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FORMING OXIDE COATINGS ON ALUMINUM

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This invention relates to processes for forming oxide coatings on aluminum by treating the metal in chemical coating solutions. The invention is particularly applicable to processes employing aqueous solutions of the carbonate type, especially carbonate-chromate solutions, with or without additions of polyvinyl alcohol or various proteins.

The invention is concerned with artificially produced oxide coatings on aluminum, and certain chemical treatments for producing them; and it is not concerned with electrolytic treatments for producing oxide coatings. As used herein, the term "aluminum" includes pure aluminum, commercial aluminum containing the usual impurities, and aluminum base alloys.

When first prepared, chemical coating solutions including those of the carbonate type referred to, have been found to be unsatisfactory for production or commercial coating of aluminum articles. Consequently, it has long been customary to "work" fresh solutions preliminarily with aluminum, preferably scrap aluminum. This practice often results in delays of many hours in getting a new solution into production or commercial use. Likewise the practice may require the unnecessary consumption of otherwise useful aluminum, especially when scrap aluminum is not available. In any event, the practice may not always be carefully followed; and, for that reason and others, coatings heretofore produced are often not uniform in weight, hardness or adsorptive properties, from piece to piece or from cycle to cycle, as the coating solution is repeatedly used.

The general object of the invention is to provide an improvement in processes for forming oxide coatings on aluminum which will permit of the coating solutions being used, with a minimum of preparatory effort and expense to produce and reproduce coatings of more uniform weight and hardness. It is particularly an object to produce more adsorptive coatings—coatings that are more easily colored or dyed. One specific object is to eliminate the necessity of working a coating solution with aluminum prior to use of the solution in producing coatings of satisfactory commercial quality.

Of the aqueous solutions used for chemically forming oxide coatings on aluminum, those containing an alkali metal carbonate as the principal constituent have proved to be the most useful in the commercial arts. These solutions usually contain about 0.5 to 6 per cent by weight of alkali metal carbonate, preferably sodium carbonate. In the use of such solutions, it is usually preferred, depending upon the ultimate properties desired in the coating and sometimes upon the presence or absence of other constituents in the solution, to provide in the solution a small quantity of an alkali metal chromate, i. e. about 0.05 to 2.0 percent by weight. A chromate such as sodium or potassium chromate is usually present in a ratio between about one part chromate to two parts carbonate and about one part chromate to thirty parts carbonate. Appropriate smaller amounts of sodium or potassium dichromate have been employed to provide the desired chromate content in the solution.

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In recent years, two improved carbonate type coating solutions have met with considerable success, and the invention is applicable to them as well as to those discussed above. One of these is the carbonate-chromate-polyvinyl alcohol solution, in which the last constituent may be present in amounts by weight between about 0.2 and 5 per cent, preferably 1 per cent. The other is the carbonate-chromate-protein solution, in which the last constituent may be present as albumen, casein, zein or gelatin in amounts by weight between about 0.5 and 5 per cent, preferably 1 per cent.

A typical carbonate type of coating solution, to which the invention is applicable, contains the following percentages by weight of coating constituents:

	Preferred	Commercial Range
Sodium carbonate	2.0	0.5–6.0
Sodium chromate	0.2	0.05–2.0

While a preferred amount and a commercial range for the chromate have been shown, it is also possible to produce satisfactory coatings, under certain conditions, without any chromate present.

When a fresh solution of the carbonate type is first prepared, it is extremely active and usually produces a heavy, relatively soft coating that is easily marked and smudged. Further use of the solution produces coatings of lesser weight and greater hardness, but the solution will not immediately produce and reproduce uniform coatings. Likewise, if ordinary practices are followed, the coatings produced will not readily adsorb dyes.

