Jan. 23, 1962 E. M. DUKE, JR 3,018,211

COMPOSITION AND PROCESS FOR BRIGHTENING ALUMINUM AND ITS ALLOYS

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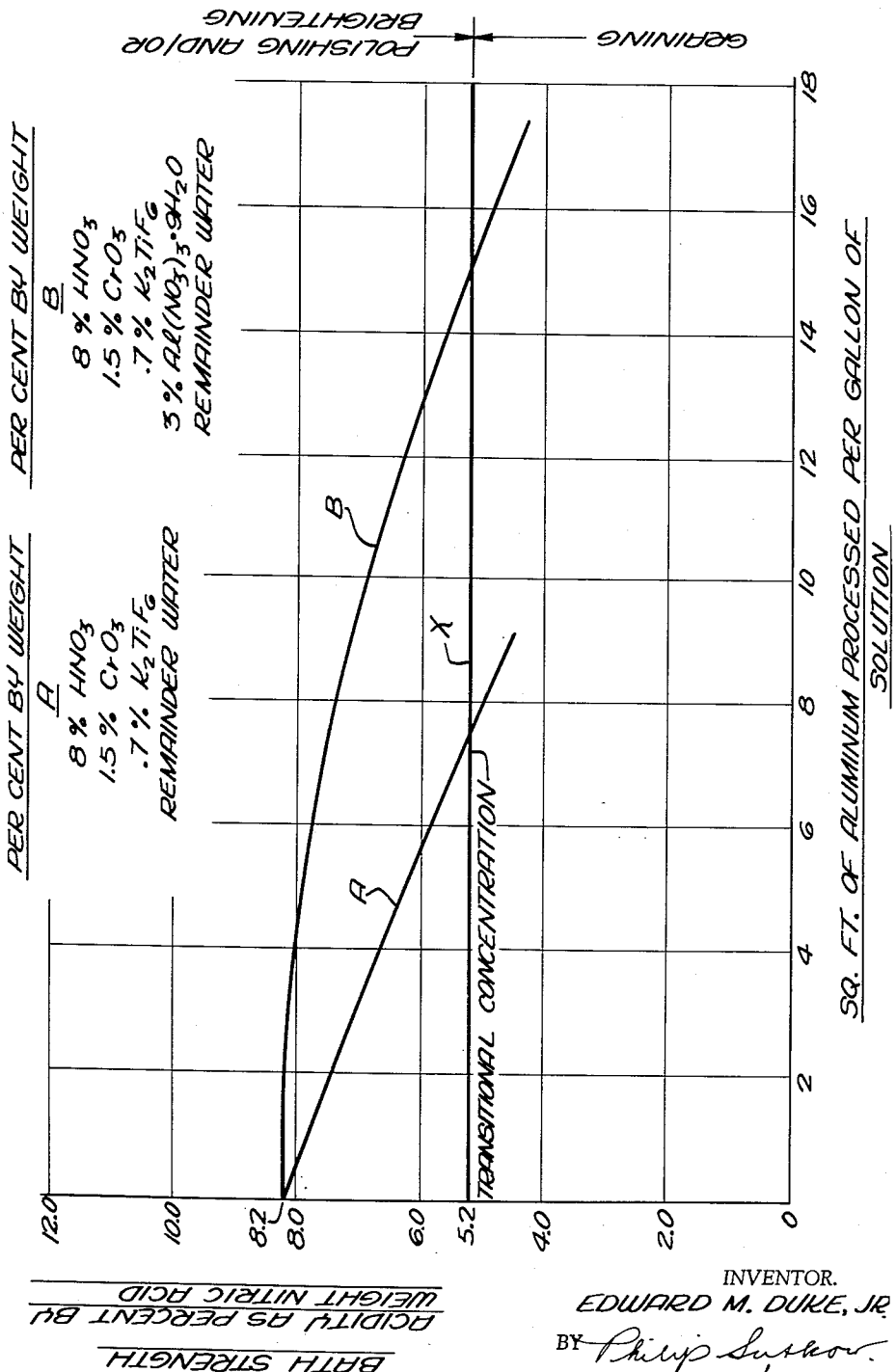


FIG. 1.

