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COMPOSITION FOR CLEANING ALUMINUM AND METHOD UTILIZING SAME

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ABSTRACT OF THE DISCLOSURE

A composition for cleaning aluminum comprises an aqueous bath of urea nitrate and ferric sulfate. The bath is effective at ambient temperature to rapidly remove smut from aluminum alloy articles, and the rate of activity is substantially uniform throughout the useful life of the composition.

BACKGROUND OF THE INVENTION

In the manufacture of articles from aluminum and aluminum base alloys, the surface of the alloy articles generally becomes oxidized, marred, or coated with grease and other impurities as a result of fabrication procedures and heat treatment. In producing a bright finish on the articles, they may be degreased and then subjected to hot alkaline etching solution to remove a surface layer of the metal. The alkaline etching will normally leave a tenacious dark deposit (smut) of insoluble alloying elements, such as copper, silicon, magnesium, manganese, or impurities which may be present in trace amounts, such as iron. Conventionally, concentrated nitric acid has been employed for removing the smut, usually in combination with hydrafluoric acid when relatively large quantities of silicon are present as in the case of some casting alloys.

Although such concentrated nitric acid baths have proven highly satisfactory and are extensively used in industry, they are subject to a number of objections. In many cases it is desirable to automate cleaning operations or to reduce variables to such a level that such operations can be carried out or supervised by relatively unskilled personnel. This requires that the rate of attack of the desmutting composition be uniform over extended periods of use, which is not true of the nitric acid baths. Also, the reaction of the metal with nitric acid during the treatment to remove the smut may be violently exothermic and may present a safety hazard and cooling problems. Furthermore, the evolution of nitrogen oxide fumes and the corrosive nature of nitric acid solutions render them quite noxious and costly in terms of equipment deterioration, in addition to which the relatively high concentrations of acid that are required for satisfactory results adds significantly to the expense of the treatment.

Accordingly, it is an object of the present invention to provide a novel aqueous composition for desmutting aluminum alloy articles, which affords a substantially uniform rate of activity throughout its useful life and which is effective at ambient temperatures.

It is also an object of the invention to provide such a composition which is relatively inexpensive, safe and convenient to use and maintain.

Another object is to provide a novel self-contained dry powder formulation for admixture with water to produce such a desmultting composition.

Still another object is to provide a novel method for effecting the removal of smut from aluminum alloy workpieces.

A futrher object is to provide such a method wherein contact is effected by a spray technique.

SUMMARY OF THE INVENTION

It has now been found that the foregoing and related objects can be readily attained in an aqueous composition for cleaning aluminum comprising about 0.1 to 1.5 gram moles per liter of the combination of urea nitrate and ferric sulfate, which combination contains about 0.5 to 20.0 moles of urea nitrate per mole of ferric sulfate. Preferably, the combination is used in a concentration of about 0.25 to 1.0 grams mole per liter and contains about 1.0 to 10.0 moles of urea nitrate per mole of ferric sulfate, and most desirably the concentration is about 0.4 to 7.75 grams mole per liter and the molar ratio is about 2.0 to 5.0:1.0. In addition, the composition may contain about 2.0 to 10.0 percent of boric acid and/or about 2.0 to 10.0 percent of fluoride salt (calculated as F), based upon the combined weight of urea nitrate and ferric sulfate.

In a preferred embodiment of the invention, a self-contained, dry powder formulation is provided containing urea nitrate and ferric sulfate (and optionally also boric acid and/or a dry, water-soluble fluoride salt) in the proportions hereinbefore set forth. The method of removing smut from an aluminum alloy workpiece utilizes the aqueous composition previously set forth and maintained at a temperature of at least about 20° centigrade. An aluminum alloy workpiece having a quantity of copper-containing smut thereon is contacted with the aqueous composition for a period of time sufficient to remove substantially all of the smut therefrom, after which the workpiece is rinsed to remove any residual amounts of smut and cleaning composition therefrom. The contact step may be effected by immersing the workpiece in the composition, or the composition may be sprayed upon the workpiece; in the former case, the period of time of contact ranges from about 2 to 120 seconds, and most desirably from about 5 to 30 seconds; in the latter case, the period of contact of any finite portion of the composition is less than about one second.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Illustrative of the efficacy of the present invention are the following examples:

EXAMPLE 1

Part A

Panels of 2024 aluminum (nominally containing 4.5 percent copper, 1.5 percent magnesium and 0.6 percent manganese) measuring two by three inches are simultaneously etched for 30 seconds at 140° Fahrenheit in an aqueous solution containing 57 grams per liter of sodium hydroxide and three grams per liter of sodium gulconate; a uniform dark grey coating of smut is thereby produced on each of them.