The difficulties mentioned above have long been known, and have been partially overcome

heretofore by working the solution with scrap aluminum, or other available aluminum, before putting the solution into production or commercial use. Such preliminary working of the solution takes many hours and often is permitted to consume aluminum unnecessarily, since it has been necessary in the past to work the solution with an arbitrary amount of aluminum, as roughly determined by experience. How "working" affects the solution is not fully understood, but the commonly accepted explanation is that some compound of aluminum is formed and dissolved in the solution, to the saturation point or beyond, in order to put the solution into condition to coat properly. It is believed that the aluminum is converted by the solution to a soluble complex, that the solution becomes saturated or supersaturated with this complex, and that then the conversion of additional aluminum causes precipitation of an aluminum compound of oxidic and hydrated nature—hydrated alumina. It has also been observed that cooling of a hot "worked" solution may result in precipitation of substantial amounts of this hydrated alumina, a result which is especially desirable if uniform coatings are later to be produced and reproduced in the solution, or if the coatings later produced are to be dyed. The language "aluminum complex" is used hereinafter to describe the aluminum conversion product, or its equivalent, which is in solution (true or colloidal) and which is adapted to be precipitated. The language "hydrated alumina" is used hereinafter to describe the aluminum compound which is precipitated from the aluminum complex of the solution.

While the foregoing practice and explanation therefor have been known for many years, no successful substitute for the practice of working the solution with aluminum has been proposed heretofore, so far as is presently known. It has been supposed that commercially available aluminum oxides, hydroxides or hydrates could be added to a new coating solution so as to eliminate the working step, but such additions have been found ineffective for the purpose.

It has now been discovered, however, that a soluble salt of aluminum can be dissolved in a coating solution of the carbonate type and the solution treated, either before or after or simultaneously with such addition, so as to produce therewith the desired aluminum complex in the solution, and also at least some precipitate of the desired hydrated alumina. This improvement in the coating process can be achieved, in general, by preliminarily providing in the solution (1) a soluble salt of aluminum in an amount sufficient to increase the aluminum content thereof by at least about 0.05 per cent by weight, or more if desired, and (2) a neutralizing compound (such as an alkali metal bicarbonate or hydroxide) selected to react with the aluminum salt in solution to produce a condition of alkalinity in the solution in which there is an appreciable amount of aluminum complex of low solubility in the solution adapted to be precipitated as hydrated alumina. The neutralizing compound is selected with reference to the alkalinity or acidity of the salt of aluminum employed, and it is preferably provided in an amount approximating the stoichiometric amount for the reaction with the amount of the salt of aluminum provided. When these materials are provided in the solution there will usually be opposing changes in the pH of the solution, but the pH of the solution will reach a point favorable to the precipitation of hydrated

alumina, usually at a value near that which would be exhibited by the solution were the additions not made. They result in the formation of an appreciable amount of aluminum complex in the solution; and, especially in the case of the larger additions and when cooling is employed, they usually also result in the precipitation of an appreciable amount of hydrated alumina.

One class of soluble salts of aluminum which can be employed in the practice of the invention is the class of soluble alkali metal aluminates. The preferred member of this class is sodium aluminate, which may be added effectively in an amount by weight of about 0.15 to 0.5 per cent, or more if desired, the weight being referred to sodium aluminate of 100 per cent purity. This addition increases the aluminum content of the solution by an amount on the order of that previously indicated as desirable. The neutralizing compounds best employed with the aluminates are the soluble alkali metal bicarbonates, which may be added in an amount sufficient to increase the carbonate content of the solution by about 0.1 to 0.3 per cent by weight, or more if desired. The preferred member of this class of compounds is sodium bicarbonate, which may be added effectively in an amount by weight of about 0.15 to 0.5 per cent, or more, depending on the amount of aluminate added. With the additions, the pH of the solution will be adjusted and readjusted, the aluminum complex will be formed in the solution, and the hydrated alumina will tend to be precipitated, as may be indicated by cloudiness in the solution.

It will be noted that the aluminate is alkaline in solution (tending to raise the pH of the solution), and that the bicarbonate has an acid reaction (tending to lower the pH of the solution). They react with each other in solution, producing some added alkali metal carbonate, as well as the aluminum complex. The added carbonate does not interfere with the coating characteristics of the solution and, in fact, it merely raises the alkali metal carbonate content of the solution. If desired, the solution may be originally made up with an initial alkali metal carbonate content less than that ultimately desired, according to the amount that will be formed in the preliminary treatment here described.

Neutralizing compounds other than the bicarbonates may also be employed with the aluminates. For example, carbon dioxide may be substituted for the bicarbonates. Likewise, the alkali metal dihydrogen phosphates, bisulphates, bisulfites, and sulfur dioxide (or sulfurous acid) may be employed. In any case these neutralizing compounds should be employed in approximately the stoichiometric amounts for the neutralizing reaction with the aluminate.