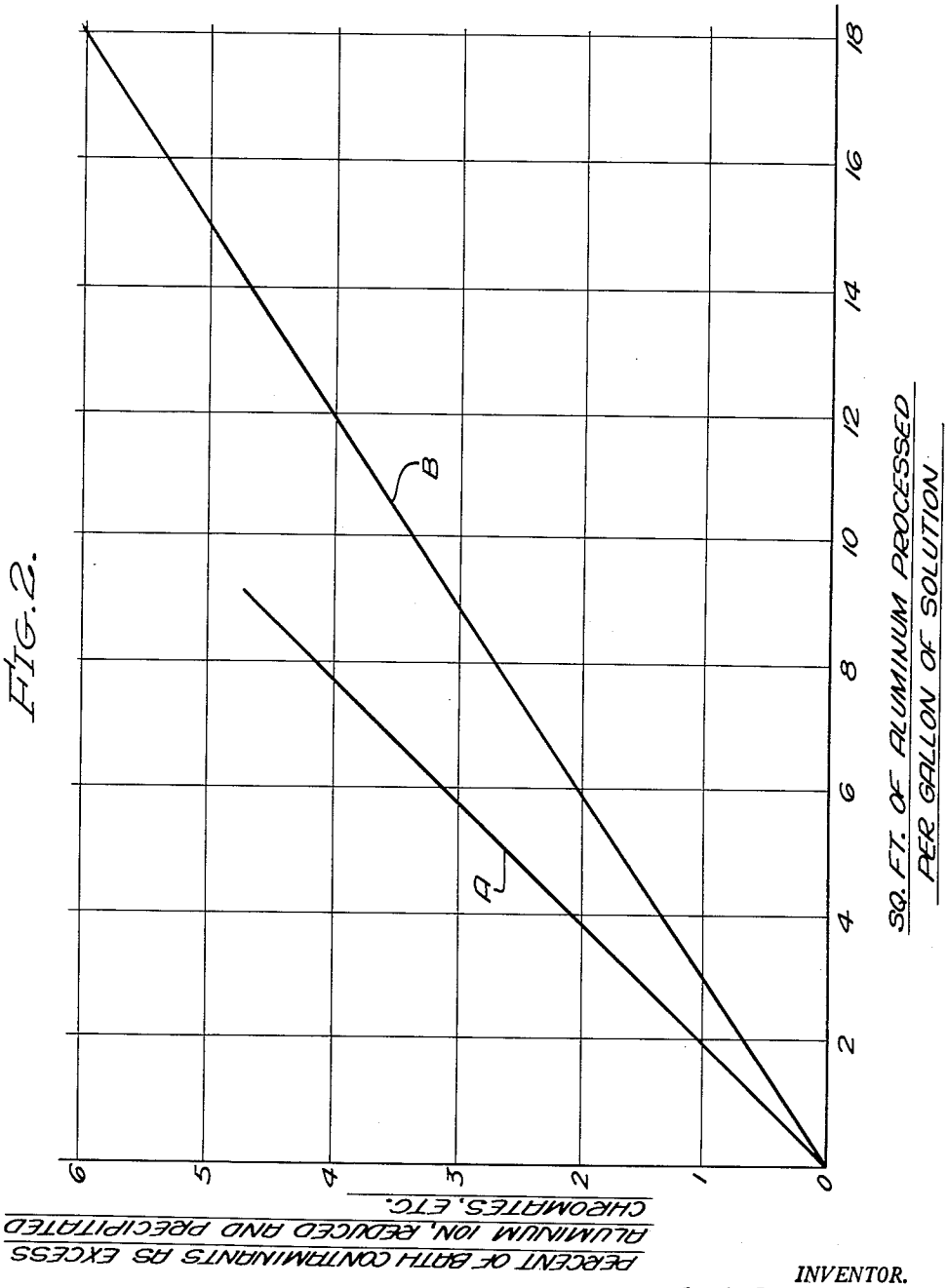
INVENTOR.
EDWARD M. DUKE, JR.
BY Philip Sussdorf
Max Gelden
ATTORNEYS

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COMPOSITION AND PROCESS FOR BRIGHTENING ALUMINUM AND ITS ALLOYS

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FIG. 2.



