Oct. 8, 1963 E. W. KENDALL 3,106,499

PROCESS AND COMPOSITION FOR CLEANING AND POLISHING ALUMINUM AND ITS ALLOYS

Filed May 11, 1959 2 Sheets-Sheet 1

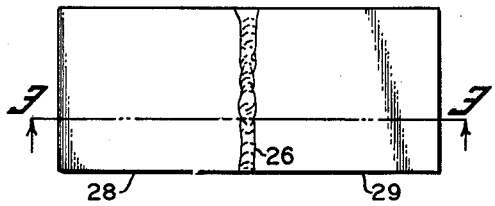


fig - 1

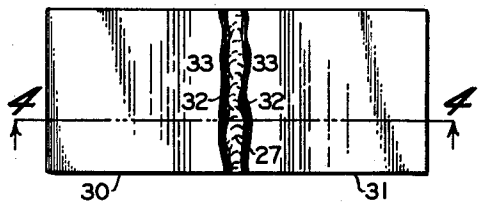


fig - 2

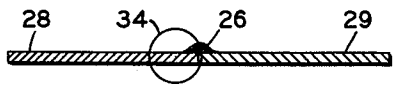


fig - 3

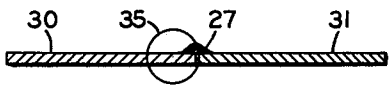


fig - 4

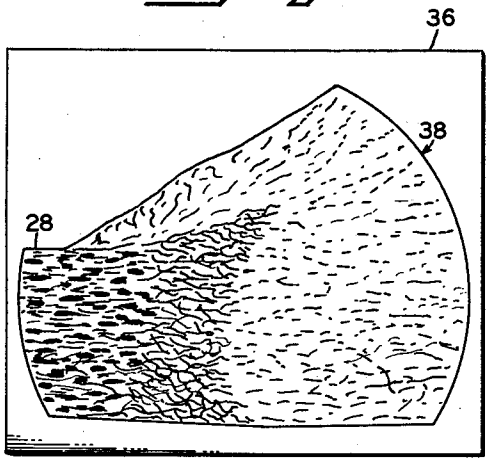


fig - 5

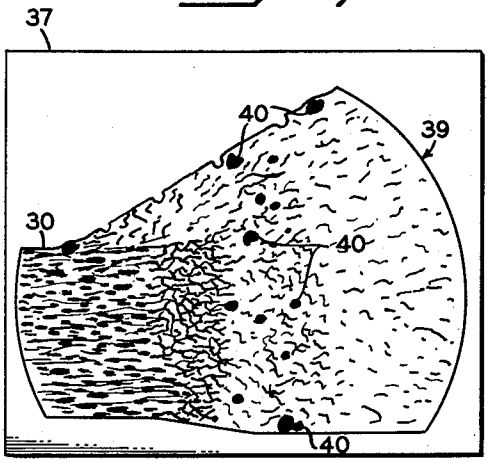


fig - 6

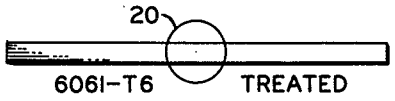


fig - 7

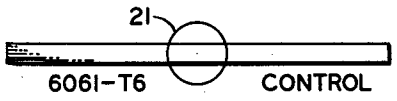
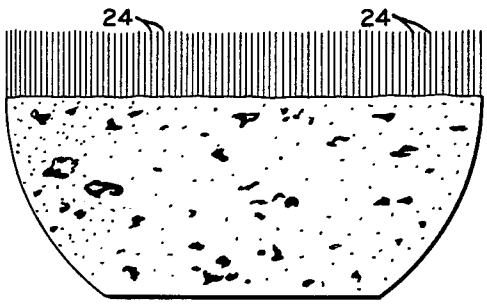


fig - 8

INVENTOR.
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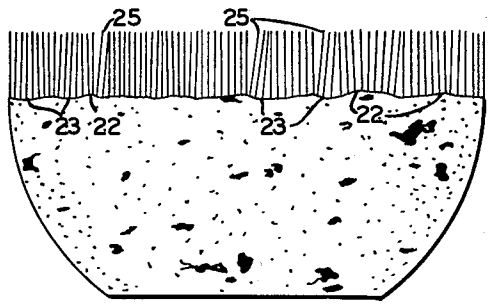
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PROCESS AND COMPOSITION FOR CLEANING AND POLISHING ALUMINUM AND ITS ALLOYS
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6061-T6 TREATED

fig - 9



6061-T6 CONTROL

fig - 10

MATERIAL	SPECIMEN	MINIMUM GAGE	MAXIMUM GAGE	AVERAGE GAGE	DIFFERENCE
2024-T3	1-1CONTROL 1-2TREATED	.03984 .03974	.04083 .04106	.04026 .04026	
7075-T6	2-1CONTROL 2-2TREATED	.04032 .04042	.04150 .04131	.04090 .04077	- .00013
3003-0	3-1CONTROL 3-2TREATED	.04074 .04131	.04291 .04304	.04192 .04195	+ .00003
6061-T6	4-1CONTROL 4-2TREATED	.04016 .04038	.04096 .04138	.04067 .04083	+ .00016
2024-T6	5-1CONTROL 5-2TREATED	.04934 .04976	.05040 .05030	.04989 .05002	+ .00013
2024-T81	6-1CONTROL 6-2TREATED	.01946 .01952	.02037 .01987	.02001 .01971	- .00030
5052-0	7-1CONTROL 7-2TREATED	.04077 .04070	.04163 .04144	.04106 .04102	- .00004

