The present invention relates to the cleaning of aluminum and aluminum base alloys and more particularly relates to a novel composition and method in the pickling of aluminum base alloys to obtain a uniformly etched finish.

In the manufacture of articles from aluminum and aluminum base alloys, the surfaces of the alloy articles generally become oxidized, marred or scaly as a result of fabrication procedures or heat treatment or by the initial casting operation. It is customary to produce a bright finish on the articles by subjecting them to a hot alkaline etching solution to remove a surface layer of aluminum or aluminum alloy, after which the etched flakes are given a chemical brightening treatment.

Aluminum alloy castings are generally given an intermediate treatment to remove a tenacious black or brownish film developed by the alkaline etch due to the presence of insoluble alloying elements such as silicon and iron remaining after the aluminum at the surface has been etched out to a small depth. Conventionally, a concentrated acid bath containing nitric and hydrofluoric acids has been employed for this purpose.

A typical bath utilized in the treatment of aluminum alloy castings is one comprised of 3 gallons nitric acid (42° Baume) and 1 gallon of hydrofluoric acid (48 percent). An immersion period of about 15-30 seconds is generally used for die castings and a period of one-two minutes for sand castings. Although the bath is not heated for the treatment, the temperature rapidly rises as a result of the relatively violent exothermic reaction and must be lowered or stabilized by use of a cooling tower located outside of the treatment tank or by other suitable means. Furthermore, as the temperature at the time of immersion increases, the rate of exothermic reaction also increases.

Such concentrated nitric-hydrofluoric acid baths have proven highly satisfactory and are very extensively used in industry although subject to the above objections. The highly exothermic reaction produced by the bath creates a safety hazard and a problem of cooling. The period of exposure of the castings to the bath must be closely controlled to obtain a white finish since over-exposure produces a dull, grey film. Furthermore, there is a substantial evolution of nitrogen oxide fumes both during treatment of the article in the bath and upon removal of the article from the bath. Also, as the percentage of water in the bath increases due to dilution by water carried over from the previous rinse, the foregoing problems become aggravated.

It is the object of the present invention to provide an acid cleaning bath for aluminum which has a controlled rate of attack upon the surface and which produces a white surface even upon over treatment.

It is also an object of the present invention to provide an economical and long-lasting pickling solution for aluminum alloy castings which is readily prepared and from which is substantially free from fuming both during actual treatment of the castings and upon removal of the castings from the bath.

A further object is to provide a novel method for the treatment of aluminum alloy castings whereby the castings may be subjected to a surface etching without loss in whiteness during extended exposure and wherein the temperature of the bath may be more easily controlled and wherein fuming is substantially eliminated both during treatment of the castings and upon removal of the castings from the bath.

Other objects and advantages will be readily apparent from the following detailed specification and claims.

It has been found that the foregoing and related objects can be obtained by use of a cleaning composition comprising a concentrated acid bath containing essentially hydroxion, fluoride and nitrate ions, and to which has been added hexavalent chromium in an amount sufficient to inhibit the rate of attack upon the metal and substantially eliminate fuming. Such a composition is prepared by adding one or both of the nitrate and fluoride ions as their respective acids, it being necessary to insure a sufficient quantity of hydroxion ions in the bath to provide a concentrated acid solution of at least 50 percent by weight acids. For example, normally nitric acid will constitute the major proportion of the bath, and a fluoride salt such as ammonium bifluoride (NH₄F-HF₂) may be added to provide the fluoride component. The hexavalent chromium is preferably added as chromic acid or as chromic acid anhydride, although other soluble hexavalent chromic salts may be utilized such as sodium and potassium chromates and bichromates.

The concentrated acid bath may vary in composition from about 1-45 percent by weight hydrofluoric acid and 30-98 percent by weight nitric acid, and may contain not more than 50 percent by weight water. Generally, as the percentage of water is increased, the amount of hydrofluoric acid in the bath must be increased in order to provide a bright white surface which is free from greying. A preferred acid bath composition is one containing about 3-15 percent by weight hydrofluoric acid, 50-96.5 percent by weight nitric acid, and less than 35 percent by weight water. In both of the foregoing ranges, the fluoride and nitrate ions are most easily calculated as their respective acids since the bath is comprised of at least 50 percent by weight acids.

The term "hexavalent chromium" as used herein refers to acid-soluble compounds, ions, or complexes containing chromium in the hexavalent state as such: CrO₃⁶⁻, CrO₄²⁻ and Cr₂O₇⁻⁻.

It has been found that hexavalent chromium may be effective at amounts from trace to saturation, the amount necessary being determined generally by the concentration of hydrofluoric acid and/or water, which components appear to require larger amounts of hexavalent chromium as the relative percentage of the composition is increased. A generally desirable range for the hexavalent chromium additive is from about 0.05-10 percent by weight of the concentrated acid bath (based upon chromium), and the preferred range is from 0.5-2.5 percent by weight. However, amounts up to 15 percent by weight may provide additional benefit depending upon the relative percentages of the acid and water components.

