CLEANING COMPOSITION FOR METAL ARTICLES

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Appl. No.: 14/651,050

PCT Filed: Mar. 15, 2013

PCT No.: PCT/US13/31819

§ 371 (c)(1), (2) Date: Jun. 10, 2015

Related U.S. Application Data

Provisional application No. 61/736,777, filed on Dec. 13, 2012.

Publication Classification

Int. Cl. C23G 1/12 (2006.01)

U.S. Cl. C23G 1/125 (2013.01)

ABSTRACT

An aqueous cleaning composition includes at least one acid fluoride salt selected from ammonium bifluoride, sodium bifluoride, potassium bifluoride, calcium fluorophosphates, sodium fluoroaluminates, and combinations of two or more thereof; at least one mineral acid adduct of urea; at least one surfactant; and at least one organic solvent. The cleaning composition is effective in removing deposited soil and corrosion products on a metal surface, particularly aluminum and aluminum alloy surfaces.
FIG. 1

FIG. 2
**FIG. 3**

**FIG. 4**
FIG. 5

% ABF

% Clean Oxidized

0 10 20 30 40 50 60 70

2 3 5 7 10
CLEANING COMPOSITION FOR METAL ARTICLES

TECHNICAL FIELD

[0001] The invention related generally to a composition for cleaning metal surfaces, and in particular, to an aqueous composition for cleaning aluminum and aluminum alloys.

BACKGROUND

[0002] Although aluminum is generally considered to be a bright metal, aluminum and aluminum alloy surfaces often present a dull appearance due to build up of grease and dirt, particularly on industrial machinery and equipment. Chemical and electrochemical solutions have been developed to create a highly-reflective surface on aluminum and aluminum alloy bodies.

[0003] Many of the available cleaning compositions require elevated temperatures, e.g., temperatures at or above 120° C, to be effective. Other cleaning compositions are alkaline, which may cause corrosion and pitting of the metal surface. Acidic cleaning compositions have been used, but many contain components that present a safety risk to the user and/or are harmful to the environment.

SUMMARY

[0004] In one aspect of the invention, there is provided an aqueous cleaning composition including: at least one acid fluoride salt selected from ammonium bifluoride, sodium bifluoride, potassium bifluoride, calcium fluorophosphates, sodium fluorosilicates, and combinations of two or more thereof; at least one mineral acid adduct with urea; at least one surfactant; and at least one organic solvent.

[0005] In one embodiment, the mineral acid adduct with urea is selected from among the adducts of urea with perchloric acid (urea perchloride); hydroiodic acid (urea hydroiodide); hydrobromic acid (urea hydrobromide); hydrochloric acid (urea hydrochloride and urea dihydrochloride); sulfuric acid (urea sulfate); nitric acid (urea nitrate and urea dinitric acid); phosphoric acid (urea phosphate) and combinations of two or more thereof.

[0006] In one embodiment, the acid fluoride salt is ammonium bifluoride.

[0007] In one embodiment, the surfactant includes a nonionic surfactant. The nonionic surfactant may include ethoxylated alcohol.

[0008] In one embodiment, the surfactant includes an amphoteric surfactant. The amphoteric surfactant may include cocamidopropyl betaine.

[0009] In one embodiment, the organic solvent includes diethylene glycol monobutyl ether.

[0010] In one aspect of the invention, there is provided an aqueous cleaning composition including: from about 1% to about 10% by weight of at least one acid fluoride salt selected from ammonium bifluoride, sodium bifluoride, potassium bifluoride, calcium fluorophosphates, sodium fluorosilicates, and combinations of two or more thereof; from about 2% to about 20% by weight of at least one mineral acid adduct with urea; from about 1% to about 10% by weight at least one surfactant; and from about 1% to about 10% by weight at least one organic solvent.

[0011] The aqueous cleaning composition may be diluted with water in a ratio of cleaning composition:water of 1:1 to 1:10. In one embodiment, the aqueous cleaning composition is diluted with water in a ratio of 1 part cleaning composition to 3 parts water.

[0012] In one aspect of the invention, there is provided a method of cleaning a metal surface, the method including: contacting the metal surface with an aqueous cleaning composition for a sufficient time to clean the metal surface, the aqueous cleaning composition including: at least one acid fluoride salt selected from ammonium bifluoride, sodium bifluoride; potassium bifluoride; calcium fluorophosphates, sodium fluorosilicates, and combinations of two or more thereof; at least one mineral acid adduct with urea; at least one surfactant; and at least one organic solvent.

BRIEF DESCRIPTION OF DRAWINGS

[0013] FIG. 1 is a plot of the percent clean of a soiled aluminum substrate vs. percent ammonium bifluoride content in a cleaning solution in accordance with the present invention.