INVENTOR.
EDWARD M. DUKE JR.
BY Philip Sutker
Max Gilden
ATTORNEYS

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3,018,211

COMPOSITION AND PROCESS FOR BRIGHTENING ALUMINUM AND ITS ALLOYS

Edward M. Duke, Jr., Richland, Wash., assignor, by mesne assignments, to Purex Corporation, Ltd., a corporation of California

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7 Claims. (Cl. 156—21)

This invention relates to brightening of aluminum and is more particularly concerned with a bright dip composition and to a method of chemically brightening aluminum with said composition.

The term "aluminum" employed in the specification and claims is intended to denote commercially pure aluminum and its alloys.

Various types of brightening compositions for aluminum and methods for producing bright aluminum surfaces are known. But much of the prior art technique has certain disadvantages. For example, some of the main problems associated with present practice for bright dipping of aluminum are excessive metal loss, grain accentuation or development which tends to hamper achievement of high specular reflectance, and smut formation. Another difficulty of the prior art has been rapid loss of bath effectiveness, requiring frequent rejuvenation and replacement, and thus increasing the cost of operation.

One object of this invention is the provision of a composition and procedure for chemically brightening or polishing aluminum, resulting in an aluminum surface of high specular reflectance.

Another object is to provide a composition and method for chemically brightening aluminum whereby metal loss at the surface, grain development and smut formation are materially suppressed.

Yet another object is to afford a composition or bath, and a process of improved efficiency for obtaining bright aluminum surfaces, while permitting a greater period of treatment in the bath before rejuvenation is required, and wherein effective bath life is increased over that of the prior art.

Other objects and advantages will be apparent hereinafter.

I have found that the above objects and advantages can be accomplished by employing an aqueous acid bath containing hydrogen, nitrate, hexavalent chromium, complex fluoride, and aluminum ions, preferably present in certain hereinafter defined concentrations. It has been observed particularly that a proper balance as between nitric acid and hexavalent chrominum should be maintained, together with a relatively high concentration of aluminum ions in conjunction with the complex fluoride ions.

I have found that a certain level of concentration of the hexavalent chrominum-containing anion is necessary in the bath in conjunction with a certain level of concentration of nitric acid, i.e. hydrogen and nitrate ions, to supply an oxidizing medium such that when the dull surface oxides of aluminum have been removed, a protective thin coating is apparently applied to the aluminum surface to inhibit any corrosive attack of the aluminum metal by the complex fluorine-containing anions. Such protective coating may be in the form of a very thin layer of oxide on the metal surface, such layer being of a nature which does not adversely affect the obtention of an aluminum surface of high specular reflectance, but rather aids achievement of this result by preventing etching or pitting action of the fluorine-containing anion on the metal surface. Hence, the presence of the chromium-containing and the nitrate ions in the acid solution renders the treating bath "safe on aluminum." Also, the employment of the hexavalent chromium and nitric acid

within certain ranges of concentration, particularly together with a relatively high concentration of aluminum ions in solution, substantially increases the effective life of the bright dip bath, and reduces the contamination level of the bath, particularly as regards formation of excess aluminum ions and reduced and precipitated chromates, e.g. as CR_2O_3.

With respect to the nitric acid, which generally functions to provide an oxidizing acid medium which does not attack aluminum metal but which aids in protecting the base metal from possible attack by fluorine-containing anions, the concentration of nitric acid in the bright dip solution of this invention should be such that the concentration of nitrate ion is about 0.60 to about 3.00 mols per liter and the concentration of hydrogen ions is about 0.60 to about 2.00 mols (gram atoms) per liter. An additional portion of the nitrate ions can be supplied by employing aluminum nitrate as the source of aluminum ions and as the source of such additional nitrate ions.

The hexavalent chromium-containing anion can be derived from chromic anhydride (CrO_3), referred to herein and in the art as chromic acid, and alkali metal and ammonium chromates and dichromates, such as, for example, sodium, potassium or ammonium chromates or dichromates. The amount of hexavalent chromium-containing ions employed in the bright dip solution of the invention should be equivalent to between about .05 and about 0.40 mol (gram atoms) per liter of hexavalent chromium.

