This invention relates to the brightening of aluminum and aluminum alloys. More particularly, the invention relates to a composition and method for chemically brightening aluminum and aluminum alloy surfaces and additionally to a method for replenishing the brightening composition. Specifically, the invention is directed to improved acid-fluoride type brightening solutions wherein complex fluorides are advantageous utilized.

Although aluminum is ordinarily considered a bright metal, it often presents a dull or matte-like finish due to the oxide films inevitably formed on its surfaces during processing. In addition, wrought surfaces exhibit fabrication marks, e.g., roll marks usually extending parallel to the rolling direction. Such fabrication marks greatly influence the light reflecting characteristics of the surfaces. Many aluminum and aluminum alloy products are fabricated from mill finished sheet or other wrought materials having such a characteristic dull and marked appearance, which leads to a demand by fabricators for means to impart to the metal surfaces a bright, lustrous finish having a relatively high specular reflectance.

Specular reflectance of a bare metal surface is a measure of the smoothness or rather flatness of the surface, whereas total reflectance is a property of the material or composition of the surface, and is of little value in indicating flatness. However, specular reflectance may provide a useful measure to be compared by reference to the measurement of the quantity. A light beam is projected on the surface at a given angle (e.g., 60°) to the apparent plane of the surface. Part or all of the incident light is reflected by the surface to a photocell located so as to receive all of the light reflected by elements of the surface that make the given angle (e.g., 60°) with the direction of the incident beam. Irregularities in the surface do not reflect light in the direction of the photocell, and thus the more irregular the surface the lower is the portion of total incident light received by the photocell. The photocell is connected to a voltmeter which directly measures the percentage of incident light reflected. Thus, the specular reflectance of the surface may be measured by comparison with a standard assumed to be a perfect reflector, e.g., a plate glass mirror, by adjusting the meter reading to 100% using the standard. For measurement of relative increments or gains in specular reflectance (hereinafter at times referred to as "gains in SR") for purposes of brevity, no assumption is involved and the plate glass mirror is merely a convenient base or standard of specular reflectance.

Successful brightening of aluminum and its alloys involves the necessity of obtaining relatively large or significant, and preferably maximum, gains in specular reflectance on the treated material. However, in chemical brightening, it has been determined that gains in specular reflectance often cannot be produced without the metal exhibiting a visibly etched or pitted condition or presenting a haziness which markedly detracts from the appearance desired. "Brightened" stock of this character is generally unsuitable for the requirements of a visibly smooth, bright surface of high specular reflectance.

One widely used method of polishing aluminum and its alloys is by mechanical buffing with a suitable abrasive. However, this mechanical polishing although productive of good results in terms of bright finish of high specularity is expensive and is not easily adaptable to articles having intricate shapes and inaccessible surfaces. Other known methods such as electropolishing and electro-brightening involve subjecting the aluminum article to an electrolytic treatment in an appropriate solution and produce a very desirable finish of high specular reflectance. However, the methods are both slow and prohibitive in cost for many end uses of the metal.

Chemical brightening of aluminum and its alloys has previously been accomplished, in some measure, by using a solution of nitric and hydrofluoric acids; however, consistently reproducible results in terms of optical gains in specular reflectance of the surface while avoiding either gross or fine etching, pitting, or haziness have not been obtainable with this two component system following the teachings and practices of the prior art. As one indicative instance, it has been determined that a given high purity aluminum, specifically 99.5% Al, exhibits a large loss in specular reflectance when treated in a nitric acid—"simple" fluoride solution even though previously determined optimum concentrations of fluoride and nitric acid were employed. By "simple" fluoride is meant those fluorides wherein fluoride exists in uncomplexed form in the anion, for example, hydrofluoric acid and its salts such as ammonium and sodium fluoride and acid fluorides. It has been found, however, that acceptable gains in specular reflectance with simultaneous avoidance of etching, pitting, haziness, or deposition of objectionable black coating on the metal could be consistently obtained by a simple fluoride-nitric acid solution wherein the absolute concentrations and the relative proportions of these two components are maintained within certain critical limits, and the two component solution is modified by the presence therein of cations of a metal electropositive to hydrogen, whether derived in the first instance from the metal being treated, or by positive addition to the solution.