fig - 11

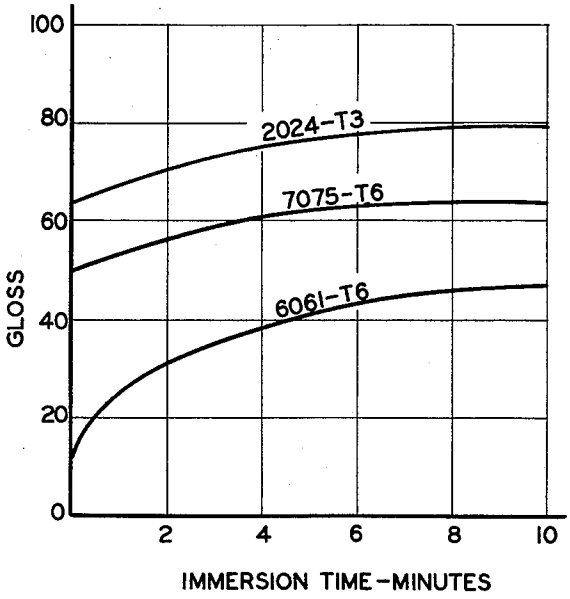


fig - 12

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United States Patent Office 3,106,499 Patented Oct. 8, 1963

3,106,499

PROCESS AND COMPOSITION FOR CLEANING AND POLISHING ALUMINUM AND ITS ALLOYS

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Filed May 11, 1959, Ser. No. 812,369
16 Claims. (Cl. 156—21)

This invention relates generally to the art of treating metals to produce desired surface characteristics such as high polish or gloss, low electrical resistance, and freedom from metallic oxide films and contaminants. More specifically, the present invention is directed to a process and composition for chemically cleaning and polishing aluminum and the alloys of aluminum by simple immersion in a chemical solution.

Due to the inherent characteristic of aluminum to combine with oxygen, the exposed surfaces of most aluminum alloys rapidly develop an oxide scale, coating or film which manifests a dull and unattractive appearance. The film exhibits a great tenacity for the retention of grease, dirt, and other forms of contamination which reduces still further the reflectance characteristics of the original surface. The exterior skins for aircraft, for example, which are generally formed of aluminum or aluminum alloys, in operation, become quite dull in appearance, and where a number of different alloys are used for the several parts and assemblies, the aircraft, as a whole, may present a varying patch work of dull and unattractive shades of gray. It is customary, however, for aircraft manufacturers to require that the exterior skins present a uniform texture and appearance and heretofore, in practice, this usually has been accomplished by rubbing and buffing the surfaces of the skins by hand.

It is also customary in the manufacture of many aircraft assemblies, to electrically weld two or more sheet metal parts together which are made of alloys composed mainly of aluminum. It has been found that thin films of oil, dirt and/or metallic oxide on the faying surfaces of the parts to be joined obstruct the passage of the electric current and cause poor welds. The electrical surface resistance increases markedly upon the formation of the oxides and contaminants on the faying surfaces of the parts to be welded and may prevent their welding altogether. In order to secure spot welds of high strength, it is usually required that the surface or contact resistance between the parts should not exceed 100 microhms.

It is also customary in the manufacture of many aircraft assemblies to employ fusion welding in the joining together of two or more sheet metal parts which are made of alloys composed mainly of aluminum. As aforementioned, the corrosion resistance of aluminum is derived from an oxide of aluminum which forms rapidly on all exposed surfaces. In order to make a sound strong weld, this oxide must be removed as well as any grease, oil, or dirt which may be on the surfaces to be welded. In preparing for welding, it usually has been the practice to scrub the parts with a stiff wire brush and hot water or, if any oil or grease is present, with a non-flammable solvent such as sodium hydroxide or tri-sodium phosphate in hot water. In welding the parts, a specially prepared flux is necessary to remove the aluminum oxide which forms rapidly on the molten weld metal. The flux combines chemically with the aluminum oxide to form a fusible slag which rises to the surface of the puddle during the welding action and is thus readily removed. After welding and cooling, it is necessary that the parts be thoroughly brushed and treated to remove all traces of adhering flux. It has been found in fusion welds that the presence of oxides and contaminants on the surfaces of the parts to be joined become manifest by a high degree of porosity in the welded joint

and this, in turn, greatly impairs and reduces the strength of the joint.

It is also the practice following working or reworking of aircraft parts and assemblies in the form of aluminum sheet stock, extrusions, forgings, etc., to clean, polish, or otherwise treat the surfaces and thereafter apply chemical conversion coatings, or anodic films, or the like, to protect the exposed surfaces against corrosion during periods of storage or between work operations on the parts and assemblies. In many cases it may be necessary to apply, remove, and reapply such protective coatings several times during the work process. The presence of surface oxides and contaminants, however, seriously impairs the ability of the protective coatings to adhere to and resist corrosion of the surface metal. Many of the etching solutions employed to remove chemical conversion coatings, or the like, or otherwise prepare the metal surfaces for work operations or application of protective coatings thereon, do not produce a clean bright surface after being applied to the metal, or the etches may fail to thoroughly clean certain surface areas where the parts and assemblies have complex and intricate configurations. Consequently, the quality of the work operation and of the protective coating applied are both frequently impaired by the etching solutions employed to prepare the metal surfaces. So-called spotweld etches, for example, employed to prepare aluminum surfaces for spot welding, while producing satisfactory electrical resistance for welding, due to too drastic etching action, may leave the surface with a dull appearance or coated with a film of some undesirable chemical product which resists adherence of a protective coating which may subsequently be applied.