The initial presence in the bath of at least .02 mol, preferably .02 to .20 mol (gram atoms) of free aluminum ions as cation per liter, is of particular importance, in that it reduces the overall activity of the bath, reduces the galvanic potential between aluminum and other metal ions that may contaminate the bath, and permits the complex fluoride ions to more readily function to remove the dull oxides of aluminum without any material amount of metal loss, and reduces or prevents development of smut. The aforementioned high concentration of aluminum ions initially present in the bath and maintained throughout effective operation of the bath, decreases the consumption of nitric acid and aids in maintaining the proper acidity of the bath, and reduces contamination thereof. The source of aluminum ions for introduction into the bath can be aluminum compounds which are soluble in the bath, such as, for example, aluminum fluoride, aluminum nitrate, hydrated aluminum oxide (Al_2O_3—$3H_2O$), aluminum phosphate, aluminum sulfate or alum.

The complex fluoride ions in addition to functioning for removal of dull surface oxides of aluminum from the metal surface, have the additional advantage of aiding in obtaining the high concentration of aluminum ions required in the bath initially and during treatment of aluminum articles in the bath for obtaining the invention results. Without the complex fluoride ions the high concentration of aluminum ions cannot be achieved in a practical manner, even at high bath temperatures.

The soluble complex fluorides employed according to the invention are preferably fluorine compounds furnishing in solution complex double fluoride ions having the formula MF_x where M is a member of the group consisting of metals and non-metals other than hydrogen, and x is an integer of from 4 to 6. These complex fluorides are of the type in which the fluorine atoms have coordinate links to the metal or non-metal of the complex ion, and hence excludes, for example, bifluorides. Illustrative specific examples of these complex anions are the SiF_6, TiF_6, ZrF_6, BF_4 and AlF_4 ions. The preferred complex fluoride ions are the TiF_6, ZrF_6 and AlF_4 ions. It is of course understood that the invention is not limited, however, to those complex fluoride ions specifi-

cally mentioned. One or more than one of these complex fluoride ions can be present. The source materials for these complex fluorides can be, for example, the alkali metal or ammonium salts of the complex fluorides or any sufficiently soluble complex fluoride salts of a metal which does not form insoluble material with any of the other anions present in the solution, such as the hexavalent chromium-containing anion.

Specific illustrative examples of such complex fluorides are sodium, potassium or ammonium fluoborates and silicofluorides, potassium titanium fluoride, sodium titanium fluoride, potassium zirconium fluoride, ammonium beryllium fluoride, ammonium cadmium fluoride, ammonium aluminum fluoride, ammonium chromium fluoride, potassium molybdenum fluoride, potassium rhenium fluoride, ammonium zirconium fluoride, potassium zirconium pentafluoride, sodium zirconium pentafluoride, potassium ferric fluoride, potassium zinc fluoride, ammonium titanium fluoride, potassium hafnium fluoride, potassium columbium fluoride, and potassium tantalum fluoride.

In the case of the AlF_4 complex anion, this can be formed either from the double salt, e.g., alkali metal or ammonium aluminum fluoride, or from the simple aluminum fluoride which in the nitric acid solution of the invention forms the complex AlF_4 ion. However, where AlF_3 is used as the source of both aluminum ions and complex fluoride ions, because of the tendency of some aluminum fluoride to form the aforementioned AlF_4 ions, thus reducing the concentration of free of disassociated aluminum ions, it is preferred to employ aluminum fluoride in conjunction with other aluminum salts, e.g., aluminum sulfate, to supply sufficient concentration of aluminum ions. The concentration of complex fluoride ions in the solution is preferably about 0.01 to about 0.10 mol per liter of solution. It has been found particularly advantageous to employ a weight ratio of free aluminum ions to complex fluoride ions of about 2 to 1.

The pH of the brightening solutions of the invention having the aforementioned ingredients, is usually about 0.5 or less, and in most cases about 0.4 or less. The temperature of the solutions is preferably maintained between 180 and about 210° F., although lower temperatures can be employed. The employment of such elevated temperatures not only serves to increase the efficiency of operation and reduce time of treatment, but also aids in conjunction with the complex fluoride ion, and the aforementioned concentration of nitric acid, to maintain in solution the relatively high concentration of aluminum ion required for proper functioning of the bath. Time of treatment in my brightening bath is usually from about 5 to 20 minutes, depending on temperature of the bath, the concentration of the specific components thereof, and the age of the bath. It will be understood that the temperature and time of treatment are not critical and can vary from the aforementioned ranges.