The present invention is particularly directed to an improved composition and method for the chemical brightening of aluminum and aluminum base alloys wherein a soluble complex fluoride is employed as the effective fluoride ion producing constituent and to a method for replenishing the brightening composition.

It has been found that the complex fluoride constituent increases the efficiency in brightening power of the solution, as compared to the simple fluoride type, in terms of maintaining higher gains in specular reflectance as the area of aluminum surface treated, per given volume of solution, increases.

The term "complex" fluoride as used in the specification and claims is intended to mean any more or less stable soluble fluoride wherein the fluoride of the anion is complexed with a metal or metalloid.

Accordingly, it is a primary object of the invention to provide a complex fluoride-nitric acid brightening composition whereby chemical brightening to produce a desirable specular reflectance may be consistently accomplished on aluminum and aluminum alloys without any marrowing of the appearance of the surface by pitting, etching or haziness. This mars the surface and detracts from the general appearance,
thus rendering the treated metal more or less unacceptable for many decorative applications. Therefore, another object of the invention is to eliminate this disadvantageous combination of results often obtained with the prior art hydrofluoric acid-nitric acid brightening solutions by provision of an improved composition and process for chemically brightening of aluminum and aluminum alloys.

Another object of the invention is to provide an improved chemical brightening composition of the complex fluoride-nitric acid type which is characterized by its economy in use, being a relatively dilute solution with low drag-out losses, and capable of producing surfaces of high specular reflectance combined with a clear, visually smooth appearance.

A still further object of the invention is to provide a novel replenishing method for maintaining the brightening effectiveness of the improved chemical brightening composition of this invention.

The invention also provides a process for chemical brightening of aluminum and its alloys to produce surfaces of high specular reflectance and devoid of etching, pitting, haziness or the deposition of an objectionable black coating having adverse effects on the treated metal appearance even though said coating is subsequently removed.

Other objects and advantages of the present invention will become apparent from the detailed description set forth below.

It was discovered that the production of acceptable gains in specular reflectance without etching, pitting or haziness is consistently obtained with a composition comprising an aqueous solution containing complex fluoride ions and nitric acid in certain well-defined proportions and ranges of concentrations, and a small but effective concentration or amount of a dissolved metal electropositive to hydrogen.

The term "electropositive" as used in the specification and appended claims is based upon the definition and values of single electrode potentials on the hydrogen scale given in the "Chemical Engineers' Handbook," John H. Perry, Editor-in-Chief, 2nd edition, eighth impression (1973) (McGraw-Hill Book Company), pages 2746 to 2748, inclusive. It is there indicated that "in solutions containing their own ions, noble metals (e.g. with electrolytic solution pressures lower than that of hydrogen) acquire a positive potential, while base metals (e.g. with electrolytic solution pressures greater than that of hydrogen) acquire a negative potential."

The presence of effective amounts of dissolved metal electropositive to hydrogen as a constituent of the aqueous brightening solution may readily be accomplished by the addition of a soluble salt of the selected metal or the dissolved metal may be introduced into the solution from the aluminum or aluminum alloy upon exposure thereof to the complex fluoride-nitric acid solution, when the aluminum or alloy contains the electropositive metal in sufficient quantity. In any event, the presence of such dissolved metal is deemed necessary to obtain the desired brightening without etching.

Copper is the preferred electropositive metal from the standpoint of cost while producing optimum results, together with the fact that in many cases this metal is present in the aluminum or aluminum alloy as a positively added alloying constituent or as a residual.

It has been determined that in general the desired results of brightening without etching are obtained with a concentration of dissolved copper, i.e. copper ions, not substantially less than about 0.001 gram per liter (1.6 x 10⁻⁴ molar) or about 0.004 gram per liter expressed as Cu(NO₃)₂.3H₂O. Other suitable electropositive metals may be employed when present in minimum concentrations approximately equivalent to that above set forth for copper. For example, silver and other metals electropositive to hydrogen whose nitrate salts are sufficiently soluble (i.e. adequate solubilities in nitric acid) are productive of satisfactory results.

