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METHOD OF CHEMICALLY COATING
ALUMINUM

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The use of aluminum and the various aluminum base alloys, i. e., those containing about 70 per cent or more by weight of that metal, has been widened and promoted by the application to surfaces composed of that metal, or its alloys, of various coatings which have many functions including decoration, resistance to abrasion, reflection, resistance to corrosion, lubrication and hardness. In large part, but by no means exclusively, these coatings are of the class commonly termed "oxide coatings" and consist largely of an aluminum oxide component artificially produced on the aluminum or aluminum alloy surface. The methods of producing such oxide coatings are numerous, but the most successful methods of producing hard, adherent and absorptive oxide coatings are the so-called electrolytic or anodic methods in which the surface to be coated is made anode in an electrolytic cell, the electrolyte of which is the coating solution, and electric current is applied.

There is, however, another type of oxide coating treatment which is usually referred to as the chemical or non-electrolytic treatment and which does not employ electric current as a coating force. In such treatments, the surface to be coated is immersed in, or otherwise exposed to, the coating forming solution until a coating of desired thickness is produced. These non-electrolytic treatments are usually less expensive in operation and do not require the use of special electrical apparatus, but the coating thereby produced is usually not as hard, adherent and compact as those produced by properly operated electrolytic treatments. The non-electrolytic coatings often have other disadvantages, among which may be noted those most pertinent to the present invention, that is, the color of coating produced, the ability of the coating to respond to treatment with organic dyes to yield various shades of color and the comparative ability of the coating to withstand abrasion or handling without wearing or flaking off, the latter being a quality best expressed by the term "toughness."

Despite these and other well known drawbacks of the non-electrolytic oxide coatings, such coating have found widespread application in the art, since there are many instances where, because of the size, shape and relative cost of the product to be coated, the existing facilities of manufacture, the amount of material to be coated at a given time, and similar or related factors, the electrolytic type of coating cannot be economically used. There are, likewise, instances where the relative disadvantages of the non-electro-

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lytic type of oxide coating is not of controlling importance, as where the coated aluminum or aluminum alloy surface is to be put to uses which do not place severe demands upon the coating.

The general object and purpose of this invention is to provide an improved method of making a coating of the oxide type and one which is applied to aluminum or aluminum alloy surfaces by the chemical or non-electrolytic process. Since in aluminum base alloys the principal responding factor to the treatment is the aluminum, the term "aluminum" shall hereinafter and in the appended claims be used to define both aluminum and aluminum base alloys, unless otherwise specifically stated.

The coatings which are made by the present method are of the oxide coating class in the sense that the principal component thereof is aluminum oxide. Like such coatings, these coatings may also contain traces or small amounts of copper or other metal present in the aluminum surface treated and may also contain traces or small amounts of elements present in the coating solution, such as chromium compound when the coating solution has contained chromium. However, the coatings are different from said class in that they contain proteins in a minor but effective amount. Whether this protein content of the coating exists as such or is combined in some way with the other elements of the coating is not presently clear, but in any event its presence in the coating may be ascertained by the usual qualitative tests for proteins, such as the biuret reaction or the xanthoproteic reaction.

The after-treatments generally applied by the art to oxide coatings to improve or modify their characteristics, such as, for instance, sealing, plugging or coloring treatments, treatments designed to increase corrosion resistance and treatments in the course of which a substance is deposited on or within the formed coating for a special purpose, may be applied to these oxide-protein coatings, since the coatings are porous and exhibit in some degree the general properties of oxide coatings on aluminum. Thus these coatings may be applied to aluminum surfaces to serve the general functions of the prior oxide coatings. However, the coatings are not electrolytic coatings and find particular application in those fields of use where for various reasons, as above stated, the electrolytic type of oxide coatings is not preferred.

There are certain fields of usefulness in which these oxide-protein coatings are superior to prior chemical or non-electrolytic oxide coatings.