The compounds serving as the source for the essential ions of the bright dip composition of the invention, can be added separately to a water solution in amounts sufficient to form the acid bath having the preferred aforementioned ranges of said ions, or alternatively, a solid composition composed of a mixture of two or more of said compounds in proper proportions can be added to an aqueous nitric acid solution in proper concentration to form the bright dip bath.

When processing aluminum parts to be brightened according to the invention, it is first preferred to remove sols from the surface of the parts by treatment in a precleaning composition, such as, for example, a solution formed by dissolving in water a composition composed of 95% tetrasodium pyrophosphate, 3% sodium chromate and 2% sodium dodecyl benzene sulfonate, in a concentration of 6 ounces of the composition per gallon of solution. The parts should then be rinsed thoroughly in cold or warm running water to remove any residue from the parts. If desired, the parts can then be pre-etched in a caustic alkali solution, e.g., 10% NaOH solution, for a few minutes. When such pre-etching is employed, this tends to increase the tank life of the bright dip bath of the invention.

The aluminum parts can then be deoxidized by treatment, e.g., for 2 to 5 minutes, in a deoxidizer of the type disclosed in U.S. application Serial No. 710,403 of Isidore Pollack, filed January 22, 1958. An illustrative bath of this nature is composed of 91% sodium bisulfate, 8% chromic acid (CrO_3) and 1% potassium titanium fluoride dissolved in water in an amount of 8 ounces of said composition per gallon of solution. The parts are then rinsed thoroughly in cold running water.

The parts are then treated in the bright dip bath of the invention, preferably under the pH conditions, temperature and time period noted above. Gentle mechanical agitation o fthe work pieces in the bath, or agitation of the bath itself, enhances the specular brightness. However, excessive agitation is to be avoided, especially in aged baths, as it tends to accelerate graining therein. To prolong the bath lige, it is recommended that about 1.0% of the bath be discarded for each 10 sq. ft. of aluminum processed per working gallon of solution.

After the aluminum parts have been brightened according to the invention, the parts are rinsed thoroughly in cold, agitated, overflowing water. The work surface can then be passivated in a chromic acid passivating solution, e.g., 0.5% chromic acid (CrO_3) solution, adjusted to pH of 2.0 with nitric acid, for a short period, e.g., 10 to 20 seconds, to form a thin inert layer of oxide on the brightened aluminum surface without adversely affecting the specular brightness thereof.

It will be understood that treatment in any one or more of the aforementioned auxiliary treating baths, that is, pre-cleaner, pre-etching, deoxidizer or passivating baths, is optional, and can be omitted if desired.

It has been found that treatment in the bright dip bath of the invention produces a highly polished mirror-like surface on commercial aluminum, e.g., 1100 and 3003 aluminum, and on alloys such as 2024 and 6061, a bright smooth surface of high specular reflectance is obtained, which is not quite as reflective as the surface formed on 1100 or 3003 aluminum. However, the bright dip bath hereof is effective on various aluminum alloys in addition to those specifically mentioned above.

The following examples illustrate practice of the invention and the advantages thereof:

EXAMPLE 1

Two solutions A and B are made up as follows:

	Percent by Weight	
	A	B
Nitric acid (HNO_3)	8.0	8.0
Chromic acid (CrO_3)	1.5	1.5
Potassium titanium fluoride (K_2TiF_6)	0.7	0.7
Aluminum nitrate ($Al(NO_3)_3.9H_2O$)		3.0
Water	89.8	86.8

Solution A contains 1.27 mol hydrogen ion, 1.27 mol nitrate ion, .15 mol hexavalent chromium and .039 mol TiF_6 ion, based on a liter of solution. Solution B contains 1.27 mol hydrogen ion, 1.39 mol nitrate ion, .15 mol hexavalent chromium, .039 mol TiF_6 ion and .14 mol aluminum ion, based on a liter of solution.