Although it has been indicated that the aluminum or aluminum alloy alone may suffice for the required concentration of the electropositive metal, the invention includes the positive addition of such metal to the solution in solube form regardless of the composition of the aluminum being treated. On the other hand, consistently good results are obtained without positive additions of copper as copper is present in the aluminum or aluminum alloy in amount at least corresponding to the lower portion of the range normally present as a residual in commercially pure aluminum, for example 0.05%. In tests recorded below, excellent results were produced with 28-% H₂ aluminum alloy containing only 0.1% copper by weight. However, optimum gains in the specular reflectance are observed upon increasing the copper ion concentration up to approximately 0.01 to 0.02 gram per liter (about 0.5 to 0.8 gram per liter expressed as Cu(NO₃)₂.3H₂O), above which no significant improvement is noted.

The copper content of the solution, however, is not limited to the above-mentioned concentration, and much higher amounts may be used without any adverse effects. For example, about 2 grams per liter (about 8 grams per liter of Cu(NO₃)₂.3H₂O as a positive addition), which is one hundred times the above-mentioned figure, has been used with excellent results. Also the aluminum alloy may contain copper in amount producing much higher dissolved copper concentrations without adverse effect. In regard to positive additions, however, it serves no useful purpose, and is uneconomical to increase the dissolved copper concentration above about 0.1 or 0.2 gram per liter. The foregoing statements also apply to equivalent amounts of other positively added electropositive metals.

The suitable form for positive addition of the electropositive metal is any soluble salt obtainable with the solution, for example, one wherein the anion will not form a precipitate with other solution constituents, and will not adversely affect brightening. In order to simplify the solution composition, it is preferred to add the copper or other electropositive metal as a nitrate. It may, however, be added as a fluoride, provided that the total effective free fluoride ion concentrations and proportions relative to nitric acid are maintained within the limits defined below.

The invention further provides for certain concentrations of nitric acid, both absolute and relative to the complex fluoride which should be rather closely observed to obtain the desired results set forth above to the greatest extent possible. The nitric acid is the primary source of the hydrogen ions necessary for the oxidation (dissolution) of the aluminum which must occur to produce leveling of the surface and the consequent gains in specular reflectance. This reaction may be illustrated as follows:

\[
2\text{Al} + 6\text{H}^+ = 2\text{Al}^3+ + 3\text{H}_2\text{O}
\]

It has been found that the nitric acid content of the brightening solution should be from at least about 1.3 cc. per liter up to about 100 cc. per liter HNO₃ (70% by weight). Within this range, which properly correlates with the concentration of complex fluoride, as set forth below, substantial gains in specular reflectance are obtained without etching or pitting. The preferred range for nitric acid concentrations is from about 1.5 to about 53 cc. per liter HNO₃ (70% by weight). Within this range, optimum specular reflectance is obtained and sugar ratios of HNO₃ to complex fluoride are observed and haziness as well as etching and pitting is avoided.

The complex fluoride component of the brightening solution may be any soluble complex fluoride which does not produce an objectionable precipitate with the aluminum ion introduced into the solution by metal dissolution as indicated by the foregoing equation. It is preferred, however, to employ fluoboric acid or any fluoroborate soluble in nitric acid and whose cations are not
2,719,079

deleterious to the brightening bath as the source of complex fluoride ions, although other complex fluorides, such as fluosilicic acid, fluorotitanic acid and salts thereof soluble in nitric acid and whose cations are not deleterious to the brightening bath in equivalent amounts in respect to effective fluoride concentration, are preferable to produce excellent brightening without marring of the surface appearance by etching, pitting or haziness. In the case of fluosilicic acid, however, a precipitate of silica is formed due to hydrolysis. Although this precipitate does not affect the efficiency of the solution in respect to specular gain or brightening, it may interfere with the efficiency of the process by requiring a mechanical operation, such as filtration of the solution. The fluoroboric acid may be added as such to the bath, or as separate additions of boric acid and hydrofluoric acid in stoichiometric amounts to form fluoroboric acid. Slight excesses of hydrofluoric acid or boric acid over stoichiometric quantities may be tolerated provided the proper total fluoride concentrations and fluoride-nitric acid ratios are maintained. Other boron and fluorine containing substances may also be used to form the fluoroboric acid, provided that deleterious ions are not introduced in the bath. Alkali metal salts of boron, such as sodium tetraborate and sodium perborate, or ammonium borate may be added to the bath in addition to alkali metal fluorides or bifuorides, or ammonium fluorides and bifluorides, to produce fluoroboric acid. Although the alkali metal salts are usable with good brightening, their use is not preferable not to employ them because of the insolubility of the aluminum complex salts that they may form in the bath. Effective brightening results can also be obtained, as before stated, by the use of any fluoroborate soluble in nitric acid and whose cations are not deleterious to the brightening solution. An example of these fluoroborates is ammonium fluoroborate. The alkali metal fluoroborates may also be employed with good results; however, they may form insoluble aluminum complex salts in the bath.