Another class of soluble salts of aluminum which can be employed in the practice of the invention is the class of soluble normal aluminum salts. The preferred member of this class is aluminum sulfate, but other similar aluminum salts such as the chloride or the nitrate, or the like, may be found suitable. Aluminum sulfate, for example, may be added effectively in an amount by weight of about 0.3 to 1 per cent, or more if desired, the weight being referred to the anhydrous salt. Hydrated aluminum sulfate will usually be employed and the corresponding larger weight of that form of aluminum sulfate would, of course, be added, the appropriate actual weight of either form being contemplated herein. This addition likewise increases the

aluminum content of the solution by an amount on the order of that previously indicated as desirable. The neutralizing compounds best employed with the normal aluminum salts are the soluble alkali metal hydroxides, which may be added in an amount sufficient to increase the hydroxyl content of the solution by about 0.1 to 0.3 per cent by weight, or more if desired. The preferred member of this class of compounds is sodium hydroxide which may be added effectively in an amount by weight of about 0.2 to 0.7 per cent by weight, or more, depending on the amount of normal aluminum salt added. With the additions, the pH of the solution will be adjusted and readjusted, the aluminum complex will be formed in the solution, and the hydrated alumina will tend to be precipitated, as may be indicated by cloudiness in the solution.

It will be noted that the aluminum salt in this last class is acid in solution (tending to lower the pH of the solution), and that the hydroxide is alkaline (tending to raise the pH of the solution to a point favorable to formation of the aluminum complex). They react with each other in solution, producing an alkali metal salt, as well as the aluminum complex. The alkali metal salt does not interfere with the coating characteristics of the solution, but it does not raise the alkali metal carbonate content of the solution.

Soluble aluminum salts other than the normal salts may also be added to the solution. When an acid aluminum salt is employed, additional hydroxide is needed in the solution to neutralize the aluminum salt. The provision of an acid salt and the necessary additional hydroxide in the solution is equivalent to the provision of a normal salt in the solution. When a basic aluminum salt is employed, part of the hydroxide required in the solution is supplied by the hydroxide content thereof. The provision of part of the hydroxide by way of a basic salt and a smaller amount of alkali metal hydroxide is equivalent to the provision of a normal salt and a corresponding total amount of alkali metal hydroxide in the solution.

A typical coating solution including the first-mentioned class of soluble salts of aluminum might contain the following percentages by weight of coating and stabilizing constituents:

	Preferred	Commercial Range
Sodium carbonate	1.5	0.5–6.0
Sodium chromate	0.1	0.05–2.0
Sodium aluminate	0.4	0.15–0.5 or more
Sodium bicarbonate	0.4	0.15–0.5 or more

whereas a typical coating solution including the second-mentioned class of soluble salts of aluminum might contain the following percentages by weight of coating and stabilizing constituents:

	Preferred	Commercial Range
Sodium carbonate	1.9	0.5–6.0
Sodium chromate	0.1	0.05–2.0
Sodium hydroxide	0.5	0.2–0.7 or more
Aluminum sulfate	0.8	0.3–1.0 or more

it being noted that the preferred amounts of the salts of aluminum indicated contain aluminum in amounts of about 0.12 per cent by weight, referred to the weight of the solution.

With the preferred solutions given in the above examples, the adjustment and readjustment of the pH of the solution may take place as follows. If a solution of carbonate and chromate only is first made up, it will exhibit a pH of about 11. If sodium aluminate is then added, the pH will rise above approximately 11.2. Then, if sodium bicarbonate is added, the pH will fall below about 10.5, slightly below the original value of 11. Likewise, if sodium hydroxide is first added, the pH will rise above approximately 11.6. Then, if the aluminum sulfate is added, the pH will fall below about 10.5, slightly below the original value of 11. Similar changes take place if the order of adding the salt of aluminum and the alkali, is reversed, in either case.

In either of the examples given above, the two constituents listed last may well be added last; the chromate addition, however, may be conveniently deferred to a point after the addition of aluminate or hydroxide. As to the order, between themselves, of adding the two constituents listed last, it is desirable to add the aluminate and later the bicarbonate in the first example, and to add the hydroxide and later the sulfate in the second example. The stabilizing constituents are best added in the preferred amounts to a hot solution held at temperatures above about 100° F., preferably a solution held at about 175 to 195° F. Thereafter, the solution is best cooled, preferably to room temperature, to precipitate appreciable quantities of hydrated alumina. Then the solution may be reheated to temperatures suitable for coating, preferably temperature between about 175 and 195° F.