Various methods heretofore used or proposed for removing the objectionable oil, dirt and metal oxide films, and the chemical conversion coatings and anodic films, have generally employed mechanical or manual abrasion, electro-chemical means, or chemical solutions. Manual buffing and polishing is laborious, tedious, and time consuming and, because of the human element involved, the effects of texture, color and gloss are non-uniform from one surface area to another. In addition, the abrasive action removes excessive metal, scratches the surface, and leaves a visible pattern of the abrasive marks and strokes.

Electrolytic burnishing or polishing methods are known to produce surfaces having a high reflective capacity on aluminum and aluminum alloys. Electrolytic methods, however, have increased initial and maintenance costs imposed by the expenditure of electrical energy in the process. Chemical solutions including the so-called "bright dip" solutions have also been tried and used with varying degree of success, but these, in common with the electrolytic solutions, have exhibited marked tendency to attack and etch the metal surface with accompanying loss of metal, to preferentially polish certain alloys while being completely ineffective when used with others, to preferentially attack certain partially disassociated alloy constituents, to generate noxious fumes and odors, and to comprise rare and expensive constituent materials, or substances dangerous to handle. In so-called "aqueous solutions," for example, a costly concentrated acid etch may be the predominant ingredient in the solution in which the only water is that which is provided with the acid.

According to the present invention there is provided a process and composition which imparts a handsome luster and mirror-like surface to aluminum and the alloys of aluminum. In its preferred form, the composition consists mainly of water in an aqueous solution of ammonium bifluoride, nitric acid and boric acid. The solution preferably is operated at a temperature of 160°–190° F.

with the immersion time being from 5 to 10 minutes. After a period of immersion of 10 minutes at 170° F., the alloys of aluminum undergo negligible loss of weight and dimensional volume and manifest a high metallic luster, uniform texture, and similar color. The solution is highly effective in preparing aluminum and its alloys for the reception of chemical conversion coatings or anodic films, or will remove these coatings when this is desired. The solution also serves as an excellent pre-spotweld etch for aluminum and its alloys, and when used to prepare parts for fusion welding, provides joints of low porosity without requiring a welding flux.

It is an object of the present invention therefore to provide a new and improved process and composition for cleaning and polishing aluminum and the alloys of aluminum by simple immersion in a chemical solution.

Another object is to provide a process and composition for imparting a high gloss on the surface of aluminum and its alloys with negligible loss of metal weight and dimensional volume.

A further object is to provide a method and composition for treating alloys having a high aluminum content which will remove all surface dirt and metallic oxides and only such minimal amount of surface metal as necessary to enhance the reflectance characteristics of the surface.

Another object is to provide such a treatment which leaves the surfaces of commercial aluminum alloys of many different chemical compositions smooth and glossy with relatively uniform color, texture, and reflectance characteristics.

Still another object is to provide a treatment of the type described which may be used effectively on aluminum and the alloys of aluminum as a pre-spotweld etchant.

Still another object is to provide a chemical process and solution for preparing aluminum and its alloys for fusion welding in which fluxes are not required during the welding operation and porosity in the welded joint is minimized.

Still another object is to provide a chemical solution which is effective in preparing aluminum and its alloys for the reception of chemical conversion coatings and anodic films. Still another object is to provide a solution of this type which is effective in removing chemical conversion coatings and anodic films and, additionally, leaves the surface smooth and glossy and free of all metallic oxides and contaminants.

Another object is to provide an aqueous solution for cleaning and polishing aluminum and its alloys in which inexpensive constituent materials are employed and in which water is used in predominant proportions.

An additional object is to provide a chemical process and composition for cleaning and polishing aluminum and its alloys which uses minor proportions of inexpensive chemicals in an aqueous solution and operates at moderately hot temperatures and relatively short periods of time to produce a high gloss finish with minimal loss of metal and without the production of obnoxious fumes and odors.

Still another object in a treatment of the type described is to provide compositions in dry mix or liquid concentrate form which may be placed in aqueous solution for the purpose of cleaning and polishing aluminum and its alloys by immersion therein.

Still other objects, features and advantages of the present invention will become more clearly apparent as the description proceeds, reference being had, in part, to the accompanying drawings wherein:

FIGS. 1 and 2 are views illustrating two fusion welded joints as they appear on a photomicrograph and in which the parts comprising the joint depicted in FIG. 1 were cleaned preparatory to welding in accordance with the process of the present invention and the parts comprising the joint depicted in FIG. 2 were cleaned prior to welding in accordance with a prior art etching process;

FIGS. 3 and 4 are diagrammatic views representative of cross-sections of the welded joints of FIGS. 1 and 2 as they would appear along the lines 3—3 and 4—4 thereof respectively;

FIGS. 5 and 6 are views illustrating photomicrographs of the welded joints taken at 25 times magnification within the fields of view respectively depicted by the circles of FIGS. 3 and 4;

FIGS. 7 and 8 are end views of halves of an aluminum alloy sheet in which the half depicted in FIG. 7 was treated in accordance with the polishing process of the present invention after both halves were treated with an alkaline cleaner;

FIGS. 9 and 10 are views respectively depicting the surface conditions of the plates of FIGS. 7 and 8 as they appear on a pair of photomicrographs taken at 500 times magnification within the fields of view respectively depicted by the circles of FIGS. 7 and 8;

FIG. 11 is a view illustrating in tabular form the differences in sheet thickness resulting from treatment of Control and Treated specimens of various aluminum alloys in which the Treated and Control specimens have been treated in the same manner as the plates of FIGS. 7 and 8 respectively, and

FIG. 12 is a graph illustrating the effect of immersion time on the relative gloss obtained from representative aluminum alloys when polished in the solution of the present invention.