It is believed that the complex fluorides in the solution are formed by the reaction of free fluoride ions which latter are necessary for the dissolution of the oxide film on the aluminum surface, and that the complex ion dissociates as the free fluoride ion is used in reacting with the aluminum oxide. Thus, the required concentration of free fluoride ions is maintained while excessive initial fluoride ion concentration or numerous replenishment additions of fluoride ion source may be avoided. As the metal aluminum on the surface is dissolved by the hydrogen ion after removal of the oxide film, some of the free fluoride ion is apparently rendered ineffective probably by complexing with the aluminum ion. However, the invention is not to be considered as limited to the foregoing or any other theory of mechanism.

Due to the fact that the relative stabilities of the complex fluorides at working temperatures are unknown, and therefore the effective fluoride ion concentration cannot be directly expressed, the limits of amounts of fluoride are best defined in terms of the complex fluoride ion concentration corresponding to that equivalent in fluoride to a stated amount of fluoroboric acid added in preparing the solution. The effective concentrations of complex fluoride ion in terms of fluoroboric acid are from about 0.3 cc. to about 26 cc. per liter (45% HBF₄) when maintained in the proper ratio with respect to the amount of nitric acid employed. The preferred concentrations for highest specular reflectance without haziness, as well as avoidance of pitting or etching, are from about 0.3 cc. to 24 cc./l. (45% HBF₄).

As indicated above, it was found that not only must the above concentrations of nitric acid and complex fluoride be observed, but the proper relative proportions of HNO₃ to complex fluoride must also be observed to obtain high specularity with no etching, pitting or haziness. In addition, it was determined that in certain solutions to which no positive copper was added, a black coating was deposited on the aluminum surface. Although readily removed in a subsequent nitric acid dip, the presence of the black coating during brightening prevented attainment of specular reflectance gains of the order possible with some of the complex fluoride concentration in which the black coating formation was avoided. In addition, test panels, on which the coating appeared, exhibited more haziness. Control of the complex fluoride to nitric acid ratios and/or positive additions of copper nitrate prevented this objectionable black coating.

In those instances wherein the complex fluoride to nitric acid ratio was sufficiently high to cause the formation of the objectionable black coating, addition of nitric acid while maintaining the complex fluoride concentration constant prevented the coating. In other words, lowering of the complex fluoride to nitric acid ratio to values within the limits set forth below effectively obviated the black coating problem. In addition, the black coating is also effectively eliminated by positive addition of copper as nitrate when operating at a complex fluoride to nitric acid ratio representing the maximum permissible while avoiding etching and/or haziness.

In regard to copper deposition (or other metal electro-positive to hydrogen e. g. silver), which occurs during the brightening operation, it may be visible or not discernible depending upon the concentration of the dissolved metal. In any event, it is readily removed by a subsequent nitric acid dip, even at room temperature. However, if the work is to be anodized in a conventional electrolyte, such as sulfuric acid, immediately after brightening the use of the nitric acid dip is obviated since the deposit is readily removed during anodizing without affecting the anodic coating formation.

The critical relative proportions of complex fluoride to nitric acid may be best defined by reference to the attached figure which represents a plot of various concentrations of fluoroboric acid and nitric acid, expressed in cubic centimeters of 45% HBF₄ per liter and cubic centimeters of 70% HNO₃ per liter, respectively. As indicated on the figure, aluminum 25-HF₄ panels treated in solutions whose compositions fell above the line R, S, T, U, V exhibited decreases in specular reflectance with etching. Panels treated in solutions falling in the area below the line R, S, T, U, V, but outside of the closed areas exhibited gains in specular reflectance, but were visibly etched.