[0014] FIG. 2 is a plot of the percent clean of an oxidized aluminum substrate vs. percent ammonium bifluoride content in a cleaning solution in accordance with the present invention.

[0015] FIG. 3 is a bar graph of the percent clean of a soiled aluminum substrate for cleaning solutions containing various mineral acid adducts with urea in accordance with the present invention.

[0016] FIG. 4 is a bar graph of the percent clean of an oxidized aluminum substrate for cleaning solutions containing various mineral acid adducts with urea in accordance with the present invention.

[0017] FIG. 5 is a bar graph of the percent clean of an oxidized aluminum substrate for comparative cleaning solutions containing different concentrations of ammonium bifluoride.

DETAILED DESCRIPTION

[0018] The composition of the present invention is an aqueous acidic composition that is useful in cleaning metal surfaces, and in particular, aluminum and aluminum alloy surfaces. More specifically, the composition described herein is particularly useful for cleaning evaporator coils, heating coils and air-cooled condensers to remove deposits that build up on the coils, which can interfere with proper operation of the coils. The cleaning composition is effective in producing a brightened surface for aluminum and aluminum alloys.

[0019] The invention described herein includes a concentrated cleaner that safely removes dirt and oxidation in a uniform manner resulting in a brightening effect on aluminum fin stock used in the HVAC industry. More specifically, the composition of the present invention provides for an effective cleaning composition that removes accumulated dirt and oxidation in a manner that is safer for the manufacturer, end user and the environment than conventional hydrofluoric acid and mineral acid compositions.

[0020] Hydrofluoric acid has been a staple ingredient in HVAC coil cleaning for many years. This is mainly because it effectively dissolves aluminum metal very rapidly at a rate unlike any other commonly used acid. It also has a brightening effect on the cleaned metal that is typically better than most conventional compositions. Any residual unreacted hydrofluoric acid quickly reacts with calcium in the environment and forms an inert compound that has very low solubil-
ity in water, thereby does not enter the water supply in a significant way. These HF compositions usually contain a mineral co-acid such as sulfuric or phosphoric acids or other acid of a lower pKa to push the equilibrium for HF to the left as:

\[
\text{HF} + \text{H}^+ \rightarrow \text{H}_2\text{F}^-
\]

\[
\text{HF} + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{F}^- + 2\text{H}^+ + \text{SO}_4^{2-}
\]

\[
3\text{HF} + \text{Al}^3+ (6\text{H}_2\text{O})\text{F}^- + 3/2\text{H}_2\text{O}
\]

[0021] The above equations show that it is the HF species that attacks the aluminum metal underneath the oxide layer. Any soluble oxide is removed in the process along with oxide attached to the aluminum metal surface. When this reaction is quenched with rinse water, an aluminum fluoride film is left on the remaining fin stock giving an appearance of a brighter surface than an aluminum oxide surface. However, the downside to using hydrofluoric acid is that it is extremely hazardous. Hydrofluoric acid is dangerous to use because of the reactivity with calcium ion in the body that can cause heart failure. It is very penetrating through the skin and is very volatile so as to be an inhalation hazard as well as a skin corrodent. In addition, hydrofluoric acid is a dangerous product to manufacture, to store, to blend into a formula, to dilute and during application.

[0022] Some of the hazards of using hydrofluoric acid may be circumvented by the use of ammonium bifluoride and a co-acid. Co-acids are typically chosen from two groups: mineral acids such as sulfuric and phosphoric acids; and organic co-acids such as citric and hydroxyacetic acids. However, the cleaning performance and the brightening effect have been unsatisfactory with the available non-HF/organic acid formulations.

[0023] The benchmark for performance in aluminum cleaning and brightening as mentioned above, are the hydrofluoric acid containing formulations with the aforementioned hazards. An example of a commercially available cleaning composition is Acti-Brite from Virginia Corporation, which contains about 15-18% hydrofluoric acid, 5-7% phosphoric acid and surfactants. An example of a commercially available ammonium bifluoride with organic co-acid product is Calbrite from NoCalgon Corporation. Analysis of Calbrite shows it to contain about 10-13% ammonium bifluoride, about 5-5% hydroxyacetic acid, and surfactants.

[0024] As used herein, the term “brightening” means improving the clarity or distinctness of an image reflected by a metal surface.

[0025] As used herein, the term “substantially free of” means the composition is completely lacking the component or having such a small amount of the component that the component does not affect the performance of the composition. The component may be present as an impurity or as a contaminant, and is present in an amount that is less than 0.5% by weight. In another embodiment, the component is present in an amount that is less than 0.1% by weight, and in yet another embodiment, the component is present in an amount that is less than 0.01% by weight.

[0026] The cleaning composition of the present invention includes an acid fluoride salt, a mineral acid adduct of urea, at least one surfactant, a water miscible organic solvent and water.