According to the present invention, a preferred three-constituent acid composition composed predominantly of water with minor proportions of nitric, hydrofluoric, and boric acids, and an alternative two-constituent acid composition composed predominantly of water with minor proportions of nitric and fluoboric acids are prepared which, in practice, produce exceptional cleaning and polishing effects, particularly on aluminum alloys, although other metals such as titanium are effectively cleaned thereby. Although the alternative aqueous solution may be prepared with the two-constituent acid composition, the cleaning and polishing effects obtained therefrom are substantially the equivalent of that obtained from use of the three-constituent acid composition for the reason that the fluoboric acid in solution breaks down and forms hydrofluoric and boric acids. It is preferable, however, that a quantity of boron calculated as boric acid, be in excess of the amount required for reaction with all of the fluorine present for reasons hereinafter more fully to appear. To this end, boric acid or its water soluble salts may be added to the two-constituent acid solution.

In the preferred three-constituent acid composition, the solution is prepared using ammonium bifluoride ($NH_4F.HF$) which, in solution, forms hydrofluoric acid (HF) and ammonia (NH_3). In its most desired form, the composition consists of a solution composed of 0.2 gram of ammonium bifluoride, 1.0 gram of boric acid (H_3BO_3) and 3 milliliters (mls.) of nitric acid

(HNO_3) (42° Bé.)

(specific gravity 1.42) dissolved in 100 mls. of water.

The concentration and constituent formulation of the salts and acids may be varied within certain limits from the optimum as represented in the above formulation, as may be seen in the following examples.

Example I

	Per 100 mls. of aqueous solution
HF	grams 0.15–0.35
H_3BO_3	do 1.0–10.0
HNO_3	mls 2.0–5.0

Example II

	Per 100 mls. of aqueous solution
H_2SiF_6	grams— 0.55–1.25
H_3BO_3	do— 1.00–10.00
HNO_3	mls— 2.0–5.0

Example III

	Per 100 mls. of aqueous solution
$NH_4F.HF$	grams— 0.2–0.5
H_3BO_3	do— 1.0–10.0
HNO_3	mls— 2.0–5.0

Example IV

	Per 100 mls. of aqueous solution
Alkali metal fluoride (NaF, KF) (calculated as $NH_4F.HF$)	grams— 0.2–0.5
Alkali metal or ammonium borates ($Na_2B_4O_7$, $NH_4HB_4O_7$) (calculated as H_3BO_3)	grams— 1.0–10.0
HNO_3	mls— 2.0–5.0

From the foregoing, it will be apparent that a weight to volume ratio of about 10:1 exists between the nitric acid and the ammonium bifluoride. When this ratio is observed there will be no smut formed on parts treated in the solution. It will also be apparent that the boric acid may vary from 2 to 50 parts by weight to one part by weight of the ammonium bifluoride. The boric acid and alkali metal fluoride calculated as ammonium bifluoride in these proportions may be prepared as a dry powdered mixture from commercial grade materials and marketed as a dry mix or as a solid in order to promote economies in packaging and shipping.

In preparing the solution, the dry mix is dissolved in water and the nitric acid preferably is added last. The nitric acid in the solution composition should have a specific gravity of 1.42, and any commercial grade or dilution may be employed provided the required weight of acid is obtained in the resulting solution and due compensation is made for any difference in water volume. The approximate range of materials in solution may thus be:

Alkali metal fluoride calculated as—	Percent by weight of aqueous solution
$NH_4F.HF$	0.2–0.5
H_3BO_3	1.0–10.0
HNO_3	2.0–5.0

A preferred dry mix comprises 1 part by weight of alkali metal fluoride calculated as ammonium bifluoride to 5 parts by weight of boric acid. Thus, a preferred solution will be formed when the equivalent of the preferred ultimate 2% volume of nitric acid is added to form about 96 mls. of water having alkali metal fluoride calculated as 0.2 gram $NH_4F.HF$ and 1.0 gram H_3BO_3 dissolved therein. Ammonium bifluoride and boric acid solids having these weights will not dissolve in 2 mls. of nitric acid without the addition of approximately 10 mls. of water. Accordingly, the preferred solution may be concentrated only to the extent that at least 10% of the 96% water that goes into final solution is retained in the concentrated solution in order to get the solids ($NH_4F.HF$ and H_3BO_3) to dissolve with the nitric acid. This concentrated solution will then comprise:

$NH_4F.HF$	grams— 0.2
H_3BO_3	do— 1.0
HNO_3	mls— 2
H_2O	mls— 10

and may be used for each 100 mls. of ultimate solution. It therefore only becomes necessary to add 86 mls. of water to the liquid concentrate to form each 100 mls. of solution and bring the same to the desired formulation. The concentrated solution conveniently may be marketed in polyethylene bottles, or the like, to prevent deterioration from the hydrofluoric acid.

The materials of the concentrated solution may fall within the following ranges:

	Percent of ultimate solution by weight
$NH_4F.HF$	.2 to .5.
H_3BO_3	1.0 to 10.0.
HNO_3	12.0 to 25.0 (16 to 20% acid).

The solution, the liquid concentrate, or the dry mix, as the case may be, may be prepared from hydrofluoric (HF), fluoboric (HBF_4), and hydrofluosilicic acids (H_2SiF_6) and the water soluble salts thereof, provided that the total weight of fluoride ion is comparable to that hereinbefore specified for the optimum formulation. Thus, in place of the foregoing fluo acids, water soluble fluo compounds such as alkali metal or ammonium fluorides, fluosilicates, and fluoborates may be used in proper amounts to liberate an equivalent concentration of hydrofluoric acid. These may include among others sodium and potassium fluoride (NaF, KF), sodium fluosilicate (Na_2SiF_6), sodium fluoborate ($NaBF_4$), ammonium bifluoride ($NH_4F.HF$), ammonium fluoborate

(NH_4BF_4)

and ammonium fluosilicate ($(NH_4)_2SiF_6$).