The aqueous acid brightening solutions, which produce substantial increases in specular reflectance without pitting or etching are those which contain fluoride ions and nitric acid equivalent to the relative concentrations of fluoroboric acid in cubic centimeters of 45% HBF₄ per liter and nitric acid in cubic centimeters per liter (70% HNO₃ by weight) which are present within or include the area defined approximately in the accompanying diagram by the solid lines J, J, K, K, L, M, MN, NO, OP, PQ and QL. Some haziness is noticed in certain instances on panels treated by solutions lying in this range, particularly at the higher nitric and complex fluoride concentrations. Optimum results in terms of highest gain in specular reflectance and freedom from haziness as well as etching or pitting are obtained by solutions whose constituent concentrations are within the area defined by solid lines AB, BC, CD, DE, EF, FG, GH, and HA.

Accordingly, the diagram of the drawing accurately and definitely establishes the approximate limits of complex fluoride and nitric acid concentrations and their relative proportions for consistently reproducing the high gains in specular reflectance without etching, pitting, or haziness in accordance with the invention. The diagram further contains contour lines (shown in dashed lines) which are drawn through those points in the areas, above-defined, corresponding to fluoroboric acid-nitric acid solutions which produce approximately equal gains in specular reflectance measured parallel to the rolling direction, the values of
such gains being indicated for each contour line on the diagram.

The data for the diagram were obtained by treating test panels of 2S-H12 aluminum alloy having a copper content of 0.1% with 0.45% iron and 0.1% silicon by weight, each panel being 4 x 6 x 0.084 inches. The panels were suspended in the various solutions, having the compositions indicated in Table I below, by means of an aluminum wire hook inserted through a hole punched in the center of one end of the panels. The wire hook in turn was suspended from a shaft in a freely turning bearing. Mechanical agitation of the solution caused the panel to revolve with the production of more evenly brightened work than in the case of stationary panels.

The time of treatment of the panels was five minutes, after which they were dipped in nitric acid, water rinsed and dried. The operating temperature of the bath was from 200 to 210° F, maintained by a hot plate or burner. Specular reflectance values were obtained on the mill finish panels and again on the panels after treatment by means of a Henry A. Gardner 60° glossmeter. The meter reading was adjusted to 100 with the instrument operating on a plate glass mirror. Then the specular reflectance (S. R.) of the panels before and after treatment was measured and read directly from the meter at a value under 100, the chosen S. R. for the standard. The gain in specular reflectance determined by difference is represented on the diagram by the "contour" lines.

In the test solutions from which the diagram was prepared, 0.26 gram of copper nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>3H<sub>2</sub>O) per liter of solution were added to ensure the presence of sufficient copper ion to bring about the increased gains in specular reflectance that have been found to be characteristic of a solution containing copper.

The ranges of fluoroboric and nitric acid defined by the accompanying diagram were determined by means of the above-described specular reflectance measurements, and by visual observation to determine the presence or absence of etching and/or haziness irrespective of measured gains in S. R. The plotted coordinates for the lines on the diagrams are set forth below in terms of solution composition.

TABLE I
Solution composition

<table>
<thead>
<tr>
<th>Line in</th>
<th>Area J, JK, KL, LM, MN, NO, OP, PQ, RI</th>
<th>Area AB, BC, CD, DE, HI, MN, OP, QR, RA</th>
</tr>
</thead>
<tbody>
<tr>
<td>450 HBF&lt;sub&gt;4&lt;/sub&gt; m/l.</td>
<td>70% HNO&lt;sub&gt;3&lt;/sub&gt; m/l.</td>
<td>450 HBF&lt;sub&gt;4&lt;/sub&gt; m/l.</td>
</tr>
<tr>
<td>20.0</td>
<td>1.3</td>
<td>11.0</td>
</tr>
<tr>
<td>40.0</td>
<td>13.0</td>
<td>15.0</td>
</tr>
<tr>
<td>50.0</td>
<td>21.0</td>
<td>7.9</td>
</tr>
<tr>
<td>60.0</td>
<td>31.0</td>
<td>7.9</td>
</tr>
<tr>
<td>70.0</td>
<td>40.0</td>
<td>13.0</td>
</tr>
<tr>
<td>80.0</td>
<td>50.0</td>
<td>21.0</td>
</tr>
<tr>
<td>90.0</td>
<td>60.0</td>
<td>21.0</td>
</tr>
<tr>
<td>100.0</td>
<td>70.0</td>
<td>21.0</td>
</tr>
<tr>
<td>110.0</td>
<td>80.0</td>
<td>21.0</td>
</tr>
<tr>
<td>120.0</td>
<td>90.0</td>
<td>21.0</td>
</tr>
<tr>
<td>130.0</td>
<td>100.0</td>
<td>21.0</td>
</tr>
<tr>
<td>140.0</td>
<td>110.0</td>
<td>21.0</td>
</tr>
</tbody>
</table>

