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PROCESS AND COMPOSITION FOR PRODUCING ALUMINUM SURFACE CONVERSION COATINGS

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This invention relates to the art of chemically coating aluminum surfaces, for production of corrosion resistant and paint bonding coatings upon surfaces. The invention is especially concerned with novel procedure and compositions for producing high quality aluminum conversion coatings continuously from a given bath by maintaining the working efficiency of such bath at a high level over an extended period of use.

The term "aluminum" as employed herein is intended to denote substantially pure aluminum or an alloy of aluminum in which aluminum is the major component.

One of the many known methods of producing chemical films on aluminum surfaces includes the treatment of the aluminum in acidic baths containing an acid which attacks aluminum, together with other components effective to form a fixed integral film upon the aluminum surface. This type of film is known in the art as an aluminum conversion coating.

Typical chromate type conversion coating baths for aluminum are aqueous acidic solutions containing hexavalent chromium and fluoride anions, together with cations of hydrogen, and usually some other metal cations. These ions may be introduced as combined parts of many diverse compounds. A typical bath of this nature may comprise, for example, a mixture of chromium trioxide, zinc silico-fluoride and boric acid.

The coating operation preferably is performed by immersing, or otherwise contacting cleaned, and sometimes deoxidized aluminum surfaces with the bath for periods of time ranging, for example, from 15 seconds to 5 or 6 minutes. A very thin, amorphous, gelatinous film is produced on the aluminum surface. The film is usually dry, firm, lustrous, yellow in color and more or less iridescent. It should be uniform, well adherent and continuous over the entire surface, including crevices and recesses. The film is believed to be composed of oxides and hydroxides of aluminum and trivalent chromium, and also compounds of fluorine plus occluded hexavalent chromium compounds.

As the bath continues to work on aluminum surfaces, the essential constituents gradually become exhausted and are usually replenished frequently so as to maintain substantially the original concentrations of the constituents. Another characteristic of working baths is that the bath pH rises progressively. After the pH exceeds about 2, the color of the films becomes weaker and the corrosion resistance decreases. To offset this condition, occasional pH adjustments are made with acid, such as nitric acid, in addition to the regular necessary replenishments with the original make-up chemicals.

It is believed probable that the various active ions of the bath are exhausted at differing rates. Thus, the hydrogen ions may be expended more rapidly than the other ions. This may be one cause of the pH rise.

Another important condition affecting the efficiency of the working bath is the continuous solution of aluminum and of the various minor constituents used to form the aluminum alloys. Still another contaminating side reaction is the continual reduction of some of the hexavalent chromium to the trivalent form and its retention in the solution in the form of trivalent chromium compounds.

The dissolved aluminum gradually accumulates in the

processing bath and after an extended period of time depending on how heavily the bath is worked, the aluminum accumulates to the point where it begins to affect the quality of the coatings produced. Eventually, the aluminum will reach a level high enough to inhibit the formation of a yellow coating. The accumulation of trivalent chromium in the bath will, if allowed to reach a sufficiently high concentration, degrade the coating to the point where it is no longer satisfactory. Hence, the effect of these accumulating extraneous and by-product cations is to progressively deteriorate the quality of the films produced, particularly as to color and corrosion resistance. Frequent replenishments with the original make-up chemicals, and frequent pH adjustments may partially alleviate these adverse conditions. However, after the detrimental aluminum and trivalent chromium ions, along with minor aluminum alloying ions, have accumulated beyond certain substantial proportions, the remedies of replenishment and pH adjustment are of little avail. In attempting to rejuvenate a chromate type conversion coating bath before the latter condition occurs, the removal of both the aluminum and trivalent chromium contaminants must be considered. Such removal need not be complete as long as the contaminating ions are maintained at a sufficiently low concentration so that the quality of the film is not affected adversely.

It is an object of this invention to provide improved novel acidic chromate type aluminum conversion coating compositions, and process for producing aluminum conversion coatings therewith.

Another object is the provision of aluminum conversion coating compositions and baths of the above noted type which remain effective over extended periods of time for producing high quality conversion coatings continuously on aluminum parts, without replenishment of such baths with fresh make-up chemicals.

Yet another object is to afford aluminum conversion coating compositions and baths which are substantially self rejuvenating and provide rapid efficient coating action over extended periods of operation.

A further object is the provision of novel aluminum conversion coating compositions and baths including hexavalent chromium, hydrogen and fluorine ions, and containing components effective to counter the adverse effects of dissolved aluminum and trivalent chromium produced in such baths during treatment of aluminum therewith, without adversely affecting the quality of the conversion coating produced.

