to form at high voltages say from 250 to 500 volts or over as a peak for corrosion resistant coatings.

It is this apparent ability of our system to cause the oxide layer to extend itself surface-wise on articles being anodized which furthermore accounts for the fact that even where articles are being anodized under our system in contact with or touching one another there is no gap in the oxide layer at such points and no resultant contact scar is evident where the pieces being anodized were touching.

Another possible explanation may be that using higher voltage electrolytes the growth of the oxide layer at contact points is not blocked because of the high field intensity at these points

forcing the transformation of the exposed metals at these points.

Undoubtedly the looseness of contact with the source of positive current also assists film formation at the contact points because it permits the electrolyte to fill in or flow in between the articles being anodized and adjacent articles in a minute layer and also between articles near the source of positive current and said source. Thus although we describe articles being anodized as in contact with a source of positive current none the less it must be understood that a layer of electrolyte of minute thickness intervenes at said points of contact.

From the above explanation and reasoning we believe that we have developed the first correct method of anodizing articles immersed in a film forming electrolyte because according to ordinary practice whereby mechanical contact pressure is ordinarily exerted on articles being so anodized we have eliminated this false and unnecessary mechanical pressure and by so doing have eliminated the scars or marks ordinarily on articles so anodized from articles anodized by our method.

We find that it is most advantageous to operate near or preferably at or above the sparking voltage of the electrolytic system employed but do not wish to be limited thereby since a longer exposure to electrolysis under the methods disclosed and with the electrolytes of the class specified will in some cases give good results.

Our method of mass formation without a mechanical pressure electrical contact to articles being formed and our method of developing throwing power in electrolytic oxidation to produce porous corrosion resistant-coatings is novel. Ordinary high voltage films on aluminum are shiny, hard and brittle and not highly absorptive or white as ours are.

We have also found that electrolytes may be used comprising a ketone such as acetone and formaldehyde and an ionizing film forming salt such as boric acid and ammonium hydroxide to give suitable results.

We claim:

1. The method of forming corrosion resistant coatings on aluminum which includes the steps of subjecting the aluminum to electrolysis as an anode in an aqueous solution of a potential condensation product of urea and formaldehyde having boric acid and ammonium hydroxide added thereto and carrying out the electrolysis at a voltage such that sparking takes place on the surface of the aluminum.

2. The method of forming corrosion resistant coatings on aluminum which includes the steps of subjecting the aluminum to electrolysis as an anode in an aqueous solution of a potential condensation product of formaldehyde and a material of the class consisting of urea and phenol, and a film forming electrolyte, carrying out the electrolysis at a voltage such that sparking takes place on the surface of the metal, and continuing the electrolysis until an absorbent, adherent, flat coating is produced on such surface.

3. The method of forming corrosion resistant coatings on aluminum which includes the steps

of subjecting the aluminum to electrolysis as an anode in an aqueous solution of a potential condensation product of formaldehyde and a material of the class consisting of urea and phenol, and having a film forming electrolyte added thereto, and carrying out the electrolysis at a voltage greater than the breakdown voltage of the film.

4. The method of forming corrosion resistant coatings on film forming metal from the group consisting of aluminum, magnesium, tantalum and their alloys, which includes the steps of subjecting the metal to electrolysis as an anode in an aqueous solution of a potential condensation product of formaldehyde and a material of the class consisting of urea and phenol, and having a film forming electrolyte added thereto, and carrying out the electrolysis at a voltage such that sparking takes place on the surfaces of the metal.

5. The method of forming corrosion resistant coatings on aluminum pieces which comprises simultaneously subjecting a plurality of pieces to electrolysis as an anode in an aqueous solution of a film forming electrolyte and a potential condensation product of urea and formaldehyde at such a voltage that sparking takes place on the surfaces of the pieces, and keeping the pieces in motion and in loose contact with a source of current during the electrolysis.

6. The method of forming a corrosion resistant coating on pieces composed of film forming metal from the group consisting of aluminum, magnesium, tantalum and their alloys which comprises simultaneously subjecting a plurality of pieces to electrolysis as an anode in an aqueous solution of a film forming electrolyte and an organic potential resinous condensation product of the formaldehyde type at such a voltage that sparking takes place on the surfaces of the pieces, and keeping the pieces in motion and in loose contact with a source of current during the electrolysis.

7. The method of forming a corrosion resistant coating on aluminum pieces which comprises simultaneously subjecting a plurality of pieces to electrolysis as an anode in an aqueous solution of a film forming electrolyte and an organic potential resinous condensation product of the formaldehyde type at such a voltage that sparking takes place on the surfaces of the pieces, and keeping the pieces in motion and in loose contact with a source of current during the electrolysis.

8. Aluminum having an electro-formed coating of an oxide film containing aluminum and oxygen thereon, said coating being adherent, corrosion resistant and absorbent, presenting a flat, substantially white, non-metallic appearance, and being produced by subjecting the aluminum to electrolysis as an anode in an aqueous solution of a film forming electrolyte and a potential condensation product of formaldehyde and a material of the class consisting of urea and phenol, and carrying out the electrolysis at a voltage greater than the breakdown voltage of the film.

JOSEPH B. BRENNAN.
LEONA MARSH.