Similarly, the boric acid may be replaced by its water soluble salts, such as the alkali metal and ammonium borates including sodium borate ($Na_2B_4O_7$) (Borax) and ammonium borate ($NH_4H.B_4O_7$), in amounts capable of supplying boric acid of the required concentration in water.

The two-constituent acid composition aforedescribed may simply be prepared by adding nitric acid and fluoboric acid, or the water soluble salts thereof, to the proper amount of water by observing the fluoride and borate ion concentrations required in the three-constituent acid composition, the nitric acid being in the same proportions and the fluoboric acid or its salts, as the case may be, supplying both the fluorine and boron required in the solution. It may be preferable to calculate the quantity of fluoboric acid, or one of its water soluble salts, as the case may be, in terms of the fluoride ion required, and making up any deficiency, or augmenting the supply, of boron in the solution by the addition of boric acid in order preferably to keep the borate ion concentration in excess of that required for buffering the fluoride ion, since the boric acid may be lost, in part, through volatilization and this, in turn, may result in too severe activity of the hydrofluoric acid on the metals under treatment in the solution.

Nitric and fluoboric acids or nitric acid and one or more water soluble fluoboric salts may separately be added to the proper amount of water or the same added in the form of a concentrated solution of these compounds.

It will be apparent that concentrated solutions of these acids in these proportions, or equivalent concentrated solutions of the nitric acid with suitable fluoborates may be prepared in form suitable for marketing for the purposes of this invention, as hereinbefore described.

In the case of each of the foregoing solutions, which are operated as so called "hot solutions," the acid composition is critical both as to the components and their proportions, particularly with respect to the relative concentrations of the fluoride and borate ions, and is also critical as to the range of operating temperature.

In these solutions, the hydrofluoric acid is considered to be the sole etchant and, by itself, will vigorously attack aluminum and its alloys. A passivating agent or buffer is required to retard and inhibit this etching action in order to minimize the attack on the surface metal and thus remove only that amount of metal essential for cleaning and/or polishing, as the case may be. The borate ion in the solution provides this retarding and inhibiting effect such that little or no visible action of the acid on the metal may be observed when the soluton is

at ambient temperature (70° F.) and contains the proper concentrations of the fluoride and borate ions.

As ionization of the hydrofluoric and boric acid solution (nitric acid being absent) is increased by raising the temperature of the soluton up to the order of 200° F., the action of the acid on the metal increases but is insufficient to adequately polish the metal or otherwise serve the purposes of the invention. An oxidizing agent is required to oxidize the surface contaminants and make them soluble in the solution. This function is supplied by the nitric acid which apparently attacks the surface contaminants, releasing nitric oxide in the process. This action of the nitric acid is inappreciable below 160° F. As the temperature is increased above 160° F., the nitric acid apparently breaks down and an evolution of hydrogen is visible. Nitric oxide also is released from the solution and, although this is in such small volume as to be hardly detectable and therefore unobjectionable, the fact that the nitric acid is functioning may be detected near the surface by the slight odor of the nitric oxide gas which is escaping from the solution.

As aforementioned, the hydrofluoric, boric, nitric acid solution may be operated at temperatures of the order of 200° F. and upwards. The loss of the boric acid through volatilization at the elevated temperatures, however, makes an operating range of the order of 160 to 190° F. preferable, a specific preferred operating temperature in this range being 170° F. It will also be understood that in operation, the solution is maintained at this temperature and such additional amounts of nitric acid and fluoride and/or borate ion must be added from time to time as necessary to maintain the desired concentration of the acid constituents.

The aforedescribed hot solutions when employed to clean and polish aluminum and its alloys by simple immersion therein produce superior results and are effective on all aluminum alloys provided the alloying constituents at the surface of the metal do not exceed the order of 5 to 6% of the alloy. The process and composition have been found to be effective with the following widely used aluminum alloys in all physical conditions and having the approximate compositions noted in percent by weight:

	Type 2024	Type 5052	Type 6061	Type 7075
Cu	3.8 to 4.9	0.1	.15 to .40	1.2 to 2.0.
Mn	0.3 to 0.9	0.1	.15	0.3.
Mg	1.2 to 1.8	2.2 to 2.8	0.8 to 1.2	2.1 to 2.9.
Cr	0.25	.15 to .35	.35	.15 to .40.
Zn	0.1	0.1	.2	5.1 to 6.1.
Fe+Si	0.5	0.45	1.1	1.2
Al	balance	balance	balance	TI 0.2, Al balance.

Referring now to the drawings, and first more particularly to FIG. 11, there is shown a tabulation of aluminum alloys in which a test sample (approximately 3 x 4 inches) for each alloy depicted was divided along the 4 inch axis to provide the designated Control and Treated specimens. By reason of this arrangement, the initial gage thickness of both specimens were substantially the same. The control and treated specimens were both subjected to a cold alkaline cleaner to remove foreign matter such as would effect the optical micrometer thickness measurements, and the treated specimens thereafter were subjected to the immersion polish and cleaner of the present invention for 10 minutes at 170° F. The reduction in gage measurements providing the minimum, maximum, and average gage readings depicted were then made and the difference noted. It will be appreciated that in each case there is either no reduction in gage, or such reduction as occurs is negligible or at the most, as in the case of 2024–T81, is of the order of less than 1.5% of the average gage of the untreated specimen. The increase in gage thickness has no known significance and may be attributable to errors in the use of the optical micrometer.