In the use of any of the solutions simply to produce ordinary oxide coatings that may be relatively hard and protective, but not necessarily uniform from piece to piece nor readily dyeable, some of the advantages of the invention may be obtained by simply preparing a new carbonate type solution, with even the smaller indicated amounts of the soluble salt of aluminum and the neutralizing compound, preferably while the solution is hot, and directly using it to produce coatings on aluminum. This procedure at least eliminates the step of working the solution with aluminum metal.

However, in the use of any of the solutions to produce and reproduce uniform and dyeable coatings, the best results are obtained by preparing a new carbonate type solution, with the preferred or larger indicated amounts of the soluble salt of aluminum and the neutralizing compound, while the solution is hot; and, in this case, allowing the solution to cool, preferably to room temperature, by standing for several hours, preferably overnight. This fully stabilizes the solution by the precipitation of appreciable quantities of hydrated alumina. Thereafter, the solution may be heated to operating temperature and used to coat aluminum articles in the usual way. The articles coated in the stabilized solution, in successive cycles, have more uniform coatings, and the coatings dye well.

It will be seen that an improved method of utilizing carbonate type coating solutions has been provided.

What is claimed is:

1. In a process for forming an oxide coating on aluminum by treating in an aqueous carbonate type solution containing about 0.5 to 6 per cent by weight of alkali metal carbonate, the improvement comprising preliminarily providing in the solution a soluble salt of aluminum in an amount sufficient to increase the aluminum content of the solution by at least about 0.05 per cent by weight and a neutralizing compound reactive with the aluminum salt whereby to produce a condition of

alkalinity in the solution in which there is an appreciable amount of aluminum complex of low solubility in the solution adapted to be precipitated as hydrated alumina, the neutralizing compound being provided in an amount approximating the stoichiometric amount for the reaction with the amount of the salt of aluminum provided.

2. In a process for forming an oxide coating on aluminum by treating in an aqueous solution containing about 0.5 to 6 per cent by weight of alkali metal carbonate and about 0.05 to 2.0 per cent by weight of alkali metal chromate, the improvement comprising preliminarily providing in the solution a soluble salt of aluminum in an amount sufficient to increase the aluminum content of the solution by at least about 0.05 per cent by weight and a neutralizing compound reactive with the aluminum salt whereby to produce a condition of alkalinity in the solution in which there is an appreciable amount of aluminum complex of low solubility in the solution adapted to be precipitated as hydrated alumina, the neutralizing compound being provided in an amount approximating the stoichiometric amount for the reaction with the amount of the salt of aluminum provided.

3. In a process for forming an oxide coating on aluminum by treating in an aqueous solution containing about 0.5 to 6 per cent by weight of alkali metal carbonate, up to about 2.0 per cent by weight of alkali metal chromate, and about 0.2 to 5 per cent by weight of polyvinyl alcohol, the improvement comprising preliminarily providing in the solution a soluble salt of aluminum in an amount sufficient to increase the aluminum content of the solution by at least about 0.12 per cent by weight and a neutralizing compound reactive with the aluminum salt whereby to produce a condition of alkalinity in the solution in which there is an appreciable amount of aluminum complex of low solubility in the solution adapted to be precipitated as hydrated alumina, the neutralizing compound being provided in an amount approximating the stoichiometric amount for the reaction with the amount of the salt of aluminum provided.

4. In a process for forming an oxide coating on aluminum by treating in an aqueous solution containing about 0.5 to 6 per cent by weight of alkali metal carbonate, up to about 2.0 per cent by weight of alkali metal chromate, and about 0.5 to 5 per cent by weight of at least one protein selected from the group consisting of casein, albumen, zein and gelatin, the improvement comprising preliminarily providing in the solution a soluble salt of aluminum in an amount sufficient to increase the aluminum content of the solution by at least about 0.12 per cent by weight and a neutralizing compound reactive with the aluminum salt whereby to produce a condition of alkalinity in the solution in which there is an appreciable amount of aluminum complex of low solubility in the solution adapted to be precipitated as hydrated alumina, the neutralizing compound being provided in an amount approximating the stoichiometric amount for the reaction with the amount of the salt of aluminum provided.