After rinsing, each of the panels is immersed and agitated slightly in one of three desmutting baths. One bath (designated A) comprises a 0.5 molar aqueous solution of nitric acid; another (designated B) is an aqueous bath containing 0.25 mole per liter each of nitric acid and ferric sulfate, and the third (designated C) is an aqueous bath containing 0.25 mole per liter each of urea

nitrate and ferric sulfate. Different panels are treated in baths of each composition at 80° and 120° Fahrenheit, and the time required in each instance for desmutting is recorded in Table 1 which follows:

TABLE 1

	Time to desmut, seconds	
	80° F.	120° F.
Bath:		
A	[1] 120	[1] 120
B	10	5
C	15	10

[1] Incomplete.

Although the urea nitrate/ferric sulfate bath is somewhat slower than the nitric acid/ferric sulfate bath, it is observed to operate upon the entire surface in a more controlled manner.

Part B

Pieces of copper measuring approximately 1.25 by 1.75 inches are placed in each of the foregoing baths; with the copper immersed therein, the baths that are operated at 80° Fahrenheit are maintained at that temperature for 24 hours, and those operated at 120° Fahrenheit are maintained at that temperature for 6 hours. The purpose of this is to simulate prolonged operation of the baths to dissolve smut, the copper that accumulates in the baths being representative thereof.

Thereafter, a fresh etched panel with a coating of smut thereon is immersed and agitated in each of the baths, and the time necessary to remove the smut is again noted; the results are tabulated in Table 2, which follows:

TABLE 2

	Time to desmut, seconds	
	80° F.	120° F.
Bath:		
A	[1] 120	[1] 120
B	15	10
C	15	10

[1] Incomplete.

A comparison of the data in Tables 1 and 2 shows that the times to desmut using bath C (embodying the invention) have remained constant at both temperatures whereas the rate for the bath designated B has decreased significantly from its initial value. Bath C also provides uniform levels of smut removal over the entire surface of the panels throughout its useful life.

EXAMPLE 2

Panels, prepared as in Example 1 and carrying a surface layer of smut, are desmutted at 80° Fahrenheit in a series of baths containing urea nitrate and ferric sulfate in various ratios and at different concentrations. The panels are simply immersed in the baths with slight hand agitation, and the time required to completely remove the smut is noted. The bath compositions and results are tabulated in Table 3:

TABLE 3

Mole ratio (urea nitrate:ferric sulfate)	Concentration of combination (g./l.)	Time to desmut (sec.)
9.75:1.0	30	60+
3.25:1.0	30	30
1.08:1.0	30	30
9.75:1.0	60	45
3.25:1.0	60	35
1.08:1.0	60	20
9.75:1.0	120	15
3.25:1.0	120	15
1.08:1.0	120	15
9.75:1.0	180	15
3.25:1.0	180	12
1.08:1.0	180	10

EXAMPLE 3

The same compositions as were described in Example 2 are employed herein to remove smut from panels; however, in the present example contact is effected by spraying the liquids onto the panels rather than by an immersion procedure. Comparable results are obtained in terms of effectiveness of smut removal.

EXAMPLE 4

A cast article of 108 aluminum alloy (nominally containing 4.0 percent copper and 3 percent silicon) is etched in the manner described in Example 1. The rinsed and dried article is desmutted in less than about 60 seconds in an aqueous bath containing 120 grams per liter of an equimolar combination of urea nitrate and ferric sulfate and about 12 grams per liter of sodium bifluoride. Contact is by immersion and the bath is maintained at room temperature.

The compositions and method of the present invention are applicable to effect the removal of smut from both cast and wrought alloy workpieces, but they are particularly beneficially employed in connection with the wrought alloys which contain relatively large amounts of copper and little or no silicon. The term "smut" is well known in the art and relates to residues of insoluble alloying elements that remain after treatment of the workpiece to dissolve a portion of the surface thereof. As employed herein, the term particularly connotes residues which contain an appreciable amount of copper.