Yet another object is to provide a composition effective on admixture with aluminum conversion coating compositions, to rejuvenate such compositions and to increase the effective life thereof.

A still further object is to provide improved aluminum conversion coating composition having the above noted characteristics and possessing a relatively long storage life and tank life.

Yet another object is to provide procedure for producing uniform high quality aluminum conversion coatings of a succession of aluminum parts employing conversion coating bath.

Other objects and advantages will appear hereinafter.

We have now found as a feature of the invention, that the incorporation of a member of the group consisting of antimony and tin, either separately or preferably in combination, in the form of suitable compounds thereof, into acidic aluminum conversion coating compositions or baths containing hexavalent chromium, hydrogen and fluorine ions, controls or suppresses the accumulation of trivalent chromium in the bath during treatment of aluminum therein.

As an additional feature we have also found that the incorporation of sodium and potassium in the form

of suitable compounds thereof, into such acidic aluminum conversion coating compositions and baths, controls and suppresses the accumulation of dissolved aluminum in the bath.

In preferred practice all of the antimony, tin, sodium and potassium constituents are employed in combination in the conversion coating composition, and these constituents operate simultaneously to confine both dissolved aluminum and trivalent chromium in the conversion coating bath to low tolerable levels, and to maintain substantially indefinitely the working efficiency of the bath so as to produce high quality coatings continuously on a succession of aluminum parts processed in such bath. The conversion coating compositions so produced thus have markedly increased tank life.

We have discovered that the combined effect of all four of the components, antimony, tin, sodium and potassium have a markedly superior effect over the use of only antimony and tin, or of only sodium and potassium.

We do not presently know the mechanism or theory by which trivalent chromium and/or aluminum excesses are eliminated from the bath or otherwise controlled or neutralized, by the invention compositions. However, we have found that after a period of operation employing such compositions, a small but progressively increasing quantity of yellow-green solid precipitate forms at the bottom of the bath. It is believed that this solid sludge contains aluminum and trivalent chromium compounds precipitated from the bath.

It is believed that excess aluminum is precipitated as the sparingly soluble compound K_2NaAlF_6. In order to provide sufficient combined fluorine for the formation of this compound, and yet supply sufficient fluoride for the normal coating reaction, according to the invention it is thus necessary to increase the total combined fluorine content beyond the proportion ordinarily used in the conversion coating composition.

The conversion coating solutions which are improved according to the invention contain an anion containing hexavalent chromium. Such anion appears to function in conjunction with other components of the solution including the cations present, to confer greater corrosion resistance on the coating and also is believed to cause the yellow coloration of the coating at the pH of the treating solution set forth below. The source material for the anions containing hexavalent chromium may be a material such as chromium trioxide or a chromate or dichromate such as sodium or potassium chromate or dichromate.

Considerable latitude is provided as to the range of concentration of hexavalent chromium compound employed. I have found that a suitable working concentration of hexavalent chromium for purposes of the invention ranges between about 0.5 and about 9.0 grams per liter of processing solution based on the equivalent weight of chromium present in its elemental or ionic form.

The hexavalent chromium-containing anion is employed together with hydrogen and suitable proportions of an anion which effectively attacks or corrodes aluminum, preferably fluorine-containing anion. Many fluorine compounds can be successfully used as the source of said ions, including HF, NaF, NH_4HF_2, HBF_4, $NaBF_4$, NH_4BF_4, $ZnSiF_6$. These compounds vary in ionization characteristics, and hence, they are used in varying proportions, depending upon the particular compound selected.

Concerning the amounts of source material for the aluminum attacking, e.g., fluorine-containing ions preferably used along with the hexavalent chromium compound in the bath, the amounts of such material may also be varied to produce the desired results. However, here consideration should be given also to the ratio of the amounts of combined fluorine and of combined hexavalent chromium with respect to each other. It is believed that the operation of the composition of the invention first involves release of fluorine-containing ions, which serve to attack the aluminum surface as a part of the coating action. However, since the control of the accumulation of aluminum is achieved according to the invention by the precipitation of dissolved aluminum as the insoluble K_2NaAlF_6, this necessitates the incorporation of additional fluorine over and above that required in the normal coating operation of the bath. We have found that satisfactory results enabling the fluorine ion to perform its above dual functions can be achieved by employing in the range of about 0.5 to about 7 grams of fluorine per liter of processing solution, and a ratio of hexavalent chromium to fluorine in the range between about 0.5:1 and about 2.5:1, based on the equivalent weights of hexavalent chromium and fluorine either in elemental or ionic form.

