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COATING BATHS FOR ALUMINUM AND METHOD OF AND MATERIALS FOR PREPARING AND REPLENISHING SAME

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6 Claims. (Cl. 148—6.16)

This invention relates to the art of applying a chemically bonded coating to the surfaces of aluminum or alloys thereof in which aluminum is the principal ingredient.

Before enumerating the objects and advantages of the invention, it will be helpful to refer briefly to certain coating procedures which are now familiar to those skilled in this art.

It is well known that aqueous acid solutions whose principal and essential coating producing ingredients are fluorides, hexavalent chromium and phosphates are capable of producing decorative as well as corrosion resistant coatings on aluminum and typical examples of processes which employ such solutions are described in U.S. Patents 2,438,877, 2,472,864, 2,678,291 and 2,814,577.

Examination of the first three patents just mentioned will show that the solutions employed in the procedures therein disclosed have chemical constituents which are present in amounts corresponding to the following: Fluoride—0.15 to 12.5 grams/liter; hexavalent chromium expressed as CrO_3—3 to 60 grams/liter; and phosphate (PO_4)—2 to 285 grams/liter. These patents also show that the fluoride content of the bath should be maintained within certain limiting ratios to the hexavalent chromium content.

The fourth patent listed discloses that, under certain conditions, it is possible and desirable to control the fluoride content of the bath without recourse to maintaining a definite fluoride:chromate ratio. It also describes a method for the treatment of large areas of aluminum surfaces in a manner which will yield substantial uniformity of color and surface appearance which is an advantage of considerable moment in the architectural field where substantial uniformity of appearance is important.

In commercial application coating baths such as just described operate quite satisfactorily within a pH range of from 0.8 to 4.5.

Beyond the foregoing the solutions used in the methods just referred to are otherwise very important commercially and for quite a number of years past there has been, in many industries, a growing demand for aluminum the surface of which has been coated in the manner described because of the decorative and protective values which can be imparted to the surface by such coatings.

However, certain difficulties have been encountered some of which arise when the coating solutions are first prepared and others of which appear during extended or continuous use of the solutions. For example, in the processes of the prior art referred to the solutions when first prepared are sometimes erratic in behavior in that they produce coatings of varying color which sometimes tend to have an overburden of powder. The problem of powder also tends to occur during continuous use of the coating solutions especially when they are employed in the treatment of relatively large areas of aluminum surfaces. Ordinarily the powdery deposit formed on top of the coating does not impair the corrosion resistance of the surface although it definitely impairs the decorative and paint bonding value.

In the prior practice referred to still another problem develops which should be understood in connection with the objects of the present invention. In the coating of aluminum surfaces some aluminum is dissolved, of which a portion becomes a part of the deposited coating, the rest dissolving in the coating solution. Since the concentration of dissolved aluminum has been found to affect the coating properties of the solution, we have devised means to keep its concentration reasonably small and sensibly constant, because, by so doing, we find that uniform coatings can be obtained on a succession of work pieces.

With all of the foregoing in mind the principal objects of the present invention are the provision of the following:

(1) A method of preparing an aluminum coating solution of the type described which, from the time the very first piece of aluminum is treated by the solution, is capable of producing coatings which are uniform in color and without an overburden of powder.

(2) A method of and materials and solutions for coating a long succession of aluminum pieces by means of which it is possible to continuously produce satisfactory coatings both as to color uniformity and corrosion resistance.

How the foregoing, together with such other objectives as may appear hereinafter, are achieved will now be described.

Our invention is based upon the discovery that baths of the character described can be rendered capable of producing uniformly colored, powder-free coatings from the beginning if they are made up and replenished in a definite manner with respect to the concentration of fluoride and alkali metal therein. According to our invention a bath is made up and maintained by attention to the following details:

A. The baths must contain definite amounts of a mixture of sodium and potassium in relation to the fluorine present.

B. The baths must contain dissolved aluminum in an amount limited by the solubility of a solid phase of that alkali fluo aluminate, in equilibrium with the coating bath, which is characterized by a content of 6 fluorine atoms for each atom of aluminum.

C. Alkali metal in the bath must be in the proportion of 0.0026 to 0.0526 mol of sodium plus potassium for each gram of fluoride, and it has been found that of the total molar content of sodium and potassium, from 10 to 90% should be potassium. Best results have been obtained where the total number of mols of sodium and potassium is from 0.0065 to 0.0455 for each gram of fluoride present. In replenishing a coating bath (and particularly those subject to heavy loading) the alkali metal content should be restored in the approximate ratio of two mols of potassium for each mol of sodium and, for each gram of fluoride added, the total alkali metal added should be from 0.0065 to 0.0455.