5. In a process for forming an oxide coating on aluminum by treating in a hot aqueous carbonate type solution containing about 0.5 to 6 per cent by weight of alkali metal carbonate, the improvement comprising preliminarily providing in the hot solution a soluble salt of aluminum in an amount sufficient to increase the aluminum content of the solution by at least about 0.12 per cent by weight and a neutralizing compound reactive with the aluminum salt whereby to produce a condition of alkalinity in the solution in which there is an appreciable amount of aluminum complex of low solubility in the solution adapted to be precipitated as hydrated alumina, the neutralizing compound being provided in an amount approximating the stoichiometric amount for the reaction with the amount of the salt of aluminum provided, then cooling the solution to about room temperature so as to facilitate precipitation of an appreciable amount of hydrated alumina, and then reheating the solution for coating.

6. In a process for forming an oxide coating on aluminum by treating in an aqueous solution containing about 0.5 to 6 per cent by weight of alkali metal carbonate, the improvement comprising preliminarily providing in the solution a soluble alkali metal aluminate in an amount sufficient to increase the aluminum content of the solution by at least about 0.05 per cent by weight and a soluble alkali metal bicarbonate in an amount sufficient to increase the carbonate content of the solution by at least about 0.1 per cent by weight, the alkali metal bicarbonate being provided in an amount approximating the stoichiometric amount for reaction with the amount of alkali metal aluminate provided so that an appreciable amount of aluminum complex of low solubility is formed in the solution adapted to be precipitated as hydrated alumina.

7. In a process for forming an oxide coating on aluminum by treating in an aqueous solution containing about 0.5 to 6 per cent by weight of alkali metal carbonate, the improvement comprising preliminarily providing in the solution about 0.15 to 0.5 per cent by weight of sodium aluminate and about 0.15 to 0.5 per cent by weight of sodium bicarbonate so that an appreciable amount of aluminum complex of low solubility is formed in the solution adapted to be precipitated as hydrated alumina.

8. In a process for forming an oxide coating on aluminum by treating in a hot aqueous solution containing about 1.5 to 2 per cent by weight of sodium carbonate and up to about 0.75 to 1 per cent by weight of alkali metal chromate, the improvement comprising preliminarily providing in the hot solution about 0.4 per cent by weight of sodium aluminate and about 0.4 per cent by weight of sodium bicarbonate, so that an appreciable amount of aluminum complex of low solubility is formed in the solution adapted to be precipitated as hydrated alumina, then cooling the solution to about room temperature so as to facilitate precipitation of an appreciable amount of hydrated alumina, and then reheating the solution for coating.

9. In a process for forming an oxide coating on aluminum by treating in an aqueous solution containing about 0.5 to 6 per cent by weight of alkali metal carbonate, the improvement comprising preliminarily providing in the solution a soluble normal aluminum salt in an amount sufficient to increase the aluminum content of the solution by at least about 0.05 per cent by weight and a soluble alkali metal hydroxide in an amount sufficient to increase the hydroxyl content of the solution by at least about 0.1 per cent by weight, the alkali metal hydroxide being provided in an amount approximating the stoichiometric amount for reaction with the amount of normal aluminum salt provided, so that an appreciable amount

of aluminum complex of low solubility is formed in the solution adapted to be precipitated as hydrated alumina.

10. In a process for forming an oxide coating on aluminum by treating in an aqueous solution containing about 0.5 to 6 per cent by weight of alkali metal carbonate, the improvement comprising preliminarily providing in the solution about 0.3 to 1 per cent by weight of aluminum sulfate and about 0.2 to 0.7 per cent by weight of sodium hydroxide, so that an appreciable amount of aluminum complex of low solubility is formed in the solution adapted to be precipitated as hydrated alumina.

11. In a process for forming an oxide coating on aluminum by treating in a hot aqueous solution containing about 1.5 to 2 per cent by weight of sodium carbonate and up to about 0.75 to 1 per cent by weight of an alkali metal chromate, the improvement comprising preliminarily providing in the hot solution about 0.8 per cent by weight of aluminum sulfate and about 0.5 per cent by weight of sodium hydroxide, so that an appreciable amount of aluminum complex of low solubility is formed in the solution adapted to be precipitated as hydrated alumina, then cooling the solution to about room temperature so as to facilitate precipitation of an appreciable amount of hydrated alumina, and then reheating the solution for coating.

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