End views of the Treated and Control specimens for the 6061–T6 alloy are illustrated in FIGS. 7 and 8 respectively. Photomicrographs taken at 500 times magnification within the fields of view indicated by the circles **20** and **21** in FIGS. 7 and 8 are depicted in FIGS. 9 and 10 respectively. The photomicrographs comparatively reveal that the surface of the treated specimen is nearly flat whereas that of the control specimen is relatively rough having appreciable crests **22** and valleys **23**. Accordingly, assuming the light to be directed generally normal to the surfaces of the specimens, there is no breaking up of the incident rays of light as indicated by the generally parallel lines **24** depicted in FIG. 9 and, hence, a high degree of reflectance is obtained from the polished surface of the treated specimen. By contrast, many of the incident rays of light striking the surface of the control specimen are angularly displaced as depicted by the angular lines **25** in FIG. 10, this being due to the relatively rougher surface of the control specimen. Hence, the reflectance characteristics of the control specimen surface are substantially impaired.

The relative reflectance or gloss of aluminum alloys treated with the cleaning and polishing solution of the present invention in relation to the immersion time in minutes is disclosed in FIG. 12 wherein it will be seen that relatively higher gloss is obtained from the aluminum clad alloys 2024 and 7075 than from the unclad alloy 6061. It may also be noted that the greatest increase in gloss apparently takes place in the first 5 minutes and that little or no increase occurs after 10 minutes, this being generally the case for normal operating conditions and specifically for the conditions under which the alloys disclosed in FIG. 12 were treated, the temperature of the three-constituent acid solution employed for this purpose having been maintained at 170° F. and optimum proportions of the solution constituents employed. Hence, under optimum operating conditions, the optimum immersion time may be taken to be from 5 to 10 minutes.

By way of contrast between the two and three-constituent acid compositions of the present invention, a solution of nitric acid and fluoboric acid, the balance being water, was heated to 170° F. and a 2024 specimen immersed in the solution for seven minutes produced a maximum gloss reading of 58 on the scale depicted in FIG. 12.

It will be understood that the gloss values depicted in FIG. 12 are relative only. These measurements were made using a Gardner 60° Glossmeter equipped with a No. 0.9 B & L Filter, the Glossmeter first being calibrated through use of a polished black Carrara glass providing a standard reading of 94 on the meter. The interposition of the filter cut the reading approximately 87 gloss units to a reading of about 7 on the meter and, hence, the reading of 40 for 6061–T6 at about 4½ minutes would correspond to a true gloss reading of approximately 87 additional gloss units or 127.

The solutions of the present invention are also effective in preparing aluminum and its alloys for fusion welding such as by inset gas shielded arc welding, this being illustrated pictorially in FIGS. 1 to 6 wherein FIGS. 1 and 2 depict a pair of fusion welded joints **26** and **27** as seen on a single photomicrograph. The parts forming the welded joint in each case were 6061 alloy, the parts **28** and **29** of FIG. 1 having been cleaned by immersion in the optimum solution of the present invention and under optimum conditions as hereinbefore specified. The parts **30** and **31** comprising the welded joint of FIG. 2 were cleaned prior to welding with a prior art cleaner and etch such as that disclosed in my copending application for Process and Composition for Treating Aluminum Alloys, Serial No. 709,442, filed January 17, 1958.

The welded joints **26** and **27** were both formed by the Heliarc process and aluminum alloy welding rod 43S was used in each case, the usual puddling action being

employed. The 43S alloy has the following composition in percent by weight:

43S welding rod—	
Copper	.3
Iron	.8
Silicon	.45–6
Manganese	.05
Zinc	.1
Titanium	.2
Aluminum	Balance

The welded joint **26** depicted in FIG. 1 was made without the use of flux whereas flux was employed in forming the joint of FIG. 2 as evidenced by the darkened areas **32** due apparently to the capillary action or flow induced by the flux. Also in evidence in FIG. 2 are the relatively light areas **33** adjacent the darkened areas **32**, this being due to the wire brushing of the welded joint **27** which is essential for removal of the flux following completion of the welding operation.

FIGS. 3 and 4 depict cross-sections of the welded joints of FIGS. 1 and 2 and indicate by the circles **34** and **35** the fields of view within which the photomicrographs **36** and **37** of FIGS. 5 and 6 were taken at 25 times magnification.

By comparing the two photomicrographs **36** and **37** it may be observed that the region **38** of the welded joint as depicted in FIG. 5 is free of any evidence of porosity whereas the comparable region **39** of FIG. 6 is replete with large holes **40** which evince a high degree of porosity and consequently a welded joint of greatly reduced strength.

The cleaning and polishing solutions of the present invention are also effective as a pre-spotweld etch and are generally able to accomplish the same order of reduction of electrical surface resistance as obtained in the use of my process and composition disclosed and claimed in the aforesaid application, Serial No. 709,442 wherein the parts to be prepared for spot welding are first immersed in a nitric-chromic acid solution for three minutes, then after rinsing, immersed in an ammonium bifluoride-citric-acid solution for two minutes, and again after rinsing, immersed in the nitric-chromic acid solution for two minutes. This prior art process has the advantage of being operable at ambient temperature. However, the hot solutions of the present invention have the advantage that the same order of resistance reduction may be obtained while requiring only a single rinse following the single immersion treatment. In addition, a highly polished surface is obtained which is receptive to the application of conversion coatings and anodic films. The hot solutions are also, effective in removing these coatings and films preparatory to re-application thereof or in preparing parts for further work operations thereon. For example, a certain part may undergo the following operations:

(1) Vapor degrease involving immersion in or treatment with the vapor of trichloroethylene, ethylene dichloride or other known solvent to remove any surface oil or grease film.