As previously described, dissolved aluminum in the baths of the prior art adversely affects the coating properties. By suitable make up and replenishment in accordance with the specific procedures outlined above, the amount of dissolved aluminum in the bath is limited by the sparing solubility of the alkali fluo-aluminate, due to the proper concentration of sodium, potassium and fluoride as described above. The sparingly soluble fluo-aluminate is found to have a composition in which, for one atom of aluminum, there are 6 atoms of fluorine. When either sodium or potassium was the only alkali metal present in the precipitate the bath was found to have undesirable fluctuations in fluoride activity. There-

fore, it is necessary that the bath contain at all times both sodium and potassium and in order to effect this in replenishing the bath it is necessary to add from 10 to 90% of the total mols of sodium and potassium in the form of potassium and, preferably, the bath should be replenished with 2 mols of potassium for each mol of sodium as this will prevent any tendency of the bath to produce powder on the coatings under heavy loading conditions. Analyses of precipitates formed by the operating baths, when replenished in accordance with the teachings just given, indicate that the precipitate consists essentially of K_2NaAlF_6.

In connection with the method of preparing and replenishing the coating bath described just above we have also discovered that a glossy, lacquer-like coating can be produced if there be added to the bath, as formulated within the teachings just given, from 1 to 5 grams per liter of cryolite.

By way of example, but without limitation as to the specific ingredients or concentrations, a bath falling under the purview of the present invention may be formulated in accordance with the following example:

Formula #1

Chromic acid	grams	14.4
Aluminum dihydrogen phosphate ($Al(H_2PO_4)_3$) 50% solution	mls	32.0
75% phosphoric acid	mls	36.3
Sodium bifluoride (NaF.HF)	grams	9.56
Potassium bifluoride (KF.HF)	do	6.02
Cryolite	do	3.17

Water, to make 1 liter.

Such a bath is capable of producing a green, lacquer-like coating when used in a dip process at 100° F. with a treating time of approximately 5 minutes. Insofar as its fluoride content is concerned, it should be replenished in accordance with the instructions above given, namely, preferably with a material which, for each gram of fluoride introduced into the bath there is included from 0.0065 to 0.0455 mol of sodium and potassium. Preferably the molar proportion of a mixture of potassium should be from 10 to 90% of the total of alkali metals added.

In replenishing such coating baths, replenishment with respect to phosphate, hexavalent chromium, and adjustment of acidity (or pH) is carried out in accordance with the principles previously established as set forth in the patents referred to above.

Replenishment with fluoride, however, in accordance with the present invention must be accompanied by suitable replenishment with a mixture of alkali metals including both sodium and potassium in the proportions set forth above.

It has been found desirable, though not essential, for ease of bath control, to add the alkali metal and fluoride in a replenishing material separate from the other ingredients. A suitable replenishing material for these ingredients is the following:

Formula #2

	Grams
Sodium bifluoride	44.2
Potassium bifluoride	55.8

Other formulations suitable for fluoride and alkali metal replenishment are the following:

Formula #3

	Grams
Sodium fluoride	32.5
Potassium fluoride	67.5

Formula #4

Sodium fluoride	51.8
Potassium bifluoride	48.2

Formula #5

Sodium fluoride	49.7
Potassium bifluoride	46.3
Cryolite	4

Formula #6

	Percent
Sodium bifluoride	28.4
Potassium bifluoride	71.6

As previously stated, under very heavy bath loading conditions, replenishment of the alkali metal content of the bath should be made by replenishing the bath with approximately 2 mols of K for every mol of Na added. That this is highly desirable is illustrated by the fact that a commercial bath was made up in accordance with the example of Formula #1 above given and was periodically replenished in respect to the fluoride content by using Formula #5. Under normal operating conditions this worked quite well for several months. However, when the bath was subjected to heavy bath loading, its coating ability became somewhat unmanageable. When this occurred replenishment was changed from Formula #5 to Formula #6 (sodium bifluoride 28.4% and 71.6% potassium bifluoride). After this was done the bath again became manageable and produced excellent coatings under extremely heavy loading conditions such as 10,000 sq. ft. per hour.

While the admixture of Formula #2 is primarily useful in effecting replenishment of the fluoride content of the coating bath it should be understood that it will serve also as an excellent source of fluoride in initially making up a new coating bath.

Examples of other useful coating baths falling into the purview of the present invention are as follows:

Formula #7

CrO_3	grams	14.4
KF.HF	do	5.71
NaF.HF	do	4.54
Na_3AlF_6	do	4.24
$Al(H_2PO_4)_3$ (50% solution)	mls	16.0
H_3PO_4 (75%)	mls	36.3

Water, to make 1 liter.