Although the concentrations of urea nitrate and ferric sulfate may vary considerably and yet fall within the scope of the invention, it is important that at least 0.1 gram mole of the combination per liter be present in the aqueous bath in order to provide satisfactory results in a reasonably short period of time. On the other hand, increasing the quantity of the combination above about 1.5 gram moles per liter produces no significant additional benefit and tends to be wasteful. As the concentrations are increased and the levels of solubility are exceeded there will, of course, be quantities of solids in the present baths. This will not usually be detrimental, and quite commonly an amount of solid ferric sulfate will be present, which will normally be utilized during the course of operation.

The ratio of urea nitrate to ferric sulfate that exists in the combination may also vary substantially, and it will be appreciated that the total molar concentration will be dependent upon the particular ratio that is involved. If the combination contains less than about 0.5 mole of urea nitrate per mole of ferric sulfate the advantages of the invention will not be fully realized, particularly as regards the uniformity of cleaning rate which is desired throughout the useful life of the composition. If the composition contains more than about 20 moles of urea nitrate per mole of ferric sulfate the rate of activity will tend to be undesirably slow. As has been mentioned previously, the preferred compositions contain about 0.25 to 1.0 gram mole per liter of the combination and have a molar ratio of urea nitrate to ferric sulfate of about 1.0–10.0:1.0; best results will usually be obtained when the concentration is about 0.4 to 0.75 gram mole per liter and the ratio is about 2.0–5.0:1.0.

The compositions of the invention may contain numerous optional additives depending upon the particular properties which are desired therein. For example, the level of flammability and self-sustaining decomposition can be reduced significantly by the addition of about 2.0 to 10.0 percent, based upon the weight of the urea nitrate/ferric sulfate combination, of boric acid; gen-

erally, this additive will be employed in an amount of about 5.0 percent by weight. The addition of fluoride salts significantly improves the effectiveness of the compositions for cleaning smut that is produced on cast alloys containing a significant quantity of silicon. Sodium bifluoride is beneficially employed since it is not only readily soluble but also does not detract from the desired pH level of the composition. The actual weight of the fluoride salt will, of course, depend upon the particular compound that is used, but it should be present in an amount of about 2 to 10 percent, calculated as F and based upon the total combined weight of urea nitrate and ferric sulfate. Also, to provide ready flowing dry powder formulations, it is beneficial to include a small amount of an anti-caking agent or inorganic filler, such as Micro-Cel E sold by Johns-Manville Products Corp.

As will be noted from the foregoing examples, in some respects the combination of nitric acid and ferric sulfate provides a cleaning composition which is quite comparable to the compositions of the invention containing urea nitrate and ferric sulfate. However, as is shown therein, the combination with nitric acid does not produce a composition that has a uniform rate of activity over its useful life since the rate decreases significantly after a period of use, making it less desirable for use in automated operations or in manual operations without the supervision of skilled personnel. In addition to other undesirable features of the nitric acid combination, it is considerably less stable to decomposition than is the novel combination of urea nitrate and ferric sulfate. The examples also show that nitric acid alone is quite ineffective in the same molar concentrations as the present baths, and the use of nitric acid in the high concentrations that are necessary for satisfactory rates of cleaning engenders many disadvantageous features, including hazardous operation, expense, difficulty of control, high drag-out losses, etc.

The present compositions can be employed either by immersing the workpieces or by spraying them, the latter technique being particularly advantageously employed with the present compositions since no prior art composition is known that can conveniently and effectively be used in such a manner. For practical commercial reasons, when an immersion technique is employed the maximum amount of time involved should not exceed about 2 minutes, and the compositions of the invention are normally effective in considerably shorter periods. On the other hand, periods of contact less than about 2 seconds are usually of no practical significance, although in some instances the present compositions may be effective in considerably shorter amounts of time. In spray applications, the period of contact of any finite portion of the composition is generally less than about 1 second, but the total time of spraying any workpiece will generally fall within the above specified range of contact periods. Moreover, the washing effect of spraying the composition upon the workpiece enhances the efficiency of cleaning considerably, and it will be appreciated that a similar effect is achieved in immersion operations when there is provided some level of agitation of either the workpiece or the bath.

