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METAL TREATING COMPOSITIONS AND PROCESSES

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This invention relates to the art of blackening aluminum surfaces or surfaces of aluminum alloy metals in which aluminum is the major ingredient, and to the novel aluminum blackening compositions for accomplishing this result.

Aluminum and its alloys are of ever-increasing importance for the fabrication of countless items because of the lightness, workability, strength and other inherent properties of these metals.

Aluminum has a bright metallic surface which is not receptive to or retentive of applied colored coatings or protective coatings of oil or wax and which becomes whitish in color upon prolonged exposure to the atmosphere due to the oxidation of the aluminum to form a white aluminum oxide surface coating.

It is well known to electrolytically plate or anodize aluminum to form thereon a non-corrosive non-oxidizable coating which protects the underlying aluminum against contact with the atmosphere and which in turn may be dyed any desired color. While such anodizing processes are effective in accomplishing the desired results, they are nevertheless slow, costly and unavailable to those who do not possess electroplating equipment.

It is an object of the present invention to provide an aluminum blackening composition which may be applied at room temperatures or any higher or more convenient temperatures by conventional immersion techniques and in the absence of applied current to form on the aluminum surface black coatings which are strongly bonded and which resist chalking or flaking off.

It is another object of this invention to provide a rapid and inexpensive process for applying coatings to aluminum which are receptive to and retentive of protective wax or oil coatings without the disadvantages of the electrolytic anodizing process.

These and other objects and advantages are accomplished by the present invention as will be clear to those skilled in the art in the light of the following description.

The essence of the present invention resides in the discovery of an aqueous solution of certain water-soluble compounds which cooperate to deposit black or off-black coatings on aluminum surfaces which are immersed therein for relatively short periods of time and at relatively low temperatures.

The aqueous blackening compositions of the present invention are acidic aqueous solutions which contain a mixture of compounds which react with the aluminum surface to render it receptive to the blackening compound, and a mixture of blackening compounds selected from the group consisting of molybdic acid and salts thereof and sulfur-bearing compounds.

It appears that this preferred composition fulfills a twofold effect in which the aluminum surface is both etched and coated with a metallic coating, the etching step rendering the surface receptive to the deposit of black molybdic oxide and the metallic coating step forming a

coating which is reactive with a sulfur-bearing compound to form the black or gray reaction product which appears to be a sulfide.

The first blackening combination in the mixture comprises a water-soluble chlorine compound which ionizes to form chloride ions which function to etch or otherwise roughen the aluminum surface, and molybdic acid or the water-soluble salts thereof which function to deposit black molybdic oxide on the roughened aluminum surface. This combination of materials when used in an aqueous solution having a pH of about 6.5 or less has been found to form black coatings which are firmly bonded to aluminum.

Suitable chlorine compounds include the alkali metal chlorides such as sodium chloride and potassium chloride, ammonium chloride, hydrochloric acid and the like water-soluble ionizable chlorides.

Suitable molybdic oxide liberating compounds are molybdic acid or hydrogen molybdate and the water-soluble salts thereof such as the alkali metal molybdates including sodium molybate and potassium molybdate, ammonium molybdate and the like.

The second blackening combination of the mixture encompassed by the present invention comprises the water-soluble salt of a metal below aluminum in the electromotive series, and a water-soluble sulfur-bearing compound. The metal salt ionizes in solution to form metal cations which deposit in an acid medium on the aluminum surface to form a surface film which appears to be receptive to or reactive to form black metal sulfur compounds or complexes.

Metal salts found suitable for treating the aluminum surface to render it receptive to black metal sulfide deposits include the salts as broadly defined and more specifically includes the sulfates, dichromates, nitrates, chlorides, acetates and other water-soluble salts of metals such as nickel, chromium, cobalt, antimony, bismuth, arsenic and any of the other metals which have a lower electrode potential than aluminum and are therefore below aluminum in the electromotive series and which are therefore replaced from their salts by aluminum.