To produce satisfactory yellow conversion coatings the processing solution should possess a concentration of hydrogen ions such that the pH of the solution is in the range of about 1.3 to about 2.2, preferably about 1.7 to about 2.1. Various acidic materials such as nitric acid, H_2SO_4, boric acid and acid salts can be employed for this purpose provided the particular acidic material utilized does not produce excessive attack on the aluminum nor excessive insoluble material or sludge in the processing solution. However, acidic materials which form a surface film by combination of the aluminum with such acidic materials, e.g. phosphoric acid or acid salts thereof, are not suitable, and are intended to be excluded from our compositions.

Preferably, although not necessarily, the conversion coating compositions contain metal cations which aid in improving the characteristics of the conversion coating, and the operation of the conversion coating bath. For example such cations aid in producing aluminum conversion coatings characterized by possessing good corrosion resistance, being quickly formed and fixed, resistant to smearing and of uniform color. These cations may be, for example, beryllium, magnesium, calcium, strontium, or barium, or lithium cations, as disclosed in Patent 2,868,679, or the cation zinc, cadmium or mercury, as disclosed in Patent 2,948,643, or cations such as vanadium, cobalt, nickel and copper, disclosed in copending application, Serial No. 772,677, filed November 10, 1958, now U.S. Patent No. 3,066,055, of George H. Pimbley. Sodium and potassium can also be employed as cations in the working solution, to aid in producing satisfactory coatings.

The source material for such cations can be compounds also containing one of the above noted anions such as the hexavalent chromium-containing anion, or any compound at least partially soluble in and compatible with the processing solution. Examples of compounds serving as source for the above cations include magnesium chromate, barium hydroxide, calcium chloride, zinc borate, cadmium oxide, nickel fluoride, cobaltous nitrate, and the like. The amount of cation which can be employed can be in the range of about 0.1 to about 10 grams per liter of solution.

We have also found that the use of a molybdenum-containing anion, preferably in the form of a molybdate, e.g. an alkali metal molybdate such as sodium or potassium molybdate, increases the effectiveness of the conversion coating bath. Such molybdate serves a dual function: first, the molybdate, e.g. as sodium molybdate, prevents the tendency of wet freshly formed conversion coatings from smearing, and secondly, such molybdate also intensifies the yellow color of the films produced and improves the uniformity of such film. The amount of such molybdate employed in the conversion coating bath can range from about .02 to about 1.5 grams per liter of solution, calculated as sodium molybdate.

The antimony and tin components of the invention composition can be present in the conversion coating bath in the form of the antimony and tin cations, or can

be present as a component of an anion. However, in preferred practice, the antimony is present in cationic form and the tin as a component of an anion, such as the stannate anion. The amount of each of the antimony and tin employed in the processing solution can range from about .02 to about 1.0 gram per liter, based on such components in elemental form.

Various compounds can be employed as the source of the antimony and tin components employed in the conversion coating baths according to the invention. Thus, such components can be combined in the source compounds with other components of the processing bath such as fluorine. For example, source materials for the antimony constituent can be antimony trifluoride. However, other compounds such as antimony trichloride, antimoney sulfate, potassium antimonyl tartrate (tartar emetic), and the like, can also be employed. The source compounds for the tin component employed in our processing bath can be, for example, stannous and stannic chloride, fluoride and sulfate, sodium and potassium stannate, and the like.

The sodium and potassium components of our conversion coating bath can be supplied by compounds containing such cations and which may also include one or more of the other anions of the bath, e.g. fluoride, hexavalent chromium or molybdenum. For example, source compounds for sodium and potassium can include sodium stannate, sodium molybdate, and sodium bifluoride, and source materials for potassium can be, for example, potassium bifluoride or potassium dichromate. The proportions of each of the sodium and potassium employed in the conversion coating bath can be in the range of about .05 to about 2.5 grams per liter of solution, based on these components in elemental form. In preferred practice, the weight ratio of potassium to sodium employed is greater than 1, preferably in the range of about 1.2:1 to about 5:1.

The antimony and tin components, and also the sodium and potassium components can be present in the initial acidic conversion coating composition or bath containing also the hexavalent chromium and fluorine constituents, to provide a self-rejuvenating bath according to the invention. Alternatively, such components can be added to a conversion coating bath after the latter has been in use, to rejuvenate the bath and prolong its effective life. Also, as the content of hexavalent chromium and fluorine decrease to values below their effective amounts, these components can be replenished from time to time to bring them up to their effective concentrations.

The chemicals for make-up of the bath may be introduced in any convenient form into water, such as in the form of powders or liquid solutions, and either as separate compounds or as compounded products. Usually, it is most convenient to employ dry materials as a compounded, powdered product, and to introduce into the aqueous solution formed therefrom any additional acid, if necessary, such as nitric acid, or any other required liquid separately. Hence the above described novel compositions in the form of mixtures in dry powdered form as well as the solutions prepared therewith are features of the invention.