A number of panels of 3003 aluminum were treated in solution A at 200° F. and a number of other panels of the same alloy were treated in solution B maintained at the same temperature as solution A.

The square feet of aluminum processed in each of solutions A and B and the corresponding remaining strength or acidity of the bath as percent by weight nitric acid are determined at various intervals. These values are

plotted, giving the curves shown in the FIG. 1 of the accompanying drawing. The horizontal line indicated at X and corresponding to a concentration of about 5.2% by weight nitric acid represents an average concentration noted herein as the transitional concentration, above which polishing and/or brightening occurs and below which the polishing and brightening action appears to decrease substantially and graining occurs. The greater the distance above the line X, the higher the specular reflectance produced on the part surface.

From the plots shown in the drawing, it is seen that using solution A not containing aluminum nitrate initially, the bath strength, i.e., its acidity in terms of nitric acid concentration, decreases rapidly and the bath reaches the transitional concentration when less than 8 square feet of aluminum per gallon of solution is processed. When using solution B of the invention, containing the required concentration of aluminum ions, together with the required concentration of nitrate and hexavalent chromium, about 15 square feet of aluminum surface per gallon of solution are processed before the transitional concentration is reached, showing the effectiveness of the presence of such aluminum ions in increasing the life and efficiency of the bright dip. Moreover, solution B can be revivified by addition of nitric acid to process say 30 square feet or more of aluminum per gallon of solution before the solution is exhausted, whereas with addition of the same amount of nitric acid to the solution A the bath is exhausted when only 16 to 20 square feet of aluminum per gallon of solution are processed.

Further, at points above the transitional concentration indicated by line X on each of curves A and B, for any given value of square feet of aluminum processed per gallon of solution, the specular reflectance of the aluminum treated with solution B containing the requisite concentration of aluminum ions, is superior to that for solution A. For example, at the value on the abscissa corresponding to processing of six square feet of aluminum in each of the baths, the specular reflectance of parts processed in solution B is materially greater than that for solution A. As the number of square feet of aluminum processed per gallon of solution increases, the greater is the difference between the high specular reflectivity produced in solution B as compared to the inferior brightening action of solution A. Also, processing of aluminum parts in solution B in which more than 8 and less than 15 square feet of aluminum per gallon of solution have previously been processed continues to give a high polished surface, whereas after processing about 8 square feet of aluminum per gallon of solution using solution A, further operation proceeds in the region below the transitional concentration, giving inferior results, including graining.

During the processing of the aluminum panels in each of solutions A and B, as the nitric acid is consumed, aluminum from the panels is dissolved in the solution, increasing the aluminum ion concentration. However, in the case of solution A the nitric acid is consumed much faster than in solution B of the invention, placing substantially more aluminum into solution than solution B. When between 6 and 8 square feet of aluminum have been processed in solution A, there is a large amount of aluminum ion present substantially in excess of the 0.20 mol per liter upper limit for the concentration of aluminum cation according to the invention, and such excess aluminum ion functions as a contaminant in the bath. About 13 to 14 square feet of aluminum can be processed in solution B before it becomes contaminated with an excess of aluminum ion comparable to the excess aluminum ion present when only 6 to 8 square feet of aluminum have been processed in solution A. Hence it is apparent that bath A becomes quickly contaminated by excess aluminum ion due to rapid consumption of nitric acid, whereas bath B of the invention containing a predetermined concentration of aluminum ion initially in solution reduces the consumption of nitric acid and can be used for processing many more square feet of aluminum before it becomes contaminated to an equal degree with excess aluminum ion, as compared to bath A.

FIGURE 2 of the drawing is a plot of square feet of aluminum processed per gallon of solution against percentage of contaminants in the form of excess aluminum, precipitated and reduced chromates and other contaminants including fluoride precipitates, formed during the reaction.

Curve A represents the contamination level of bath A and curve B the contamination level of bath B. Thus, for example, when 8 square feet of aluminum has been processed using solution A, the contamination level is about 4.2%, and according to FIGURE 1, at this point bath A is no longer effective as a brightening bath. On the other hand, at 8 square feet of aluminum processed in solution B, the contamination level for bath B containing aluminum ion initially is only about 2.7%, and at this level of contamination, bath B is still effective as a brightener. Bath B does not reach the 4.2% contamination level until about 13 square feet of aluminum has been processed.