Since a portion of the hexavalent chromium may be reduced or complexed by elements in the bath so as to render it ineffective for the purposes of the present invention, a simple and visual method of determining the presence of an effective amount of hexavalent chromium is to add sufficient of the hexavalent chromium compound to produce a color varying from yellow-orange-red to deep purple or blue-green color characteristic of trivalent chromium. The preferred baths have a color of orange-red to brownish-red. Thus, in utilizing the baths of this novel composition, the presence of sufficient hexavalent chromium additive can readily be determined by visual observation.
In some instances, the addition of sulfuric acid has been found beneficial for increasing the brightness of the white surface on the castings. If so desired, sulfuric acid may be included in the bath in amounts up to 10 percent by volume of the nitric acid component, although it is not essential to the present invention.

As a specific example of a bath formulation which has proven to be highly desirable in the practice of the present invention, to each gallon of concentrated nitric acid (42° Baumé) is added 1-2 pounds of a dry mixture containing 87 percent by weight ammonium bifluoride (NH₄F,HF) and 13 percent by weight chromic anhydride (CrO₃).

The parts to be cleared are immersed in the acid baths of the present invention for periods of about 20 seconds. 1½ minutes, although even longer periods may be employed without undesirable effect upon the whiteness of the finish. The baths are preferably maintained at ambient temperatures of 60-95° F, and generally within the range of 60-130° F. Since the baths of the present invention are characterized by a controlled rate of attack, the exothermic reaction is greatly reduced, thus enabling the maintenance of the bath at ambient or low elevated temperatures without great difficulty. The temperature increase of the bath due to the reaction will be largely dependent upon the ratio of the volume of bath to the casting since larger volumes will absorb and dissipate heat more rapidly. However, cooling means may also be employed if desired since lower temperatures are more desirable.

Generally, the nitric acid component will be reduced at the same rate as the consumption of fluoride ion and/or hexavalent chromium. However, in some instances as the bath becomes reduced in effectiveness during use, it may be further activated by the addition of fluoride and hexavalent chromium in an amount equal to about one-fourth their amounts in the original bath.

As will be readily apparent to those skilled in the art, tanks or receptacles for the bath should be inert to the highly concentrated hydrofluoric acid-nitric acid solution and are preferably either fabricated from plastic or carbon, or coated with an inert organic material, or provided with a carbon lining.

Illustrative of the efficacy of the present invention are the following examples wherein castings of high-silicon aluminum base alloy were treated in baths of the novel formulation.

Example 1

A bath was prepared by adding to concentrated nitric acid (42° Baumé) a dry powder additive in an amount equal to 1 pound of additive per gallon of nitric acid. The powder additive was comprised of 87 parts by weight of ammonium fluoride (NH₄F,HF) and 13 parts by weight chromium anhydride (CrO₃). This bath was maintained in a polyvinyl chloride tank at ambient temperatures.

Castings of aluminum base alloy having a high silicon content were immersed in the bath for a period of 45 seconds. No fuming occurred during immersion and no fuming occurred when the castings were transferred from the bath. The treated castings were observed to have a bright white matte finish.

Example 2

A conventional pickling bath was prepared by mixing 3 gallons of nitric acid (42° Baumé) and 1 gallon hydrofluoric acid (48 percent).

Some castings of high silicon-aluminum base alloy were pre-etched in a caustic solution comprised of 6 ounces of caustic soda per gallon at a temperature of 200° F. for one minute. The castings were then rinsed and dried.

One casting was immersed in a beaker containing 320 cc. of the above pickling bath for a period of one minute, the casting completely filling the beaker. During the period of immersion, the temperature rose from 90° to 102.2° F., and there was moderately heavy fuming during the period of immersion. Upon removal of the casting from the beaker, excessive fuming occurred. The casting was found to have lost 1 percent by weight during the pickling treatment.

Ten grams of chromic acid was dissolved in the pickling bath immediately thereafter, and a second casting was immersed therein for a period of one minute, during which the temperature rose from 104° to 111° F. No fuming occurred during the period of immersion in the beaker and negligible fuming occurred on transfer of the casting from the beaker. The weight loss during the pickling treatment was found to be only 0.055 percent by weight.

It is significant to note that the temperature increase after addition of the chromic acid was only a fraction of that in the conventional solution despite the fact that immersion of the casting in the solution of the present invention occurred at a higher temperature, which generally will increase the rate of attack. As can be seen from the foregoing, the fuming was substantially eliminated by use of the bath of the present invention.