In the dry mixtures of the invention, the hexavalent chromium anion constituent may be present in the solid composition as a compound in proportions ranging from about 5 to 35% by weight of hexavalent chromium, the preferred range being about 10 to about 25%. The combined fluorine should be present in the solid composition in a proportion ranging from about 5 to about 25% by weight, and the hexavalent chromium and fluoride in the solid composition should be present in such relation to each other that the ratio of hexavalent chromium to fluorine is in the range of about 0.5:1 to 2.5:1, preferably in the range of 0.8:1 to 1.2:1. The metallic cations present such as zinc, calcium, cobalt, nickel and the like, described above, may be present in the solid composition in the proportions ranging from 0 to 30%, preferably about 2 to about 25%, by weight. The antimony and/or tin compounds used as rejuvenating agents according to the invention should be present in the solid composition in proportions each ranging up to about 5% based on the weight of the antimony or tin in elemental form, the preferred range being about 0.5 to 4%. When a molybdate such as sodium molybdate or any equivalent thereof, such as potassium or ammonium molybdate is employed, it is desirable to employ this ingredient in the solid composition in a proportion of about 0.5 to about 5% by weight calculated as sodium molybdate, the preferred range being about 2 to about 5%. When sodium and potassium are also employed as rejuvenating agents according to preferred practice of the invention, each of these components can be present in the solid compositions in amounts ranging by weight from about 0.5 to about 30%, usually 1.5 to about 30%, calculated as elemental sodium or potassium, with a combined content of sodium and potassium of preferably not more than about 35%.

Where the solid composition employed is in the nature of a rejuvenating composition which is to be added to a spent conversion coating bath, the proportions of antimony, tin, sodium and potassium therein will be in the relative proportions noted above. That is, such composition can contain up to about 5 parts by weight of each of antimony and tin, preferably about 0.5 to about 4 parts, about 0.5 to about 30 parts by weight of sodium or potassium, and preferably not more than about 35 parts of both sodium and potassium, and if employed, a molybdate in an amount of about 0.5 to about 5 parts by weight, calculated as sodium molybdate.

A completely compounded mixture of the dry ingredients is incorporated in water in a proportion of about 0.25 to about 5.0 ounces, preferably about 1 to 2 ounces per gallon of water, to form an operating bath. The operating temperature of the bath is usually between about 75 to about 95° F. with immersion time of about 3 to 5 minutes.

The aluminum surfaces to be treated in the solutions of the invention should be free from grease and other surface soils. A mild alkaline cleaning bath, e.g. one containing alkali metal carbonates, safe for aluminum, at a concentration of 6 to 8 ounces per gallon, is recommended for this purpose, at 170°–180° F.

End results will be improved if surface oxide coating is removed, after alkaline cleaning, by pretreatment in a suitable acid type deoxidizing agent, e.g. mixtures of sulfuric, chromic and hydrofluoric acids. The work should be thoroughly rinsed after each pre-cleaning and deoxidizing operation prior to treatment in the solution of the invention.

The following are examples of operation of the invention. In carrying out the procedures in the following examples, coupons of 2024–Bare aluminum were processed at the beginning of each new cycle. These coated coupons following processing were inspected as to visual features and then tested in a salt spray cabinet under standard conditions for corrosion resistance. In the event that the coupon looked satisfactory and withstood 336 hours of salt spray treatment with a rating of 90% or better with respect to freedom from corrosion and pitting, it was considered satisfactory and the preceding work cycle was deemed successful. In other words, after performing the preceding cycle of work, the bath was not yet spent.

Example 1

	Percent by weight
$ZnSiF_6 \cdot 6H_2O$	47
CrO_3	39
Boric acid	13
Antimony trifluoride	1
	100

A one liter processing bath was prepared using the

above composition at a concentration of 1½ ounces per gallon of water. The bath was used for processing aluminum to a stage where it was estimated that an equivalent of about 248 square feet of 2024–Bare aluminum alloy was successfully processed, per gallon of bath. At this stage the appearance of the aluminum test panels was still good and the salt spray resistance was rated 90% at 442 hours' exposure. When the operation was continued to the equivalent of 270 square feet of 2024–Bare aluminum surface, the salt spray resistance dropped to 360 hours and the appearance of the test panels became dark brown and blotchy. Hence it was considered that the bath was operative for processing about 250 to about 260 square feet of successful coating per gallon of bath on 2024–Bare alloy.