EXAMPLE 2

The following solutions C to K are prepared, a practical range of proportions of the components which can be used also being given for each of the specific compositions:

Table I

	Percent by Weight	
	C	Range
HNO_3	7.8	3.60 to 12.0
$Al(NO_2)_3.9H_2O$	2.3	.75 to 3.75
CrO_3	2.3	.50 to 4.00
K_2TiF_6	.8	.26 to 1.30
Water	Remainder	Remainder
	D	
HNO_3	7.8	3.60 to 12.0
$Al(NO_3)_3.9H_2O$	2.3	.75 to 3.75
CrO_3	2.3	.50 to 4.00
K_2ZrF_6	.8	.26 to 1.30
Water	Remainder	Remainder
	E	
HNO_3	8.3	3.60 to 15.0
AlF_3	1.1	.20 to 2.0
CrO_3	2.3	.50 to 4.0
Water	Remainder	Remainder
	F	
HNO_3	9.3	3.60 to 15.0
AlF_3	.55	.10 to 1.0
$Al_2(SO_4)_3$	1.0	.34 to 1.7
CrO_3	2.3	.50 to 4.0
Water	Remainder	Remainder
	G	
$NaAlO_2$	.7	.16 to .80
K_2TiF_6	.7	.26 to 1.3
Na_2CrO_4	2.4	.80 to 6
HNO_3	9.0	3.6 to 12.6
Water	Remainder	Remainder
	H	
$NoBF_4$	.3	.1 to .6
Na_2CrO_4	2.5	.8 to 6.0
$Al(No_3)_3.9H_2O$	3.0	.8 to 3.8
HNO_3	9.0	3.6 to 12.6
Water	Remainder	Remainder
	J	
Na_2SiF_6	.5	.2 to .9
Na_2CrO_4	2.5	.8 to 6.0
$Al(NO_3)_3.9H_2O$	3.0	.8 to 3.8
HNO_3	9.0	3.6 to 12.6
Water	Remainder	Remainder

Table 1—Continued

	Percent by Weight	
	K	Range
$K_2Cr_2O_6$	2.3	.9 to 5.5
K_2TiF_6	.7	.3 to 1.3
$Al(NO_3)_3.9H_2O$	3.0	.8 to 3.8
HNO_3	9	3.6 to 12.6
Water	Remainder	Remainder

1100, 3003, 2024 and 6061 aluminum alloys are treated in each of the compositions C to K noted above for a period of about 5 minutes, the temperature of each of the solutions being maintained at about 200° F.

In each case, the respective parts treated in the above solutions develop a smooth, polished bright surface of high specular reflectance, with absence of pitting and graining, and with substantially no loss of base metal. However, best results are noted with compositions containing titanium, zirconium and aluminum complexes with fluorine, that is, compositions C to G and K. Particularly with the 1100 and 3003 aluminum samples, the compositions of Table I produce mirror-like surfaces. Of the compositions E and F, wherein the fluorine complex is the AlF_4 ion, composition F containing additional free aluminum ion furnished by the aluminum sulfate produces better results. In composition G, the $NaAlO_2$ in nitric acid solution breaks down to give aluminum nitrate.

From the foregoing, it is seen that the invention provides improved novel compositions and procedure for efficient brightening and polishing of aluminum, without accentuating the formation of smut or grain, and with substantially no base metal loss.

The term "consisting essentially of" as used in the definition of the ingredients present in the composition claimed is intended to exclude the presence of other materials in such amounts as to interfere substantially with the properties and characteristics possessed by the composition set forth but to permit the presence of other materials in such amounts as not substantially to affect said properties and characteristics adversely.

The term "aluminum" employed in the claims is intended to denote commercially pure aluminum and aluminum alloys.

While I have described particular embodiments of my 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.