[0027] Suitable acid fluoride salts include metal fluorides, including alkali metal fluorides, and ammonium fluorides. Examples of such acid fluoride salts include ammonium bifluoride, sodium bifluoride, potassium bifluoride, calcium fluoro phosphates and sodium fluoro silicates, and combinations of two or more thereof. Preferably, the acid fluoride salt includes ammonium bifluoride.

[0028] As part of an effective cleaning composition, the acid fluoride salt concentration level may suitably be from about 1 to about 30% by weight, based on the total weight of the composition. In one embodiment, the acid fluoride salt concentration level is within the range of about 1 to about 25% by weight, or within the range of about 1 to about 10% by weight, or within the range of about 4 to about 6% by weight.

[0029] The composition includes at least one adduct of a mineral acid with urea. Particularly useful mineral acids are strong mineral acids. Table 1 below lists mineral acids with their respective relative strengths expressed by the pKa scale.

<table>
<thead>
<tr>
<th>Acid</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoromontonic acid</td>
<td>&lt;12</td>
</tr>
<tr>
<td>Hydroiodide</td>
<td>10</td>
</tr>
<tr>
<td>Perchloric</td>
<td>10</td>
</tr>
<tr>
<td>Sulfuric</td>
<td>2.0</td>
</tr>
<tr>
<td>Hydrochloric</td>
<td>7</td>
</tr>
<tr>
<td>Nitric</td>
<td>1.3</td>
</tr>
<tr>
<td>Phosphoric</td>
<td>2</td>
</tr>
<tr>
<td>Hydrofluoric</td>
<td>3.2</td>
</tr>
<tr>
<td>Water</td>
<td>15.7</td>
</tr>
</tbody>
</table>

[0030] Suitable adducts of mineral acids with urea include adducts of urea with perchloric acid (urea perchloride); hydroiodic acid (urea hydroiodide); hydrobromic acid (urea hydrobromide); hydrochloric acid (urea hydrochloride and urea dihydrochloride); sulfuric acid (urea sulfate); nitric acid (urea nitrate and urea dinitric acid); phosphoric acid (urea phosphate) and combinations of two or more thereof.

[0031] Adducts of mineral acids with urea may be prepared directly from the components or their solutions or by the action of mineral acids on cyanamide, in which case the latter decompose to give urea, which then enters into the adduct with the acid.

[0032] Urea hydrochloride is an organic acid salt that can be prepared by reacting urea with hydrogen chloride. In one embodiment, urea hydrochloride is added in salt form to the cleaning composition. The urea hydrochloride may be a monohydrochloride or a dihydrochloride. In another embodiment, the urea hydrochloride is formed in situ by adding urea and hydrochloric acid to the cleaning composition.

[0033] According to certain preferred embodiments, the composition is substantially free of added hydrochloric acid.

[0034] As part of an effective cleaning composition, the urea:metal acid adduct concentration level may suitably be from about 1 to about 30% by weight, based on the total weight of the composition. In one embodiment, the urea hydrochloride concentration level is within the range of about 2 to about 25% by weight, or within the range of about 2 to
about 20% by weight, or within the range of about 2 to about 15% by weight, or within the range of about 2 to about 10% by weight.

[0035] The pH of the composition is in the range of about 0.05 to 7. In one embodiment, the pH of the composition is between about 0.5 and about 6.5. In one embodiment, the pH of the composition is between about 1.0 and about 5.0. In one embodiment, the pH of the composition is between about 0.5 and 4.5.

[0036] The cleaning composition contains at least one surfactant. The surfactant or surfactant mixture may be selected from water soluble or water dispersible nonionic, anionic, cationic, zwitterionic or true amphoteric surfactants.

[0037] Exemplary nonionic surfactants include polyoxyalkylene alkyl (or alkenyl) esters obtained by adding 3 or 30 moles of an alkylene oxide having 2 to 4 carbon atoms to an aliphatic alcohol having 10 to 18 carbon atoms, wherein examples of the aliphatic alcohol used include primary alcohols and secondary alcohols in which the alkyl group thereof may also be branched, and the aliphatic alcohol is preferably a primary alcohol; polyoxyethylene alkyl (or alkenyl) phenyl ethers; fatty acid alkyl ester alkylates obtained by adding an alkylene oxide between the ester bonds of a long chain fatty acid alkyl ester; polyoxyethylene sorbitan fatty acid esters; polyoxyethylene sorbitol fatty acid esters; polyoxyethylene fatty acid esters; polyoxyethylene hydrogenated castor oil; glycerin fatty acid esters; fatty acid alkanolamides; polyoxyethylene alkylamines; alkyl glycosides; and alkylamine oxides. In certain embodiments, the nonionic surfactant includes an ethoxylated alcohol.