Example 2

	Percent by weight
$ZnSiF_6 \cdot 6H_2O$	48
CrO_3	39
Boric acid	13
	100

The above composition was dissolved in water in a concentration of 1½ ounces per gallon of water. This bath was used to process 2024 aluminum, and after the processing of an equivalent of about 215 square feet of aluminum surface per gallon of bath, the coating became chalky, dull, and brown in color, instead of the normally yellow and lustrous color.

Hence it was considered that this bath had deteriorated and was no longer useful for obtaining commercially acceptable conversion coatings.

Accordingly, the composition of Example 1 containing antimony, in the form of antimony trifluoride, was superior to the composition of Example 2, not containing this material, in increasing the tank life of the bath for producing acceptable conversion coatings.

Example 3

	Percent by weight
$ZnSiF_6 \cdot 6H_2O$	44.2
CrO_3	40.0
Zinc borate	10.2
$NH_4F \cdot HF$	2.6
Sodium stannate, $Na_2SnO_3 \cdot 3H_2O$	3.0
	100.0

A processing bath was prepared with the above composition at a concentration of 1½ ounces per gallon of water and was used for processing aluminum in the manner described in Example 1. The aluminum so processed had a good coating appearance and salt spray resistance of 456 hours at a stage equivalent to the coating of 248 square feet of 2024–Bare aluminum alloy per gallon of bath.

Hence it is seen that the tank life of the composition of Example 3 for producing acceptable aluminum conversion coatings and which contains tin as sodium stannate, was superior to the tank life of the composition of Example 2, not containing tin, which had deteriorated when an equivalent of 215 square feet of aluminum had been processed.

Example 4

	Percent by weight
$ZnSiF_6 \cdot 6H_2O$	45
CrO_3	37
Boric acid	12
Antimony trifluoride	3
Sodium stannate	3
	100

A processing bath was prepared by dissolving the above composition in water at a concentration of 1½ ounces of the composition per gallon of water. This composition was used to process aluminum as in the case of Example 1, and after processing an equivalent of 248 square feet of 2024–Bare aluminum alloy per gallon of the solution, the resulting coatings had a salt spray resistance of 90% rating at 480 hours' exposure and was yellow and lustrous, showing that the bath was still operating satisfactorily.

Hence it is seen that the above composition containing both antimony and tin has an improved tank life and produces superior conversion coatings of high salt spray resistance as compared to coatings formed in the absence of such components (Example 2) at the same stage of operation.

Example 5

	Percent by weight
Zinc borate	20
Sodium bifluoride	14
Potassium bifluoride	22
Chromium trioxide	44
	100

A processing bath was made up using the above composition at a concentration of 1½ ounces per gallon of water. The processing of aluminum was carried out in a manner similar to Example 1, and when the processing had proceeded to the equivalent of 248 square feet of 2024–Bare aluminum alloy per gallon of bath, the coating formed at this stage exhibited some tendency to produce smeary and somewhat scanty films with a salt spray resistance of only 288 hours. This formulation thus had no greater advantage than that of Example 2.

Example 6

	Percent by weight
Zinc borate	8.5
Chromium trioxide	33.1
Potassium dichromate	17.4
Ammonium acid fluoride	30.0
Potassium bifluoride	2.5
Sodium bifluoride	2.5
Sodium molybdate	2.0
Antimony trifluoride	2.0
Sodium stannate	2.0
	100.0

A bath containing the above composition was prepared by dissolving 1½ ounces of the composition per gallon of water. At a stage equivalent to the processing of 675 square feet of 2024–Bare aluminum alloy coating per gallon of the solution, the salt spray resistance was 456 hours and the coating on the test panels was still of good appearance.

Hence this formulation containing antimony, tin, sodium and potassium functioned to perform good quality coatings for a much greater period of processing time than the compositions of Examples 2 and 5, and also the compositions of Examples 1, 3 and 4. It was found that even after working the bath of this example to a stage equivalent to 810 square feet of aluminum per gallon of bath, the test films on 2024–Bare aluminum alloy were still acceptable and the salt spray resistance was at the passing grade of 90% at 336 hours.

Example 7

The baths of Examples 2 and 6 were operated simultaneously for the processing of aluminum panels by continuously subjecting such panels in cycles of treatment to the action of these respective baths. When the coatings produced employing the bath of Example 2 appeared inferior, such bath was rejuvenated by adding to the bath 3 to 5 grams per liter of the rejuvenating composition set forth below.