I claim:

1. A chemical brightener bath for aluminum, which comprises an acid aqueous solution consisting essentially of about .60 to about 2.00 mols per liter of hydrogen ions, about .60 to about 3.00 mols per liter of nitrate ions, a concentration of hexavalent chromium-containing ion equivalent to about .05 to about 0.40 mol per liter of hexavalent chromium, about .01 to about .10 mol per liter of complex fluoride ions selected from the group consisting of the SiF_6, TiF_6, ZrF_6, BF_4 and AlF_4 ions, and about .02 to about .20 mol per liter of aluminum cations, the pH of said solution being not greater than about 0.5.

2. A chemical brightener bath as defined in claim 1, wherein said complex fluoride ions are TiF_6 ions.

3. A chemical brightener bath for aluminum, which comprises an acid aqueous solution consisting essentially of nitric acid, aluminum nitrate, chromic acid and potassium titanium fluoride, the amounts of said ingredients present being such as to provide about .60 to about 2.00 mols per liter of hydrogen ions, about .60 to about 3.00 mols per liter of nitrate ions, chromate ions in a concentration equivalent to about .05 to about 0.40 mol per liter of hexavalent chromium, about .01 to about .10 mol per liter of fluotitanate ions, and about .02 to about .20 mol per liter of aluminum cations, the pH of said solution being not greater than about 0.5.

4. A chemical brightener bath for aluminum, which comprises an acid aqueous solution consisting essentially of nitric acid, aluminum fluoride and chromic acid, the amounts of said ingredients present being such as to provide about .60 to about 2.00 mols per liter of hydrogen ions, about .60 to about 3.00 mols per liter of nitrate ions, chromate ions in a concentration equivalent to about .05 to about 0.40 mol per liter of hexavalent chromium, about .01 to about .10 mol per liter of AlF_4 ions, and about .02 to about .20 mol per liter of aluminum cations, the pH of said solution being not greater than about 0.5.

5. A process for chemically brightening aluminum, which comprises treating said aluminum in an aqueous acid solution consisting essentially of about .60 to about 2.00 mols per liter of hydrogen ions, about .60 to about 3.00 mols per liter of nitrate ions, a concentration of hexavalent chromium-containing ion equivalent to about .05 to about 0.40 mol per liter of hexavalent chromium, about .01 to about .10 mol per liter of complex fluoride ions selected from the group consisting of the SiF_6, TiF_6, ZrF_6, BF_4 and AlF_4 ions, and about .02 to about .20 mol per liter of aluminum cations, the pH of said solution being not greater than about 0.5.

6. A process as defined in claim 5, wherein the temperature of said solution being maintained between about 180° and about 210° F.

7. A composition which consists essentially by weight of .50 to 6.0 parts of a soluble hexavalent chromium-containing compound, 0.1 to 2.0 parts of a soluble complex fluoride of the group consisting of soluble silicofluorides, titanium fluorides, zirconium fluorides, fluoborates and aluminum fluorides; and .16 to 3.8 parts of a soluble aluminum salt, said composition when added to an aqueous nitric acid solution having a nitric acid concentration furnishing about .60 to about 3.00 mols per liter of nitrate ions, forming a brightening bath for aluminum, comprising hexavalent chromium-containing ion equivalent to about .05 to about 0.40 mol per liter of hexavalent chromium, about .01 to about .10 mol per liter of complex fluoride ions selected from the group consisting of the SiF_6, TiF_6, ZrF_6, BF_4 and AlF_4 ions, and about .02 to about .20 mol per liter of aluminum cations, and about .60 to about 2.00 mols per liter of hydrogen ions, said bath having a pH not greater than about 0.5.

References Cited in the file of this patent

UNITED STATES PATENTS

2,276,353	Thompson	Mar. 17, 1942
2,553,937	Chambery	May 22, 1951
2,593,447	Hesch	Apr. 22, 1952
2,593,448	Hesch	Apr. 22, 1952
2,593,449	Hesch	Apr. 22, 1952
2,613,165	Fischer	Oct. 7, 1952
2,614,913	Reindl et al.	Oct. 21, 1952
2,625,468	Prance et al.	Jan. 13, 1953
2,687,346	McDonald	Aug. 24, 1954
2,719,079	Murphy	Sept. 27, 1955
2,843,513	Stricklen	July 15, 1958
2,851,385	Spruance	Sept. 9, 1958
2,948,643	Pimbley	Aug. 9, 1960