(2) Clean and polish in the heated nitric-fluoric-boric immersion bath of the present invention.

(3) Alodize by application of a chemical conversion coating such as Alodine 1000 which is a commercially available transparent film.

(4) Store for indefinite periods. In the case of parts scheduled for later spotwelding, for example, the parts may be stored for upwards of 30 days without increasing the electrical surface resistance above 25 microhms.

(5) Re-work or finish. In the presumed spot welding example, this operation may be performed without removal of the Alodine 1000 and, following spotwelding, the processing of the parts may be considered to be complete and adequately protected by the conversion coating.

(6) Remove Alodine 1000 by immersion in the heated nitric-fluoric-boric bath of the present invention, this being done, for example, in the case of detail parts which require a final protective coating such as that afforded by commercially available Alodine 1200.

(7) Alodize by application of Alodine 1200.

When desired, parts formed of aluminum and its alloys such as sheet stock, extrusions, etc., which have been cleaned and polished in the heated nitric-fluoric-boric immersion bath of the present invention, may be further treated for from 3 to 5 minutes in a nitric-chromic bath as aforementioned, such a bath preferably comprising an aqueous solution of the composition:

	Percent by weight
Nitric acid (HNO_3)	15 to 25
Chromic acid (C_rO_3)	0.5 to 1.5
Water (H_2O)	Balance

wherein the optimum content of nitric acid is approximately 22 percent. It is not necessary to heat this solution since it is effective within the temperature range of 70° to 90° F. This solution dissolves any small particles of smut which may have formed on the parts while in the nitric-fluoric-boric bath and brightens the metallic surfaces without impairing the specular gloss imparted thereto in the previous cleaning and polishing treatment.

Although the present invention is directed primarily to the treatment of articles formed of aluminum and its alloys by immersion in a heated bath solution, it will be understood that the articles may effectively be cleaned and polished by brushing, spraying, or swabbing the same with the solution for the required period of time to obtain the desired gloss provided, of course, that the required temperature and proportions of the solution are maintained.

The novel principles of this invention transcend the scope of the invention as suggested or implied by the several embodiments hereinbefore described, and the invention may be embodied in other forms or carried out in other ways which have been conceived and reduced to practice during the course of this development, without departing from the spirit or essential characteristics of the invention. The embodiments disclosed herein therefore are to be considered as in all respects illustrative and not restrictive, the scope of the invention being indicated by the appended claims, and all changes which come within the meaning and range of equivalency of the claims are intended to be embraced therein.

Having thus described my invention, what I claim as new and useful and desire to secure by Letters Patent is:

1. A dry mix additive to form a hot aqueous solution containing 2.0–5.0% nitric acid for cleaning and imparting high gloss to the surfaces of aluminum and its alloys consisting of a fluo compound selected from the group consisting of water soluble alkali metal fluorides, fluosilicates and fluoborates and a boric compound selected from the group consisting of boric acid and water soluble salts thereof, said boric and fluo compounds being in amount equivalent to form in the solution about 2 to 50 parts by weight of boric acid to 1 part by weight of hydrofluoric acid calculated as ammonium bifluoride, said fluo compound being in amount such that the hydrofluoric acid calculated as ammonium bifluoride has a volume to weight ratio of about 10 to 1 between the nitric acid and ammonium bifluoride.

2. An addition agent to be added to water to form a hot aqueous acid bath for cleaning and polishing aluminum and its alloys comprising a concentrated nitric-fluoric-boric acid composition providing the equivalent of 2.0–5.0 mls. of nitric acid, 0.15–0.35 gram of hydrofluoric acid, and 1.0–10.0 grams of boric acid in 100 mls. of aqueous solution.

3. A liquid concentrate to be added to water in the preparation of a hot aqueous solution for imparting a high gloss to articles of aluminum and its alloys immersed in said solution and consisting of water in amount providing upwards of 10.0% of the ultimate solution,

nitric acid in amount to form about 2.0–5.0% of the aqueous solution, a fluo compound selected from the group consisting of hydrofluoric, fluoboric, and fluosilicic acids and water soluble fluorides, fluosilicates, and fluoborates, said fluo compound being in amount equivalent to form about 0.15–0.35 gram hydrofluoric acid per 100 mls. of aqueous solution, and a boric compound selected from the group consisting of boric acid and water soluble salts thereof, said boric compound being in amount equivalent to form about 1.0–10.0 grams of boric acid per 100 mls. of aqueous solution.

4. A hot aqueous solution for chemically cleaning and polishing articles formed of a metal consisting principally of aluminum and formed by the addition to water of 2.0–5.0 mls. of nitric acid per 100 mls. of aqueous solution, 1.0–10.0 grams of boric acid per 100 mls. of aqueous solution, and 0.2–0.5 gram of ammonium bifluoride per 100 mls. of aqueous solution.

5. A hot aqueous solution for chemically polishing articles formed of aluminum and its alloys consisting of 2.0–5.0 mls. of nitric acid per 100 mls. of aqueous solution, 1.0–10.0 grams of boric acid per 100 mls. of aqueous solution, and 0.15–0.35 gram of hydrofluoric acid per 100 mls. of aqueous solution.

6. A hot aqueous solution for cleaning and polishing articles formed of aluminum and its alloys consisting of 2.0–5.0 mls. of nitric acid per 100 mls. of aqueous solution, 1.0–10.0 grams of boric acid per 100 mls. of aqueous solution, and 0.55–1.25 grams of fluosilicic acid per 100 mls. of aqueous solution.