	Percent by weight
Antimony trifluoride	1.0
Sodium stannate	1.0
Ammonium bifluoride	39.0
Sodium molybdate	1.0
Chromium trioxide	50.5
Zinc borate	4.8
Potassium bifluoride	2.7
	100.0

The resulting bath (designated #1) and also the bath of Example 6 (designated #2) were continued to be subjected to a cyclic schedule of coating of test aluminum panels. At the twentieth cycle, 0.1 gram per liter each of antimony trifluoride and sodium stannate were added to bath #1. Thereafter replenishments to this bath consisted of addition at intervals of the above noted composition plus 0.1 gram per liter each of antimony trifluoride and sodium stannate. Both baths were operated for 36 cycles of work.

It was found that bath #2 composed of the formulation of Example 6 maintained a generally lower trivalent chromium content than that formed using the solution of Example 2 to which the replenishing formulation set forth above was added, bath #1. After processing an area of 810 square feet of aluminum per gallon of bath, bath #1 contained 0.37 gram per liter of dissolved aluminum, and bath #2 contained only 0.11 gram per liter of dissolved aluminum.

Hence it is seen that bath #2 was superior to bath #1 in suppressing undesirably high aluminum content of the bath and thus aiding to provide a substantially longer tank life.

However, it will be noted that by rejuvenating the bath of Example 2 during processing, with the rejuvenating composition noted above and containing tin, antimony, sodium and potassium, the formulation of Example 2, which initially was effective for coating not more than 215 square feet of aluminum per gallon of solution, was improved according to the invention, so that it satisfactorily coated as much as about 800 square feet of aluminum per gallon of solution.

The following are additional examples of formulations effective for conversion coating of aluminum parts over an extended period of use according to the invention.

Example 8

	Percent by weight
Calcium chromate	61.5
Sodium fluoborate	30.0
Sodium molybdate	4.0
Antimony trifluoride	3.0
Stannous chloride	1.5
	100.0

Example 9

Calcium chromate	60
Ammonium acid fluoride $NH_4F \cdot HF$	25
Potassium bifluoride	5
Sodium molybdate	4
Antimony trifluoride	3
Sodium stannate	3
	100

Baths employing the compositions of Examples 8 and 9 above are prepared by adding 1½ ountces of the composition per gallon of water. These baths also require an addition of about ½ liquid ounce per gallon of 42 Baumé nitric acid for complete solution of solids.

Example 10

	Percent by weight
Nickelous fluoride, $NiF_2 \cdot 4H_2O$	55
Chromium trioxide, CrO_3	28
Boric acid	11
Antimony trifluoride, SbF_3	3
Sodium stannate	3
	100

Example 11

	Percent by weight
Nickelous fluoride, $NiF_2 \cdot 4H_2O$	27
Chromium trioxide, CrO_3	30
Boric acid	10
Antimony trifluoride, SbF_3	3
Sodium stannate	3
Potassium bifluoride, KHF_2	18
Sodium bifluoride, $NaHF_2$	9
	100

Example 12

Chromium trioxide	33
Potassium dichromate	18
Potassium bifluoride	25
Sodium bifluoride	15
Sodium molybdate	3
Antimony trifluoride	3
Sodium stannate	3
	100

Self-rejuvenating conversion coating baths according to the invention can be prepared from each of the above noted compositions of Examples 10, 11 and 12 by incorporating each of these formulations in water at a concentration of between about 1 and 2 ounces per gallon of water.

While we have described particular embodiments of our invention for purposes of illustration, it should be understood that various modifications and adaptations thereof may be made within the spirit of the invention as set forth in the appended claims.

We claim:

1. A process for applying a coating to surfaces of aluminum, which comprises treating said aluminum in an aqueous acidic bath consisting essentially of an anion containing hexavalent chromium, a fluorine-containing anion, and an ion containing antimony, said bath having a pH in the range of about 1.3 to about 2.2.

2. A process for applying a coating to surfaces of aluminum, which comprises treating said aluminum in an aqueous acidic bath consisting essentially of an anion containing hexavalent chromium, a fluorine-containing anion, and an ion containing antimony, said member being present in an amount in the range of about .02 to about 1.0 gram per liter, said bath having a pH in the range of about 1.3 to about 2.2.

3. A process for applying a coating to surfaces of aluminum, which comprises treating said aluminum in an aqueous acidic bath consisting essentially of an anion containing hexavalent chromium, a fluorine-containing anion, an ion containing antimony and an ion containing tin, said bath having a pH in the range of about 1.3 to about 2.2.

4. A process for applying a coating to surfaces of aluminum, which comprises treating said aluminum in an aqueous acidic bath consisting essentially of an anion containing hexavalent chromium, a fluorine-containing anion, an ion containing antimony and an ion containing tin, said antimony and tin each being present in an amount in the range of about .02 to about 1.0 gram per liter, said bath having a pH in the range of about 1.3 to about 2.2.