Formula #8

Same as above except no Na_3AlF_6.

Formula #9

CrO_3	grams	14.4
KF.HF	do	2.85
NaF.HF	do	2.27
Na_3AlF_6	do	2.12
$Al(H_2PO_4)_3$ (50% solution)	mls	8.0
H_3PO_4 (75%)	mls	36.3

Water, to make 1 liter.

Formula #10

CrO_3	grams	14.4
NaF	do	6.47
KF	do	8.95
$Al(H_2PO_4)_3$ (50% solution)	mls	16
H_3PO_4 (75%)	mls	36.3

Water, to make 1 liter.

Formula #11

CrO_3	grams	14.4
NaF	do	6.07
KF.HF	do	5.65
$Al(H_2PO_4)_3$ (50% solution)	mls	16
H_3PO_4 (75%)	mls	6.3

Water, to make 1 liter.

Formula #12

CrO_3	grams	14.4
KF.HF	do	6.17
NaF.HF	do	4.90
HF (48%)	mls	5.72
Na_3AlF_6	grams	3.93
$Al(H_2PO_4)_3$ (50% solution)	mls	34
H_3PO_4	mls	36.3

Water, to make 1 liter.

Formula #13

CrO_3	grams	14.4
NaF.HF	do	4.79
KF.HF	do	12.05
Na_3AlF_6	do	1.91
$Al(H_2PO_4)_3$ (50% solution)	mls	32
H_3PO_4 (75%)	mls	36.3

Water, to make 1 liter.

Obviously, the various coating baths given above may be replenished during use insofar as their content of sodium, potassium and fluoride is concerned by one or the other of the replenishing materials of Formulas 2 to 6, inclusive, within the general teachings above set forth. Furthermore, other replenishing combinations might also be appropriate depending upon the volume of work passing through the operating bath. Where the load is heavy, as explained, Formula #6 might be particularly indicated.

While forming no part of the present invention the phosphate and hexavalent chromium content of such baths may advantageously be restored by suitable additions of a solution in accordance with the formula appearing below:

Formula #14

	Grams
H_3PO_4 (75%)	437
CrO_3	110

Water, to make 1 liter.

This application is a continuation in part of our earlier application Serial No. 637,876, filed February 4, 1957, now abandoned.

We claim:

1. A bath for the coating of aluminum having a pH between 0.8 and 4.5 whose coating producing ingredients consists essentially of:

Ions of—	Grams/liter
Fluoride	0.15 to 12.5
Hexavalent chromium (expressed as CrO_3)	3.0 to 60
Phosphate (PO_4)	2.0 to 285

said bath being further characterized by containing a mixture of sodium and potassium in a total concentration of from 0.0026 to 0.0526 of a mol for every gram of fluorine present with potassium constituting from 10 to 90% thereof and also by containing dissolved aluminum to the point of equilibrium in the presence of the other essential ingredients whereby any precipitate which may be formed will consist essentially of K_2NaAlF_6.

2. The method of both making up and replenishing the bath of claim 1 insofar as its fluorine content is concerned which consists in adding to the bath the requisite amount of fluorine and from 0.0026 to 0.0526 of a mol of a mixture of sodium and potassium for each gram of fluorine added to the bath.

3. The method of coating a succession of pieces of aluminum which comprises successively treating the pieces with the bath of claim 1 and periodically replenishing the bath by adding thereto the requisite amount of fluorine and from 0.0026 to 0.0526 of a mol of a mixture of sodium and potassium for each gram of fluorine with potassium constituting from 10 to 90% thereof, and replenishing the hexavalent chromium and phosphate as may be required to maintain the content thereof as specified.

4. An admixture for use in preparing and replenishing a bath for coating aluminum, said admixture consisting essentially of water soluble fluorides of sodium and potassium, in which admixture, for each gram of fluorine there are from 0.0065 to 0.0455 of a mol of a mixture of sodium and potassium with the potassium constituting from 10 to 90% thereof.

5. The admixture of claim 4 in which the molar ratio of sodium and potassium is approximately 1 to 2.

6. The bath of claim 1, wherein the sodium and potassium content is from 0.0065 to 0.045 for each gram of fluorine with the ratio of sodium to potassium being about 1 to 2.

References Cited in the file of this patent

UNITED STATES PATENTS

2,438,877	Spruance	Mar. 30, 1948
2,472,864	Spruance	June 14, 1949
2,489,152	Panepinto	Nov. 22, 1949

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 43, strike out "of a mixture" and insert the same before "sodium", in line 42, same column 3.

Signed and sealed this 18th day of October 1960.

(SEAL)
Attest:

KARL H. AXLINE
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