A number of experiments were made to determine the effect of the presence of copper, in either the alloy or the solution, on the brightness efficiency of the baths. It was found that small additions of copper salt (on the order of 0.02 g./l. Cu(NO<sub>3</sub>)<sub>2</sub>3H<sub>2</sub>O which corresponds to about .02 g./l. of copper) to the fluoroboric-acid nitric acid bath produced optimum gains of S. R. for 2S-H12 aluminum alloy (containing 0.10% copper), and that amounts of copper exceeding this value produced no significant additional gains. However, substantially larger amounts do not diminish the specular reflectance gains on the metal surface, and amounts slightly larger than that required for optimum specular reflectance gains assure the presence of sufficient copper ion in the bath.

A test on the efficiency with which a solution containing 4.8 cc. of fluoroboric acid (45% HBF<sub>4</sub>) and 30 cc. of nitric acid (70% HNO<sub>3</sub>) per liter of solution improves the specular reflectance of high purity 99.8% (0.002% copper) aluminum alloy was made. The test that was found to give excellent results on 2S aluminum alloy having 0.1% copper content, when no copper salts are added to the solutions. The first 99.8% Al test panel (4 x 0.084 inches) showed a loss of 22 points (parallel to the rolling direction) in specular reflectance and an etch. The next panel dipped was one of 28 x 12 containing 0.10% copper. The following 99.8% panel showed a gain in specular reflectance of 11 points. Thus the small amount of copper that was introduced into the solution by dissolving of part of the 2S panel was sufficient to significantly change the effect of the solution on the 99.8% panel.

The copper dissolved from three panels of 2S was sufficient to bring the specular reflectance gains for the 99.8% panels up to 25 points. The gain of 25 points approached that produced on 99.8% aluminum panels by a solvent containing approximately 0.04 g./l. Cu(NO<sub>3</sub>)<sub>2</sub>3H<sub>2</sub>O per liter to the aqueous solution.

As above indicated, high purity aluminum alloy (99.8%) was also brightened in fluoroboric-acid-nitric acid solutions to which the copper was positively added as copper nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>3H<sub>2</sub>O). A series of panels (4 x 6 x 0.084 inches) were treated in solutions containing 5.3 cc./l. 45% HBF<sub>4</sub> and 32 cc./l. 70% HNO<sub>3</sub> with various concentrations of the copper salt. It was found that the additions of the soluble copper salt brought about marked improvement in the specular reflectance gains of the panels. Concentrations of the salt of approximately 0.03 g./l. Cu(NO<sub>3</sub>)<sub>2</sub>3H<sub>2</sub>O gave gains in specular reflectivity of about 15 points, while 0.05 g./l. of the salt gave gains on the order of 32 points. Concentrations of the copper salt greater than 0.05 g./l. per liter caused no improvement.

In regard to brightening of buffed work, the solu-
tions of the present invention are particularly advanta-
geous in that the metal surface is favorably conditioned in such a manner that streaking and cloudiness frequently occurring on buffed work during subsequent anodizing is obviated. Also, the very dilute solutions within the pre-
ferrings of the invention above are advanta-
g agoeously productive of excellent results on metal surfaces which have been previously buffed.

The process as generally employed is to prepare the aqueous solution with the indicated quantities of con-
stituents, with or without copper salt addition, and heat the solution to the desired operating temperature, then immerse the metal for the desired time, after which the treated metal is given a nitric acid dip, unless it is to be immediately anodized. It is then water rinsed in either event and is suitably dried. Before immersion the work is degreased or cleaned in conventional inhibited alkaline cleaners or vapor degreasers. The bright dip bath or solution is also usually agitated to produce more uniform results. Air or mechanical agitation is suitable, the latter being preferred so as not to cool the heated solution.