5. A process for applying a coating to surfaces of aluminum, which comprises treating said aluminum in an aqueous acidic bath consisting essentially of an anion containing hexavalent chromium in an amount of about 0.5 to about 9 grams per liter, a fluorine-containing anion in an amount of about 0.5 to about 7 grams per liter, the ratio of hexavalent chromium to fluorine being in the range of 0.5:1 to about 2.5:1, an ion containing antimony and an ion containing tin, said antimony and tin each being present in an amount in the range of about .02 to about 1.0 gram per liter, said bath having a pH in the range of about 1.3 to about 2.2.

6. A process for applying a coating to surfaces of alumi-

num, which comprises treating said aluminum in an aqueous acidic bath consisting essentially of an anion containing hexavalent chromium, a fluorine-containing anion, an ion containing a member of the group consisting of antimony and tin, said member being present in an amount in the range of about .02 to about 1.0 gram per liter, and sodium and potassium cations, each of said sodium and potassium cations being present in an amount in the range of about .05 to about 2.5 grams per liter, said bath having a pH in the range of about 1.3 to about 2.2.

7. A process for applying a coating to surfaces of aluminum, which comprises treating said aluminum in an aqueous acidic bath consisting essentially of an anion containing hexavalent chromium in an amount of about 0.5 to about 9 grams per liter, a fluorine-containing anion in an amount of about 0.5 to about 7 grams per liter, the ratio of hexavalent chromium to fluorine being in the range of 0.5:1 to about 2.5:1, an ion containing antimony and an ion containing tin, said antimony and tin each being present in an amount in the range of about .02 to about 1.0 gram per liter, and sodium and potassium cations, each of said sodium and potassium cations being present in an amount in the range of about .05 to about 2.5 grams per liter, said bath having a pH in the range of about 1.3 to about 2.2.

8. A process for applying a coating to surfaces of aluminum, which comprises treating said aluminum in an aqueous acidic bath consisting essentially of an anion containing hexavalent chromium in an amount of about 0.5 to about 9 grams per liter, a fluorine-containing anion in an amount of about 0.5 to about 7 grams per liter, the ratio of hexavalent chromium to fluorine being in the range of 0.5:1 to about 2.5:1, an ion containing antimony and an ion containing tin, said antimony and tin each being present in an amount in the range of about .02 to about 1.0 gram per liter, and sodium and potassium cations, each of said sodium and potassium cations being present in an amount in the range of about .05 to about 2.5 grams per liter, and a zinc cation in an amount in the range of about 0.1 to about 10 grams per liter, said bath having a pH in the range of about 1.3 to about 2.2.

9. The method of coating a succession of aluminum parts which comprises successively treating said parts with an aqueous acidic bath consisting essentially of an anion containing hexavalent chromium in an amount of about 0.5 to about 9 grams per liter, a fluorine-containing anion in an amount of about 0.5 to about 7 grams per liter, said bath having a pH in the range of about 1.3 to about 2.2, and periodically adding to said bath antimony and tin-containing ions, in an amount such that antimony and tin are each present in the bath in an amount in the range of about .02 to about 1.0 gram per liter, and sodium and potassium ions, in an amount such that each of said sodium and potassium ions are present in the bath in an amount in the range of about .05 to about 2.5 grams per liter, and replenishing said hexavalent chromium and fluorine components as required to maintain the content thereof within the amounts above specified.

10. An aqueous acidic conversion coating bath for aluminum which consists essentially of an anion containing hexavalent chromium in an amount of about 0.5 to about 9 grams per liter, a fluorine-containing anion in an amount of about 0.5 to about 7 grams per liter, the ratio of hexavalent chromium to fluorine being in the range of 0.5:1 to about 2.5:1, an ion containing antimony and an ion containing tin, said antimony and tin each being present in an amount in the range of about .02 to about 1.0 gram per liter, and sodium and potassium cations, each of said sodium and potassium cations being present in an amount in the range of about .05 to about 2.5 grams per liter, said bath having a pH in the range of about 1.3 to about 2.2.

11. An aqueous acidic conversion coating bath for aluminum which consists essentially of an anion containing hexavalent chromium in an amount of about 0.5 to about 9 grams per liter, a fluorine-containing anion in an amount of about 0.5 to about 7 grams per liter of fluorine, the ratio of hexavalent chromium to fluorine being in the range of 0.5:1 to about 2.5:1, an ion containing antimony and an ion containing tin, said antimony and tin each being present in an amount in the range of about .02 to about 1.0 gram per liter, and sodium and potassium cations, each of said sodium and potassium cations being present in an amount in the range of about .05 to about 2.5 grams per liter, and a metal cation other than sodium and potassium, in an amount in the range of about 0.1 to about 10 grams per liter, said bath having a pH in the range of about 1.3 to about 2.2.