[0038] Exemplary anionic surfactants include alcohol sulfates and sulfonates, alcohol phosphates and phosphonates, alkyl ester sulfates, alkyl diphenyl ether sulfonates, alkyl sulfates, alkyl ether sulfates, sulfate esters of an alkylphenylpolyoxyethylene alcohol, alkyl monoglyceride sulfates, alkyl sulfonates, alkyl ether sulfates, alpha-olefin sulfonates, beta-alkoxy alkane sulfonates, alkyl ether sulfonates, ethoxylated alkyl sulfonates, alkyaryl sulfonates, alkylaryl sulfates, alkyl monoglyceride sulfonates, alkylaroyl sulfonates, alkyl ether carboxylates, alkyl ether carboxylates having 1 to 5 moles of ethylene oxide, alkylpolyglycosoether sulfates (containing up to 10 moles of ethylene oxide), sulfoxocinates, octoxynol or nonoxynol phosphates, taurates, fatty taurides, fatty acid amide polyoxyethylene sulfates, acyl glycerol sulfates, fatty oleyl glycerol sulfates, alkyl phenol ethoxylate ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates, N-acyl taurates, alkyl succinonates and sulfoxocinates, alkylpolyoxyether sulfates, alkylpolyglycosoide sulfates, alkyl polyoxyethylenes, and sarcosinates or mixtures thereof. These anionic surfactants may be provided as salts with one or more organic counterions, e.g., ammonium, or inorganic counterions.

[0039] Exemplary cationic surfactants include quaternary ammonium surfactants, such as lauryl trimethyl ammonium chloride, cetaryl trimethyl ammonium chloride, stearyl trimethyl ammonium chloride, alkyl trimethyl ammonium chloride, distearyl dimethyl ammonium chloride, cetaryl trimethyl ammonium bromide, stearyl trimethyl ammonium bromide, lanolin fatty acid ampropyl ethyl dimethyl ammonium ethyl sulfate, steary trimethyl ammonium saccharine, cetaryl trimethyl ammonium saccharine, methacryloxyethyl trimethyl ammonium chloride, and behenyl trimethyl ammonium methyl sulfate.

[0040] Exemplary amphoteric surfactants include fatty acid ampropyl dimethylamino acetic acid betaine, alkyl dimethylaminoacetic acid betaine, N-acyl aminoethyl-N-2-hydroxyethyl aminocarboxylate, N-acyl aminoethyl-N-carboxymethoxy ethyl aminocarboxylate, and hydroxyalkyl (C12-14) hydroxethyl sarcosine. Examples of the fatty acid ampropyl dimethylamino acetic acid betaine include cocamidopropyl betaine, palm oil fatty acid ampropyl trimethylaminoacetic acid betaine, lutaramidopropyl betaine, and ricinoleic acid ampropyl dimethylaminoacetic acid betaine. Examples of the alkyl dimethylaminoacetic acid betaine include deyl dimethylaminoacetic acid betaine, lauryldimethylaminoacetic acid betaine, myristyl dimethylaminoacetic acid betaine, cetethyl dimethylaminoacetic acid betaine, stearyldimethylaminoacetic acid betaine, oleyldimethylaminoacetic acid betaine, behenyl dimethylaminoacetic acid betaine, and coconut oil alkyl trimethylaminoacetic acid betaine. Examples of the N-acyl aminoethyl-N-carboxymethoxy ethyl aminocarboxylate include sodium cocoamphocarboxylate and sodium cocoamphopropionate. Examples of the N-acyl aminoethyl-N-carboxymethoxy ethyl aminocarboxylate include sodium cocomodiisocetate, sodium cocamphodiisopropanolate, and sodium lauroamphodiacetate.

[0041] The surfactant concentration level of the cleaning composition may suitably be from about 0.5% to about 20% by weight, based on the total weight of the composition. In one embodiment, the surfactant concentration level is within the range of about 0.5 to about 15% by weight, or within the range of about 1 to about 10% by weight, or within the range of about 1 to about 7% by weight.

[0042] The composition includes at least one organic solvent. Suitable organic solvents include one or more alcohols, glycols, acetates, ether acetates and glycol ethers. Exemplary alcohols include isopropanol, ethanol, and methanol. Exemplary glycols include propylene glycol and ethylene glycol. Examples of ether acetates include diethylene glycol monoethyl ether acetate, and propylene glycol monomethyl ether acetate. Exemplary glycol ethers include propylene glycol methyl ether, dipropylene glycol methyl ether, tripropylene glycol methyl ether, propylene glycol monopropyl ether, propylene glycol monobutyl ether, ethylene glycol monobutyl ether, diethylene glycol monobutyl ether, diethylene glycol methyl ether, and dipropylene glycol monopropyl ether. Other organic solvents include N-methyl pyrrolidone, ketones, lactones, and terpenes such as d-limonene.