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These fields include coated aluminum buttons, clasps, eyelets, hookless fasteners, and a variety of relatively small articles of trade which may usually be produced at low cost, which must withstand in use the repetition of widely varying, relatively mild, but positive, abrasive and wearing forces and which are desirably produced in many shades of color. It is in these present fields of use that the coatings made by the processes of this invention are particularly outstanding, because they combine properties of toughness and of color not readily obtained in prior non-electrolytic coatings. Toughness is, as above mentioned, the ability of the coating to resist wearing or flaking off under stresses of use. Color is of importance, because most non-electrolytic coatings which are in commercial use are of such shades that they do not yield, when treated with organic dyes, the lighter and more subtle color shades desired. The color of the oxide-protein coatings may be generally described as light, some being darker than others, but on many alloys the coating is of such a shade that it responds to treatment with organic dyes to produce the shades of color desired. The toughness of these coatings may be a reflection of the possible functioning of the protein component as a binder for the relatively brittle aluminum oxide component of the coating, but since uncertainty presently exists as to the specific action of the protein content of these coatings, this is merely one possible explanation.

In the quality of resistance to corrosion the coating made by the processes of this invention may be said to be generally equal to that of the prior non-electrolytic coatings, because indications of superior corrosion resistance in these coatings, while present, are not consistent enough to justify any general conclusion of superiority.

The methods of this invention by which the production of these coatings is best achieved consist essentially in treating the aluminum surface with an alkali metal carbonate solution containing the proteins. Such solutions are aqueous. Observations justify the statement of the possibility that at least in some instances the protein is not actually in solution but is present, rather, in colloidal form. However, in these observed instances the protein has functioned as if it were in solution, and the word "solution" is, therefore, used to describe whatever condition exists. The proteins referred to in the practice of the methods of this invention are those selected from the class consisting of casein, albumen, zein, and gelatin. These may also be defined as the common proteins, since they are readily available and comparatively inexpensive. The term "gelatin" is used to include glue, which, although a gelatin, is sometimes referred to as a separate protein. One or more proteins selected from this group form a component of the aqueous coating solution, the other essential component being an alkali metal carbonate, preferably sodium carbonate. So far as has been observed, there is no advantage or disadvantage in using more than one of the proteins of the class mentioned, except such disadvantages as may mechanically arise out of forming and controlling the composition of the solution. The solution may also contain an amount of alkali metal hydroxide. Also the solution preferably contains, in some instances, a quantity of soluble chromium, i. e., hexavalent chromium, which is best present as alkali metal chromate, which term is likewise

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herein used to also include and describe the equivalent alkali metal dichromates.

Expressed in percentages of weight to the total solution, the basic components of the aqueous coating solution are

	Per cent
Alkali metal carbonate.....	0.5 to 6
Protein	0.5 to 5

10 Best results are generally obtained when the amount of protein in the solution does not exceed the amount of the alkali metal carbonate present; for specific proteins and specific aluminum surface compositions, variations in the amount
15 of carbonate and protein in the solution may produce better results in some cases than in others. For instance, taking as an example, solutions containing sodium carbonate and casein, best results appear to be obtained in coating aluminum metal when the carbonate to casein ratio is two to one, whereas in the case of aluminum base alloys containing about 5 per cent magnesium as the principal alloying element, a carbonate to casein ratio of five to four seemed to
20 produce the best results. In the case of aluminum base alloys containing about 4.5 per cent of copper as the principal alloying element, carbonate to casein ratios of five to three and three to one appeared to yield the best coatings. These specific variations are, however, minor and the best ratio for a given aluminum composition is readily determined by simple trial. The aluminum surface to be treated is immersed or otherwise exposed to the solution for a time necessary for
35 the coating reaction to build a coating of desired thickness. I have found that in the usual case this time will vary between 10 and 60 minutes, particularly when the temperature of the coating solution is adjusted to within 70 to 100 degrees centigrade. In most commercial applications of the invention, when the solution is maintained at the preferred operating temperatures of about 85 to 90 degrees centigrade, the time of treatment when the aluminum surface is immersed
40 in a slowly agitated solution is usually about 20 to 30 minutes.