12. An aqueous acidic conversion coating bath for aluminum, consisting essentially of antimony trifluoride, sodium stannate, potassium bifluoride, potassium dichromate, sodium molybdate, and a zinc compound, said bath containing 0.5 to about 9 grams of hexavalent chromium, 0.5 to about 7 grams of fluorine, 0.1 to about 10 grams of zinc, .02 to about 1.0 gram of antimony, .02 to about 1.0 gram of tin, .05 to about 2.5 grams of sodium, and .05 to about 2.5 grams of potassium, based on one liter of solution, said bath having a pH in the range of 1.3 to about 2.2.

13. A solid composition of matter for preparation of a bath for coating objects of aluminum, which consists essentially of a mixture of compounds including in chemically combined form hexavalent chromium and fluorine, and antimony and tin each in effective amounts by weight of up to about 5% of antimony and up to about 5% of tin.

14. A solid composition of matter for preparation of a bath for coating objects of aluminum, which consists essentially of a mixture of compounds including in chemically combined form hexavalent chromium and fluorine, and about 0.5 to about 4% of antimony, about 0.5 to about 4% of tin, about 0.5 to about 30% of sodium, and about 0.5 to about 30% of potassium, based on the weight of the composition.

15. A solid composition of matter for preparation of a bath for coating objects of aluminum, which consists essentially of a mixture of compounds including in chemically combined form, about 5 to 35% hexavalent chromium, about 5 to about 25% fluorine, 0 to about 30% of a cation other than sodium and potassium, 0.5 to about 4% of antimony, 0.5 to about 4% of tin, about 0.5 to about 30% of sodium, and about 0.5 to about 30% of potassium, the combined sodium and potassium content not exceeding about 35%, based on the weight of the composition.

16. A solid composition of matter for preparation of a bath for coating objects of aluminum, which consists essentially of a mixture of compounds including in chemically combined form, about 5 to 35% hexavalent chromium, about 5 to about 25% fluorine, about 2 to about 25% of zinc, 0.5 to about 4% of antimony, 0.5 to about 4% of tin, about 0.5 to about 30% of sodium, and about 0.5 to about 30% of potassium, the combined sodium and potassium content not exceeding about 35%, based on the weight of the composition.

17. A solid composition of matter for preparation of a bath for coating objects of aluminum, which consists essentially of a mixture of compounds including antimony trifluoride, sodium stannate, potassium bifluoride, potassium dichromate, and sodium molybdate, there being present in said composition by weight, about 0.5 to about 4% of antimony, about 0.5 to about 4% of tin, about 0.5 to about 30% of sodium, about 0.5 to about 30% of potassium, the combined sodium and potassium content not exceeding about 35%, and about 0.5 to about 5% sodium molybdate.

18. A composition of matter effective for rejuvenating a conversion coating bath containing an anion containing hexavalent chromium and fluorine-containing anion, said composition consisting essentially of a mixture of compounds containing antimony, tin, sodium and potassium, in amounts by weight of up to about 5 parts of antimony,

up to about 5 parts of tin, about 0.5 to about 30 parts of sodium, and about 0.5 to about 30 parts of potassium.

19. A composition of matter as defined in claim 18, said mixture of compounds including antimony trifluoride, sodium stannate, and potassium bifluoride.

20. A solid composition of matter for preparation af a bath for coating objects of aluminum, which consists essentially of a mixture of compounds including in chemically combined form hexavalent chromium and fluorine, and about 0.5 to about 4% of antimony, and about 0.5 to about 4% of tin, based on the weight of the composition.

21. An aqueous acidic conversion coating bath for aluminum which consists essentially of an anion containing hexavalent chromium in an amount of about 0.5 to about 9 grams per liter, a fluorine-containing anion in an amount of about 0.5 to about 7 grams per liter, the ratio of hexavalent chromium to fluorine being in the range of 0.5:1 to about 2.5:1, an ion containing a member of the group consisting of antimony and tin, said member being present in an amount in the range of about .02 to about 1 gram per liter, and sodium and potassium cations, each of said sodium and potassium cations being present in an amount in the range of about .05 to about 2.5 grams per liter, said bath having a pH in the range of about 1.3 to about 2.2.

References Cited in the file of this patent

UNITED STATES PATENTS

2,795,518	Carroll et al.	June 11, 1957
2,798,830	Newhard et al.	July 9, 1957
2,851,385	Spruance et al.	Sept. 9, 1958
2,868,679	Pimbly	Jan. 13, 1959
2,936,254	Newhard et al.	May 10, 1960