[0043] Mixtures of two or more organic solvents may be used. Alternatively, a single organic solvent may be used. In one embodiment, the organic solvent includes diethylene glycol monobutyl ether.

[0044] As part of an effective cleaning composition, the organic solvent concentration level may suitably be from about 0.5% to about 20% by weight, based on the total weight of the composition. In one embodiment, the organic solvent concentration level is within the range of about 1 to about 15% by weight, or within the range of about 1 to about 10% by weight, or within the range of about 1 to about 3% by weight.

[0045] Other components may be added to the composition, such as thickeners, gelling agents, fragrance, dispersants, anti-redeposition agents, dyes and humectants for example.

[0046] The aqueous cleaning composition may be provided in a concentrate that includes from about 1% to about 10% by weight of at least one acid fluoride salt selected from ammo-
nium bifluoride, sodium bifluoride, potassium bifluoride, calcium fluorophosphates, sodium fluorosilicates, and combinations of two or more thereof; from about 2% to about 20% by weight of at least one mineral acid adduct with urea; from about 1% to about 10% by weight at least one surfactant; and from about 1% to about 10% by weight at least one organic solvent.

[0047] In one embodiment, the concentrated aqueous cleaning composition includes from about 4% to about 6% by weight of at least one acid fluoride salt selected from ammonium bifluoride, sodium bifluoride, potassium bifluoride, calcium fluorophosphates, sodium fluorosilicates, and combinations of two or more thereof; from about 2% to about 15% by weight of at least one mineral acid adduct with urea selected from the adducts of urea with perchloric acid; hydroiodic acid; hydrobromic acid; hydrochloric acid; sulfuric acid; nitric acid; phosphoric acid and combinations of two or more thereof; from about 1% to about 7% by weight at least one surfactant; and from about 1% to about 3% by weight at least one organic solvent.

[0048] The cleaning composition may be supplied in a concentrated form or in a variety of diluted forms. Thus, the concentration of the components in the supplied composition may vary widely. Depending upon the application and the concentration of the composition supplied, the user may dilute the composition prior to use. The final concentration may be reached from a wide range of supplied concentrations, using water to dilute the supplied concentration, by using an appropriate dilution factor. For example, the composition may be diluted with water in a concentration of composition: water ratio of 1:1, 1:1.5, 1:2, 1:3, 1:4, 1:5, 1:6, 1:7, 1:8, 1:9, 1:10, or by using many other dilution ratios.

[0049] In one aspect of the invention, a process for cleaning metal surfaces is provided. The process includes cleaning the metal surface by contacting the metal surface with the cleaning composition described herein for a time sufficient to clean the metal surface. The cleaning composition can be applied to the metal surface using any of the contacting techniques known in the art. For example, the cleaning composition may be applied by conventional spraying or immersion methods.

EXAMPLES

Examples 1-7

[0050] Cleaning compositions containing varying amounts of ammonium bifluoride and the adduct of hydrochloric acid with urea are prepared as shown in Table 2. The amount of each ingredient for Examples 1-7 is given in weight percent.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Ex. 1</th>
<th>Ex. 2</th>
<th>Ex. 3</th>
<th>Ex. 4</th>
<th>Ex. 5</th>
<th>Ex. 6</th>
<th>Ex. 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium bifluoride (ABF)</td>
<td>0.0%</td>
<td>1.0%</td>
<td>3.0%</td>
<td>5.0%</td>
<td>7.0%</td>
<td>9.0%</td>
<td>10.0%</td>
</tr>
<tr>
<td>Urea hydrochloride (UHC)</td>
<td>10.0%</td>
<td>9.0%</td>
<td>7.0%</td>
<td>5.0%</td>
<td>3.0%</td>
<td>1.0%</td>
<td>0.0%</td>
</tr>
<tr>
<td>Diethylene glycol monobutyl ether</td>
<td>2.0%</td>
<td>2.0%</td>
<td>2.0%</td>
<td>2.0%</td>
<td>2.0%</td>
<td>2.0%</td>
<td>2.0%</td>
</tr>
<tr>
<td>Nonionic surfactant (Tomadol 900)*</td>
<td>1.0%</td>
<td>1.0%</td>
<td>1.0%</td>
<td>1.0%</td>
<td>1.0%</td>
<td>1.0%</td>
<td>1.0%</td>
</tr>
<tr>
<td>Water</td>
<td>87%</td>
<td>87%</td>
<td>87%</td>
<td>87%</td>
<td>87%</td>
<td>87%</td>
<td>87%</td>
</tr>
</tbody>
</table>

[0051] The effectiveness of the cleaning compositions was tested through evaluation of aluminum panels, which have been soiled and then immersed in a diluted composition of the concentrated cleaning compositions.