While the coating solution may be prepared in any convenient manner, one useful method consists in separately dissolving the alkali metal carbonate in a portion of the water desired in the final solution, separately adding the protein to a separate portion of water which has been made alkaline by the addition thereto of alkali metal hydroxide, and then mixing the two solutions.
50 When, upon mixing, some separation occurs, as is sometimes the case and is usually the case where zein is the protein used, mixing is best accomplished by slowly adding the protein solution to the carbonate solution with constant stirring.
60 The alkali metal hydroxide is added to help solubilize the protein or to help effect a complete dispersion thereof if, in fact, the protein exists as a colloid rather than a true solution. The amount of hydroxide added may be readily determined by observation of the effect of the alkali on a given protein, but, as a general rule, the addition of 0.02 gram of alkali metal hydroxide per gram of protein will be sufficient for the purpose.

The final coating solution as prepared will, when it contacts the aluminum surface, dissolve an amount of alumina as alkali metal aluminate during the coating process, and until the solution has been used for a short time and has dissolved such alumina, the best coating conditions
75 are not achieved. It is, therefore, desirable but

not necessary to contact a fresh coating solution made in accordance with this invention with some scrap aluminum prior to using the solution in the coating process.

The presence of chromate in the coating solution is sometimes desirable, since usually the coating produced in solutions containing chromate will have a harder surface. Often, however, chromate in the coating solution will produce a coating of a darker shade than is desired. When the presence of chromate in the coating solution is desired, it should be present as alkali metal chromate in amounts of about 0.05 to 0.5 per cent by weight of the total solution.

It has been observed that, although the coatings of this invention when once formed on the aluminum surface contain, as compared to the aluminum oxide content, relatively small amounts of protein, the coatings are nonetheless increased somewhat in abrasion resistance or hardness when treated with agents known to harden or insolubilize proteins. Whether such after-treatment is useful will depend upon the use to which the coated surface is to be put, but where maximum hardness or abrasion resistance is desired, some increase in these properties can usually be induced by such a treatment. Such hardening agents include tannin, formaldehyde and also heavy metal salts, such as chromium salts.

Some examples of the practice of this invention follow:

Example 1.—Aluminum alloy sheet containing about 4.5 per cent by weight of copper as the principal alloying element was treated in an aqueous solution containing 1 per cent by weight of sodium carbonate and 1 per cent by weight of albumen. The solution was held at 85° C. and the duration of the treatment was 20 minutes. A uniform adherent, tough coating was obtained.

Example 2.—Aluminum alloy sheet containing about 5.8 per cent zinc, 2.5 per cent magnesium and 1.6 per cent copper as the principal alloying elements was treated for 30 minutes in an aqueous solution containing 1 per cent by weight of zein and 3 per cent by weight of sodium carbonate. The solution was held at 90° C. for compari-

son with the coated surface thus formed, another aluminum alloy sheet of the same composition was anodically treated, according to standard methods, in an electrolyte containing about 15 per cent by weight of sulphuric acid. Each of the sheets thus coated was then placed in an abrasion machine in which the sheet was rotated against a revolving, weighted iron wheel. Under these comparative conditions the coating on the sheet prepared in accordance with this invention had almost twice the life, before failure, of the coating anodically prepared in the sulphuric acid solution.

Having thus described my invention, I claim:

1. The method of forming an adherent, tough, chemically produced oxide coating upon an aluminum surface by treating said surface with an aqueous solution containing, as active coating former, about 0.5 to about 6 per cent by weight of alkali metal carbonate, said solution also containing about 0.5 to about 5 per cent of at least one substance selected from the group consisting of casein, albumen, zein and gelatin.

2. The method of claim 1 characterized by the fact that said aqueous solution also contains, as active coating former, about 0.05 to about 0.5 per cent by weight of alkali metal chromate.

3. The method of claim 1 characterized by the fact that the said alkali metal carbonate is present in amount at least equal to the amount of substance selected from said group.

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