Example 3

Since the fuming problem becomes more acute when the bath is diluted by water transferred in from the rinsing following the etching bath, a second test was run wherein a bath was formulated containing 192 cc. nitric acid (42° Baumé), 64 cc. hydrofluoric acid (48 percent) and 64 cc. water. An aluminum base alloy casting etched as in the previous example was immersed in the foregoing bath. This test was interrupted after only 40 seconds because the bath was overflowing the beaker and the fuming was extremely copious. During this short period of immersion, the temperature rose from 108° to 153° F. and the casting was found to have lost 2.2 percent by weight.

Ten grams of chromic acid was added to 320 cc. of the same formulation and another casting immersed therein for a period of one minute. The temperature rose from 114° to 147° during the period of immersion, and there was no fuming during the pickling treatment. A slight tendency to fume was observed during transfer from the bath. The casting was found to lose only 1.1 percent by weight during the pickling operation.

This test is significant in that the casting could not even be completely treated in the conventional bath containing added water and that the temperature rise and metal loss for the casting treated in the bath of the present invention was significantly less than that for the incomplete treatment of the casting in the conventional bath.

Example 4

A conventional pickling bath was prepared according to the following formulation: 250 cc. nitric acid (42° Baumé), 50 cc. water and 75 grams ammonium bifluoride. A casting etched as described in Example 2 was immersed in the bath for a period of one minute, during which the temperature rose from 80 to 92° F. There was substantial fuming both during the period of immersion and upon transfer of the casting from the bath. The resultant surface on the casting was observed to be grey, and the casting was found to have lost 0.58 percent by weight.

Ten grams of chromic acid was added to the above pickling bath, and a second etched casting was immersed therein for a period of one minute, during which the temperature increased from 88° to 98° F. No fuming occurred during the period of immersion of the bath, and there was only a very slight tendency to fume upon transfer from the bath. The resultant surface on the casting was observed to be a very bright white matte, and the
casting was found to have lost only 0.06 percent by weight.

As will be apparent from the foregoing description and examples, use of the novel pickling baths of the present invention enables immersion of castings for periods in excess of normal treatment time without loss in brightness of the finish and, in fact, the castings will normally become a brighter white during extended exposure to the bath, although there is no significant, if any, continued attack upon the base metal other than that necessary to removed the desired small depth at the surface. The solutions of the present invention are characterized by elimination of or substantial freedom from nitrogen oxide fumes not only during the actual pickling operation when the castings are immersed in the bath but also upon removal of the castings from the bath. Furthermore, the controlled reaction is considerably less exothermic and problems of cooling the bath are eliminated although a coolant bath may be employed if so desired. The resultant advantages from both quality and hygienic standpoints are obvious and significant.

I claim:

1. The method of cleaning aluminum castings comprising immersing castings of aluminum alloy having an alloying element insoluble in alkali in a highly alkaline bath to etch a portion of the surface and produce a dark smut thereon comprised of the alkali-insoluble alloying element; and thereafter immersing said castings in a concentrated acid bath containing 1–45 percent by weight hydrofluoric acid, 30–98 percent by weight nitric acid, 0.05–10.0 percent by weight hexavalent chromium ion (calculated as Cr) and not more than 50 percent by weight water, for a period of time sufficient to impart a white surface thereto.

2. The method in accordance with claim 1 wherein said concentrated acid bath contains essentially 3.0–15.0 percent by weight hydrofluoric acid, 50.0–96.5 percent by weight nitric acid and 0.5–2.5 percent by weight hexavalent chromium ion (calculated as Cr) and less than 35.0 percent by weight water.

3. The method of cleaning aluminum castings comprising adding to concentrated nitric acid a hexavalent chromium compound and ammonium acid fluoride to provide a concentrated acid bath containing essentially 1.0–45.0 percent by weight hydrofluoric acid, 30.0–98.0 percent by weight nitric acid, 0.05–10.00 percent by weight hexavalent chromium ion (calculated as Cr) and not more than 50.0 percent by weight water; maintaining said bath at a temperature of 60–130°F.; immersing castings of aluminum alloy having an alloying element insoluble in alkali in a highly alkaline bath to etch a portion of the surface and produce a dark smut thereon comprised of the alkali-insoluble alloying element, said alkali-insoluble alloying element selected from the group consisting of silicon and copper; and thereafter immersing said castings in said concentrated acid bath for a period of time sufficient to impart a white surface thereto, said immersion being characterized by substantial freedom from fuming and controlled rate of aluminum etch.

4. The method in accordance with claim 3 wherein said concentrated acid bath contains essentially 3.0–15.0 percent by weight hydrofluoric acid, 45.0–96.5 percent by weight nitric acid and 0.5–2.5 percent by weight hexavalent chromium ion (calculated as Cr) and less than 35.0 percent by weight water.

5. The method in accordance with claim 3 wherein said alloying element is silicon.

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