Formula for Lab Prepared Deposit Soil:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized Water</td>
<td>51.3%</td>
</tr>
<tr>
<td>Bentone EW (Elementis Corp.)</td>
<td>1.5%</td>
</tr>
<tr>
<td>Sodium Tripolyphosphate Low Density</td>
<td>0.2%</td>
</tr>
<tr>
<td>Microsil 5 (US Silica Corp.)</td>
<td>25.0%</td>
</tr>
<tr>
<td>Aluminum Oxide # 19 (Graptor Corp.)</td>
<td>21.0%</td>
</tr>
<tr>
<td>CW 5317 Black (Elementis Corp.)</td>
<td>1.0%</td>
</tr>
</tbody>
</table>

[0052] The water and bentone are stirred until gel formation, approximately 30 minutes, using a regular overhead 3 bladed stirrer (ETK Model) at approximately 2500 rpm. The remaining ingredients are then added with good mixing to disperse.

[0054] One square foot of fin stock (aluminum fin stock from JW Aluminum Corp.) is cut into a panel and cleaned using toluene followed by acetone, and then rinsed with deionized water. The lab prepared soil is applied to cover the entire one foot square aluminum panel surface using a paint brush. The panel is baked overnight in a 110°C lab oven. The panel is then removed from the oven and allowed to cool to room temperature. The panel is then rinsed with water until the unattached soil is removed.

Testing of Formulations 1-7:

[0055] The effectiveness of each of the cleaning compositions of Examples 1-7 was evaluated using the soiled aluminum fin stock panel. Each composition was diluted 1 part to three parts water by weight. Panels of the aluminum soiled with the lab prepared soil were cut into coupons of approximately 1 inch x 2 inches and immersed in the diluted cleaner for 30 seconds. After 30 seconds the coupons were immediately rinsed with deionized water.

[0056] FIG. 1 shows the results of the evaluation. The percent clean was determined by using a grid count under 22.5x magnification. The graph shows that the composition containing 10% ABF (with no added urea hydrochloride) cleaned the surface 55% clean. The composition containing 10% of the urea hydrochloride adduct (with no ABF) had zero % cleaning. These results were surprising, as it was expected that the % cleaning would increase as the amount of ABF was increased.

Example 8-14

[0057] Cleaning compositions containing varying amounts of ammonium bifluoride and the adduct of hydrochloric acid with urea are prepared as shown in Table 3. The amount of each ingredient for Examples 8-14 is given in weight percent.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Ex. 8</th>
<th>Ex. 9</th>
<th>Ex. 10</th>
<th>Ex. 11</th>
<th>Ex. 12</th>
<th>Ex. 13</th>
<th>Ex. 14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium bifluoride</td>
<td>0.0%</td>
<td>1.0%</td>
<td>3.0%</td>
<td>5.0%</td>
<td>7.0%</td>
<td>9.0%</td>
<td>10.0%</td>
</tr>
</tbody>
</table>
Testing of Formulations 15-18:

[0064] The effectiveness of each of the cleaning compositions of Examples 15-18 was evaluated using the lab prepared soiled aluminum fin stock panel. Each composition was diluted 1 part to three parts water by weight. Panels of the aluminum soiled with the lab prepared soil were cut into coupons of approximately 1 inch x 2 inches and immersed in the diluted cleaner for 30 seconds. After 30 seconds the coupons were immediately rinsed with deionized water.

[0065] FIG. 3 shows the results of the evaluation on the lab prepared soil surface. The percent clean was determined by using a grid count under 22.5x magnification.

Examples 19-22 and Comparative Examples A-B

[0066] Cleaning compositions containing adducts of various mineral acids with urea are prepared as shown in Table 5. The amount of each ingredient for Examples 19-22 is given in weight percent.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Ex. 15</th>
<th>Ex. 16</th>
<th>Ex. 17</th>
<th>Ex. 18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium bifluoride</td>
<td>2.0%</td>
<td>2.0%</td>
<td>2.0%</td>
<td>2.0%</td>
</tr>
<tr>
<td>Urea:HCl adduct</td>
<td>10.0%</td>
<td>10.0%</td>
<td>10.0%</td>
<td>10.0%</td>
</tr>
<tr>
<td>Urea:HNO₃ adduct</td>
<td>—</td>
<td>8.0%</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Urea:H₂SO₄ adduct</td>
<td>—</td>
<td>8.0%</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Urea:H₃PO₄ adduct</td>
<td>—</td>
<td>—</td>
<td>8.0%</td>
<td>—</td>
</tr>
<tr>
<td>Diethylene glycol monobutyl ether</td>
<td>2.0%</td>
<td>2.0%</td>
<td>2.0%</td>
<td>2.0%</td>
</tr>
<tr>
<td>Nonionic surfactant (Tomadol 900)</td>
<td>1.0%</td>
<td>1.0%</td>
<td>1.0%</td>
<td>1.0%</td>
</tr>
<tr>
<td>Water</td>
<td>85%</td>
<td>85%</td>
<td>85%</td>
<td>85%</td>
</tr>
</tbody>
</table>