The process may be operated on a continuous or semi-
continuous basis, or it may be conducted as a batch process. During operation of the process the compo-
ents, that is, fluoroboric acid and nitric acid are gradually depleted and calculated additions of the compounds sup-
plying the ions are periodically added to maintain proper concentrations. Where copper is positively added, it is also replenished by small additions of soluble salts.

The maintenance additions should be carefully con-
trolled to ensure continued optimum brightening results. In using the brightening process as a pre-treatment pro-
cess for anodizing or other processes in which the increase in specular reflectance is of secondary importance the maintenance additions, particularly the complex fluoride addition, need not be so carefully controlled.

The chemical brightening treatment may be conducted in any suitable tank or other apparatus provided with a lining impervious to the corrosive action of the nitric acid and complex fluoride ions at the operating tempera-
tures. Stainless steel of certain specifications is very satisfactory for this purpose. A particularly useful lining is Karbate—a treated carbon product resistant to attack by all chemicals except those which are highly oxidizing. Karbate is manufactured in molded slabs, blocks or other shapes.

The heating of the solution may be accomplished by the use of Karbate tubes or heat exchangers, or, if electrical heating is desired, Karbate-shielded immersion heaters may be employed.

The chemical brightening compositions of the present invention advantageously provide an economical means for obtaining desired decorative finishes on aluminum and aluminum alloy surfaces which in appearance are bright, visibly smooth and clear, and have specular reflectances nearly comparable to those obtainable with the much more expensive electropolishing. The solutions are well adapted for use on mill finish stock or previously buffed metal where highest specularity is the objective.

The highly dilute nature of the solutions incurs very low drag-out losses and low maintenance costs, while productive of consistently reproducible results when the solution compositions are maintained approximately within the concentrations and relative proportions of fluoroboric acid and nitric acid set forth above, and with the presence of the very small concentration of electro-
positive metal ion.

Various modifications of processing conditions and in solution compositions permitting the substantial realiza-
tion of the results herein set forth are deemed within the spirit of the invention and the scope of the appended claims.

What is claimed is:

1. A composition for the chemical brightening of aluminum and aluminum alloys comprising an aqueous acid solution containing complex fluoride ions in concentra-
tions equivalent in fluoride to the concentrations of fluoroboric acid and nitric acid in concentrations equivalent to the nitric acid included in the area defined in the accompanying diagram by the solid lines II, JK, KL, LM, MN, NO, OP, PQ and QI, and also containing not substantially less than about 0.001 gram per liter of copper.

2. A composition according to claim 1 in which the complex fluoride is selected from the group consisting of fluoborate, fluotitanate and fluosilicate.

3. A composition according to claim 1 in which the concentrations of fluoroboric acid and nitric acid include the area defined approximately in the accompanying diagram by the solid lines AB, BC, CD, DE, EF, FG, GH, and HA.

4. A composition according to claim 2 in which the complex fluoride is selected from the group consisting of fluoborate, fluotitanate and fluosilicate.

5. A composition for the chemical brightening of aluminum and aluminum alloys comprising an aqueous acid solution containing hydrogen, nitrate and fluoride ions derived from complex fluoride ions in concentrations equivalent in fluoride to those produced by fluoroboric acid and nitric acid in concentrations equivalent to the nitric acid included in the area defined approximately in the accompanying diagram by the solid lines II, JK, KL, LM, MN, NO, OP, PQ and QI, and also containing a metal electropositive to hydrogen in amounts equivalent to not substantially less than about 0.001 gram per liter of copper.

6. A composition according to claim 5 in which the concentrations of fluoroboric acid and nitric acid include the area defined approximately in the accompanying diagram by the solid lines AB, BC, CD, DE, EF, FG, GH and HA.

7. A composition for the chemical brightening of alu-
minum and aluminum alloys having a copper content not substantially less than about 0.1% by weight comprising a dilute aqueous acid solution consisting essentially of complex fluoride ions in concentrations equivalent in fluo-
ride to the concentrations of fluoroboric acid and nitric acid in concentrations equivalent to the nitric acid included within the area defined approximately in the accompanying diagram by the solid lines II, JK, KL, LM, MN, NO, OP, PQ and QI, balance substantially all water.