One of the outstanding advantages of the present invention is the fact that the compositions described are satisfactorily employed at ambient temperatures (i.e., about 20° centigrade); however faster results can usually be achieved when the compositions are heated to temperatures somewhat thereabove. Although temperatures considerably in excess of 120° Fahrenheit may be utilized, operation at such high temperatures is not generally warranted by the concomitant improvements that may be realized.

Thus, it can be seen that the present invention provides a novel aqueous composition for desmutting aluminum alloy articles, which affords a uniform rate of activity throughout its useful life and which is effective at ambient temperatures. The composition is relatively inexpensive, safe and convenient to use and maintain, and may be furnished as a self-contained dry powder formulation for admixture with water. The invention also permits the removal of smut from aluminum alloy workpieces by a spray technique.

Having thus described the invention, we claim:

1. An aqueous composition for cleaning aluminum, comprising about 0.1 to 1.5 gram moles per liter of the combination of urea nitrate and ferric sulfate, said combination containing about 0.5 to 20.0 moles of urea nitrate per mole of ferric sulfate.

2. The composition of claim 1 wherein the concentration of said combination is about 0.25 to 1.0 gram mole per liter, and wherein said combination contains about 1.0 to 10.0 moles of urea nitrate per mole of ferric sulfate.

3. The composition of claim 1 wherein the concentration of said combination is about 0.4 to 0.75 gram mole per liter, and wherein said combination contains about 2.0 to 5.0 moles of urea nitrate per mole of ferric sulfate.

4. The composition of claim 1 additionally containing about 2.0 to 10.0 percent of boric acid, based upon the weight of said combination.

5. The composition of claim 1 additionally containing about 2.0 to 10.0 percent of fluoride salt, calculated as F and based upon the weight of said combination.

6. A self-contained dry formulation for producing an aqueous aluminum cleaning composition comprising urea nitrate and ferric sulfate, said formulation containing about 0.5 to 20.0 moles of urea nitrate per mole of ferric sulfate.

7. The formulation of claim 6 containing about 1.0 to 10.0 moles of urea nitrate per mole of ferric sulfate.

8. The formulation of claim 6 containing about 2.0 to 5.0 moles of urea nitrate per mole of ferric sulfate.

9. The formulation of claim 6 additionally containing about 2.0 to 10.0 percent of boric acid, based upon the combined weight of ferric sulfate and urea nitrate.

10. The formulation of claim 6 additionally containing about 2.0 to 10.0 percent of a dry water-soluble fluoride salt, calculated as F and based upon the combined weight of urea nitrate and ferric sulfate.

11. In a method of removing smut from an aluminum alloy workpiece, the steps comprising:

(a) preparing an aqueous cleaning composition comprising about 0.1 to 1.5 gram moles per liter of the combination of urea nitrate and ferric sulfate, said combination containing about 0.5 to 2.0 moles of urea nitrate per mole of ferric sulfate;

(b) maintaining said cleaning composition at a temperature of at least about 20° centigrade;

(c) contacting an aluminum alloy workpiece having a quantity of copper-containing smut thereon with said cleaning composition for a period of time sufficient to remove substantially all of said smut therefrom; and

(d) rinsing said workpiece to remove any residual amounts of smut and of said composition therefrom.

12. The method of claim 11 wherein said workpiece is immersed in said cleaning composition to effect said contact therebetween, and wherein said period of time ranges from about 2 to 120 seconds.

13. The method of claim 11 wherein said composition is sprayed upon said workpiece to effect said contact therebetween, and wherein the period of contact of any finite portion of said composition is less than about one second.

14. The method of claim 11 wherein said period of contact ranges from about 5 to 30 seconds.

15. The method of claim 11 wherein said composition comprises about 0.4 to 0.75 gram moles per liter of said combination, and wherein said combination contains about 2.0 to 5.0 moles of urea nitrate per mole of ferric sulfate.

16. The method of claim 11 wherein said composition contains about 2.0 to 10.0 percent of fluoride salt, calculated as F and based upon the weight of said combination, and wherein said smut also contains a significant amount of silicon.

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