Testing of Formulations 19-22—Oxidized Surface:

[0067] The effectiveness of each of the cleaning compositions of Examples 19-22 was evaluated using the oxidized aluminum fin stock strips. In addition, Comparative Example A containing about 10-13% ammonium bifluoride, about 3-5% hydroxyacetic acid, and surfactants (Calbrite) and Comparative Example B containing about 15-18% hydrofluoric acid, 5-7% phosphoric acid and surfactants (Acet-Brite) were also evaluated. Each composition was diluted 1 part to three parts water by weight. Strips of the oxidized aluminum were cut into coupons of approximately 1 inch x 2 inches. The oxidized coupons were immersed in the diluted cleaner for different lengths of time and then immediately rinsed with deionized water.
Table 6 shows the results of the evaluation on the oxidized surface. The percent clean was determined by using a grid count under 22.5x magnification.

<table>
<thead>
<tr>
<th>Example</th>
<th>10 sec.</th>
<th>15 sec.</th>
<th>30 sec.</th>
<th>45 sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>10</td>
<td>80</td>
<td>85</td>
<td>90</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
<td>75</td>
<td>90</td>
<td>95</td>
</tr>
<tr>
<td>Comp. A</td>
<td>10</td>
<td>—</td>
<td>40</td>
<td>55</td>
</tr>
<tr>
<td>Comp. B</td>
<td>50</td>
<td>—</td>
<td>95</td>
<td>100</td>
</tr>
</tbody>
</table>

Testing of Formulations 19-22—Double Oxidized Surface:

Strips of aluminum fin stock were prepared by immersing the strips in a 10% sodium chloride solution at 50°C for 48 hours. This produced a much deeper layer of a dark oxide into the aluminum metal strips of fin stock.

Each of the composition of Examples 19-22 and the composition of Comparative Example B were diluted 1 part to three parts deionized water by weight. The prepared strips of double oxidized aluminum were immersed in the diluted cleaner for one minute and then immediately rinsed with deionized water.

Table 7 shows the results of the evaluation on the double oxidized surface. Reflectance was measured using a Photovolt Model 577-A reflectometer in accordance with ASTM D 4488-95.

<table>
<thead>
<tr>
<th>Example</th>
<th>% Reflectance</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>85</td>
</tr>
<tr>
<td>20</td>
<td>90</td>
</tr>
<tr>
<td>21</td>
<td>90</td>
</tr>
<tr>
<td>22</td>
<td>95</td>
</tr>
<tr>
<td>Comp. Ex. B</td>
<td>100</td>
</tr>
</tbody>
</table>

The results obtained with the compositions prepared in accordance with the present invention are very similar to the results obtained with the hydrofluoric acid containing composition of Comparative Example B.

Comparative Example C

A cleaning composition is prepared containing various amounts of ammonium bifluoride in combination with the organic acid hydroacetic acid.

Table 8

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium bifluoride</td>
<td>2.0%</td>
<td>3.0%</td>
<td>5.0%</td>
<td>7.0%</td>
<td>10.0%</td>
</tr>
<tr>
<td>Hydroacetic acid</td>
<td>8.0%</td>
<td>7.0%</td>
<td>5.0%</td>
<td>3.0%</td>
<td>0</td>
</tr>
<tr>
<td>Diethylene glycol monobutyl ether</td>
<td>2.0%</td>
<td>2.0%</td>
<td>2.0%</td>
<td>2.0%</td>
<td>2.0%</td>
</tr>
<tr>
<td>Amphoteric surfactant (Amphosol CA)</td>
<td>2.0%</td>
<td>2.0%</td>
<td>2.0%</td>
<td>2.0%</td>
<td>2.0%</td>
</tr>
<tr>
<td>Nonionic surfactant (Tomolad 900)</td>
<td>1.0%</td>
<td>1.0%</td>
<td>1.0%</td>
<td>1.0%</td>
<td>1.0%</td>
</tr>
<tr>
<td>Water</td>
<td>85%</td>
<td>85%</td>
<td>85%</td>
<td>85%</td>
<td>85%</td>
</tr>
</tbody>
</table>

The effectiveness of the cleaning compositions of Comparative Example C was evaluated using oxidized aluminum fin stock strips. Each composition was diluted 1 part to three parts water by weight. Strips of the oxidized aluminum were cut into coupons of approximately 1 inch x 2 inches and immersed in the diluted cleaner for 1 minute. After 1 minute the coupons were immediately rinsed with deionized water.