8. A composition according to claim 7 in which the relative concentrations of fluoroboric acid and nitric acid lie within the area defined approximately in the accompanying diagram by the solid lines AB, BC, CD, DE, EF, FG, GH, and HA.

9. A composition for the chemical brightening of alu-
minum and aluminum alloys containing less than about 0.05% copper comprising a dilute aqueous acid solution consisting essentially of complex fluoride ions in concentra-
tions equivalent in fluoride to the relative concentra-
tions of fluoroboric acid and nitric acid equivalent to the nitric acid lying within the area defined approximately in the accompanying diagram by the solid lines II, JK, KL, LM, MN, NO, OP, PQ and QI, and as a third positively added constituent, ions of a metal electropositive to hydro-
gen in concentration equivalent to the copper ion concen-
tration produced by addition of not substantially less than about 0.05 gram per liter Cu(NO₃)₂·3H₂O, balance substantially all water.

10. A composition for the chemical brightening of alu-
minum and aluminum alloys comprising an aqueous acid solution consisting essentially of nitric acid, and complex fluoride ions in concentrations equivalent in fluoride to the relative concentrations of fluoroboric acid and nitric acid lying within the area defined approximately in the accom-
paigning diagram by the solid lines II, JK, KL, LM, MN, NO, OP, PQ and QI, and also containing copper ions in amount equivalent to that produced by addition of not substantially less than about 0.05 gram per liter Cu(NO₃)₂·3H₂O, balance substantially all water.
11. A composition according to claim 10 wherein the complex fluoride is selected from the group consisting of fluoborate, fluorotitanate and fluosilicate.

12. A composition for the chemical brightening of aluminum and aluminum alloys comprising an aqueous acid solution containing nitric acid and fluoborate ions in concentrations equivalent to the relative concentrations lying within the area defined approximately in the accompanying diagram by the solid lines II, JK, KL, LM, MN, NO, OP, PQ and QI, said solution also containing a metal electropositive to hydrogen in amounts equivalent to not substantially less than about 0.001 gram per liter of copper.

13. A composition according to claim 12 wherein the electropositive metal is copper.

14. A composition according to claim 12 wherein the relative concentrations of nitric acid and fluoboric acid lie within the area defined approximately in the accompanying diagram by the solid lines AB, BC, CD, DE, EF, FG, GH and HA.

15. A composition according to claim 14 wherein the solution contains copper ions in amount equivalent to that produced by addition of 0.05 gram Cu(NO₃)₂·3H₂O per liter.

16. A composition for the chemical brightening of aluminum and aluminum alloys comprising a dilute aqueous solution consisting essentially of fluoboric acid and nitric acid in concentrations included within the area defined approximately in the accompanying diagram by the solid lines AB, BC, CD, DE, EF, FG, GH and HA, and copper ions in amount equivalent to that produced by not substantially less than 0.05 gram Cu(NO₃)₂·3H₂O per liter, balance substantially all water.

17. A process for chemically brightening aluminum and aluminum alloys which comprises contacting the metal surfaces with a heated aqueous acid solution containing complex fluoride ions and nitric acid in concentrations equivalent in fluoride to the relative concentrations of fluoboric acid and nitric acid lying within the area defined approximately in the accompanying diagram by the solid lines II, JK, KL, LM, MN, NO, OP, PQ and QI, and ions of a metal electropositive to hydrogen in concentration equivalent to not substantially less than 0.001 gram per liter of copper, for a time sufficient to brighten the metal.

18. A process for chemically brightening aluminum and aluminum alloys which comprises immersing the metal in an aqueous acid solution maintained at from 130° F. to boiling and containing fluoborate ions and nitric acid in concentrations equivalent to the relative concentrations of fluoboric acid and nitric acid lying within the area defined approximately in the accompanying diagram by the solid lines AB, BC, CD, DE, EF, FG, GH and HA, said solution containing also copper ions in amount equivalent to not substantially less than 0.05 gram Cu(NO₃)₂·3H₂O per liter for a time sufficient to brighten the metal, and thereafter rinsing and drying the metal.

19. A process according to claim 18 in which the metal is treated with nitric acid to remove any deposited copper from the brightened surfaces.

20. A process according to claim 18 in which the temperature of the solution is maintained from about 190 to about 210° F.

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