7. An aqueous solution for chemically cleaning and polishing articles formed of aluminum and its alloys and consisting of about 2–5% of nitric acid and of fluoboric and boric acids in amounts equivalent to .15 to .35 gram hydrofluoric acid and 1.0 to 10.0 grams boric acid in 100 mls. of aqueous solution.

8. The process of chemically polishing the surfaces of articles formed from a metal consisting principally of aluminum which comprises the steps of forming an aqueous solution of from 2.0–5.0 mls. of nitric acid per 100 mls. of aqueous solution, 1.0–10.0 grams of boric acid per 100 mls. of aqueous solution, and 0.2–0.5 gram of ammonium bifluoride per 100 mls. of aqueous solution, maintaining the temperature of said aqueous solution between 170°–190° F., and immersing the articles to be polished in said solution for a period of from 5 to 20 minutes.

9. The process of treating aluminum and its alloys to clean and impart high gloss to the surfaces of articles formed therefrom which comprises the steps of immersing said articles in an aqueous acidic solution formed essentially of water, about 2.0–5.0 mls. of nitric acid per 100 mls. of aqueous solution, a boric compound selected from the group consisting of boric acid and water soluble salts thereof and in an amount equivalent to form about 1.0–10.0 grams of boric acid per 100 mls. of aqueous solution, and a fluo compound selected from the group consisting of hydrofluoric acid, fluoboric acid, fluosilicic acid, and water soluble fluorides, fluosilicates and fluoborates, said fluo compound being in amount equivalent to form about 0.15–0.35 gram of hydrofluoric acid per 100 mls. of said aqueous solution, and wherein the treatment is conducted with said aqueous solution at a temperature of about 160°–200° F. for from about 5 to 20 minutes.

10. A process for cleaning an article composed of an aluminum-rich alloy which comprises the steps of subjecting the article to the action of a heated aqueous solution consisting of from 2.0–5.0 mls. of nitric acid per 100 mls. of said aqueous solution, 1.0–10.0 grams of boric acid per 100 mls. of said aqueous solution, and 0.15–0.35 gram of hydrofluoric acid per 100 mls. of said aqueous solution, rinsing the article with water, and thereafter subjecting the article to the action of a solution consisting essentially of about 22% nitric acid, 0.5% chromic acid, 77.5% water by weight followed by rinsing in water and drying.

11. A process for cleaning an article composed of an aluminum-rich alloy which comprises the steps of subjecting the article to the action of a heated solution consisting essentially of water, nitric acid in about 2.0–5.0% by volume of said solution, and fluoboric and boric acids equivalent to about .15 to .35 gram hydrofluoric acid and about 1.0 to 10.0 grams of boric acid per 100 mls. of said solution, rinsing with water, and thereafter treating said article with a solution consisting essentially of about 22% nitric acid, 0.5% chromic acid, 77.5% water by weight.

12. The process for cleaning and preparing articles composed of an aluminum-rich alloy for electrical resistance or fusion welding which comprises the steps of forming a solution composed of 2.0–5.0 mls. of nitric acid per 100 mls. of solution, 1.0–10.0 grams of boric acid per 100 mls. of solution, and 0.2–0.5 gram of ammonium bifluoride per 100 mls. of solution, maintaining the temperature of the solution between 160°–190° F., immersing said articles in the solution for a period of from 5 to 20 minutes, rinsing the articles in water, and thereafter immersing the articles in a non-etching nitric-chromic acid bath consisting essentially of about 22% nitric acid, 0.5% chromic acid, 77.5% water by weight, followed by rinsing in water and drying.

13. The process of removing chemical conversion and anodic films from the surfaces of articles formed principally of aluminum comprising the steps of forming an aqueous solution of about 2.0–5.0 mls. of nitric acid, 1.0–10.0 grams of boric acid, and 0.2–0.5 gram of ammonium bifluoride dissolved in 100 mls. of said aqueous solution, maintaining the temperature of the solution between 170°–190° F., immersing said articles in said aqueous solution for a period of from 5 to 20 minutes, rinsing said articles with water following removal from said solution, and drying said articles following rinsing.

14. A liquid concentrate to be added to water in the preparation of a hot aqueous solution for imparting a high gloss to articles of aluminum and its alloys immersed in said solution and consisting of the following percentages of ultimate solution by weight:

	Percent
HF (calculated as $NH_4F.HF$)	.2 to .5
H_3BO_3	1.0 to 10.0
HNO_3	12.0 to 25.0
	(16 to 20% acid)

15. A dry mix additive to form a hot aqueous solution including 2.0–5.0 percent nitric acid for cleaning and imparting high gloss to the surfaces of aluminum and its alloys and comprising a fluoboric compound selected from a group consisting of water soluble fluoborates in amount equivalent to 0.15–0.35 gram of hydrofluoric acid per 100 mls. of aqueous solution, and a boric compound selected from the group consisting of boric acid and water soluble salts thereof, said fluoboric and boric compounds being in amounts equivalent to form in the solution about 2 to 50 parts by weight of boric acid to 1 part by weight of hydrofluoric acid calculated as ammonium bifluoride.

16. A dry mix additive to form a hot aqueous solution including 2.0–5.0 percent nitric acid for cleaning and imparting high gloss to the surfaces of aluminum and its alloys and comprising an alkali metal fluoride calculated as ammonium bifluoride and a boric compound from the group including boric acid and its salts and calculated as boric acid, said fluoride and boric compound being in the ratio of 1 part by weight ammonium bifluoride to from 2 to 50 parts by weight of boric acid, said fluoride being in amount sufficient to provide from 0.15–0.35 gram of hydrofluoric acid in the ultimate solution.

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