Figure 5 shows the results of varying the concentration of ammonium bifluoride in a cleaning composition containing hydroxyacetic acid. By comparing the results shown in Figure 5 to those of Figure 2, it can be seen that a performance boost is obtained by using a cleaning composition containing a safe urea/mineral acid adduct in combination with ammonium bifluoride in place of a cleaning composition containing a safe organic acid, such as hydroxyacetic acid in combination with ammonium bifluoride. Similar results are expected with the safe organic acid citric acid.

While the invention has been explained in relation to various embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading this specification. Therefore, it is to be understood that the invention provided herein is intended to cover such modifications as may fall within the scope of the appended claims.

1. An aqueous cleaning composition comprising:
   - at least one acid fluoride salt selected from ammonium bifluoride, sodium bifluoride, potassium bifluoride, calcium fluorophosphates, sodium fluorosilicates, and combinations of two or more thereof;
   - at least one mineral acid adduct with urea;
   - at least one surfactant; and
   - at least one organic solvent.

2. The aqueous cleaning composition of claim 1 wherein the acid fluoride salt is ammonium bifluoride.

3. The aqueous cleaning composition of claim 1 wherein the mineral acid adduct with urea is selected from among the adducts of urea with perchloric acid; hydroiodic acid; hydrobromic acid; hydrochloric acid; sulfuric acid; nitric acid; phosphoric acid and combinations of two or more thereof.

4. The aqueous cleaning composition of claim 1 wherein the surfactant comprises a nonionic surfactant.

5. The aqueous cleaning composition of claim 4 wherein the nonionic surfactant comprises an ethoxylated alcohol.

6. The aqueous cleaning composition of claim 1 wherein the surfactant comprises a cationic surfactant.

7. The aqueous cleaning composition of claim 6 wherein the cationic surfactant comprises dioctadecyldimethyl ammonium chloride.

8. The aqueous cleaning composition of claim 1 wherein the surfactant comprises an amphoteric surfactant.

9. The aqueous cleaning composition of claim 8 wherein the amphoteric surfactant comprises cocamidopropyl betaine.

10. The aqueous cleaning composition of claim 1 wherein the organic solvent comprises diethylene glycol monobutyl ether.

11. The aqueous cleaning composition of claim 1 wherein the composition is diluted with water in a ratio of cleaning composition:water of 1:1 to 1:10.

12. An aqueous cleaning composition comprising:
   - from about 1% to about 10% by weight of at least one acid fluoride salt selected from ammonium bifluoride, sodium bifluoride, potassium bifluoride, calcium fluorophosphates, sodium fluorosilicates, and combinations of two or more thereof;
from about 2% to about 20% by weight of at least one mineral acid adduct with urea;
from about 1% to about 10% by weight at least one surfactant; and
from about 1% to about 10% by weight at least one organic solvent.

13. The aqueous cleaning composition of claim 12 comprising:
from about 1% to about 10% by weight of ammonium bifluoride;
from about 2% to about 20% by weight of at least one mineral acid adduct with urea selected from the adducts of urea with perchloric acid; hydroiodic acid; hydrobromic acid; hydrochloric acid; sulfuric acid; nitric acid; phosphoric acid and combinations of two or more thereof;
from about 1% to about 10% by weight at least one surfactant; and
from about 1% to about 10% by weight at least one organic solvent.

14. A method of cleaning a metal surface, the method comprising:
contacting the metal surface with an aqueous cleaning composition for a sufficient time to clean the metal surface, the aqueous cleaning composition comprising:
at least one acid fluoride salt selected from ammonium bifluoride, sodium bifluoride, potassium bifluoride, calcium fluorophosphates, sodium fluoroaluminates, and combinations of two or more thereof;
at least one mineral acid adduct with urea;
at least one surfactant; and
at least one organic solvent.

15. The method of claim 14 wherein the acid fluoride salt is ammonium bifluoride.

16. The method of claim 14 wherein the mineral acid adduct with urea is selected from among the adducts of urea with perchloric acid; hydroiodic acid; hydrobromic acid; hydrochloric acid; sulfuric acid; nitric acid; phosphoric acid and combinations of two or more thereof.

17. A method of cleaning a metal surface, the method comprising:
contacting the metal surface with an aqueous cleaning composition for a sufficient time to clean the metal surface, the aqueous cleaning composition comprising:
from about 1% to about 10% by weight of at least one acid fluoride salt selected from ammonium bifluoride, sodium bifluoride, potassium bifluoride, calcium fluorophosphates, sodium fluoroaluminates, and combinations of two or more thereof;
from about 2% to about 20% by weight of at least one mineral acid adduct with urea;
from about 1% to about 10% by weight at least one surfactant; and
from about 1% to about 10% by weight at least one organic solvent.

18. The method of claim 17 wherein the mineral acid adduct with urea is selected from among the adducts of urea with perchloric acid; hydroiodic acid; hydrobromic acid; hydrochloric acid; sulfuric acid; nitric acid; phosphoric acid and combinations of two or more thereof.