Water-soluble sulfur-bearing compounds found suitable for the formation of black metal sulfur reaction products in an acid medium include sulfides, thiocyanates, thiosulfates, thioureas, 2-mercaptobenzothiazole, benzothiazyl disulfide, 2-mercaptoimidazoline and the like, and including most preferably sodium thiocyanate, sodium sulfide, sodium hyposulfate and the like.

According to the present invention, an aqueous blackening composition is formulated so as to include both blackening compositions heretofore set out. It has been found that when a single blackening composition is so formulated it provides a bath which blackens aluminum more deeply and more evenly and smoothly than is possible using either of the other compositions alone. From these standpoints the behavior of the combination aqueous blackening composition is synergistic.

This preferred blackening composition includes at least two chemicals which affect the aluminum surface in different manners to render it receptive to the deposit of blacking agents. These chemicals are the chlorides which tend to etch or otherwise attack the aluminum surface, and the salts of metals below aluminum in the electromotive series which displace the aluminum to form a metallic film which is reactive to form black metal sulfur compounds or complexes on the surface thereof.

The composition also includes at least two blackening compounds, one of which deposits black molybdic oxide on the aluminum and the other of which contains sulfur and is reactive with the deposited metal film to form the black metal sulfur compounds or complexes.

The blackening compositions contain the following ingredients in the following proportions:

Ingredient	Range in Percent by Weight	
	Broad	Preferred
Molybdic acid or salt	2 to 25	3 to 10
Metal salt	3 to 40	3 to 20
Water-soluble chloride	40 to 80	50 to 60
Sulfur-bearing compound	0.5 to 20	1 to 5
Acid	5 to 60	10 to 30
Fluorine-bearing compound	0 to 20	5 to 15

The following example is illustrative of a preferred composition for use according to the present invention. However the specific ingredients and proportions are set forth as illustrative and should not be considered limitative, possible variations being clear to those skilled in the art in the light of the disclosure set out hereinbefore in connection with the previous formulation.

Example 1

Ingredients:	Percent by weight
Molybdic acid	5
Nickel sulfate	5
Potassium chrome sulfate	5
Ammonium chloride	58.5
Sodium thiocyanate	1.5
Sodium bisulfate	15
Ammonium silico fluoride	10

These ingredients are dissolved in water in a concentration ranging from about 1 ounce per gallon up to about 3 or more pounds per gallon depending upon the results desired. In most cases it is preferred to use a concentration in the area of from 2 to 10 ounces per gallon and most preferably about 6 ounces per gallon of water.

The fluoride ingredient is found to cooperate with the chloride in etching the aluminum surface. Similar results are obtained through the use of soluble fluoborates, fluorides and bifluorides. If hydrofluoric acid is used for this purpose it may also function to replace some of the acidifying agent such as the sodium bisulfate.

A blackening bath prepared in this manner is preferably heated to a temperature of between about 120° F. and 180° F. and most preferably between 150° F. and 160° F. for use, although it has been found effective in accomplishing the desired result at temperatures as low as about 50° F. and as high as its boiling temperature which is somewhat in excess of 212° F. Low temperatures require longer immersion periods while high temperatures result in deposition too rapidly and quite unevenly.

The aluminum pieces are immersed in the blackening composition for a period of from 1 to 30 minutes depending upon the specific acidity of the solution and its temperature. Generally an immersion time of from 10 to 15 minutes is sufficient to form a dark black deposit which is smooth and even and which is firmly anchored to the aluminum surface. The aluminum is removed from the composition and washed or rinsed.

In cases where it is desired to further treat the aluminum to provide it with an oxidation-resisting, corrosion-resistant coating, the blackened aluminum pieces are immersed in any conventional wax, oil or resin composition to deposit over the blackened surface a protective coating or shield. This is not practical with untreated aluminum since the surface has no affinity for an oil, wax or resin coating and attempts to apply and retain such coatings thereto are unsuccessful. However the present blackened deposits on aluminum are found to provide a

perfect receptive surface for such protective coatings and appear to become integrated therewith to form a solid bond.

As protective coatings it is preferred to use thin solutions of oils and waxes which penetrate the blackened deposit on the aluminum and displace any water remaining therein as a residue of the aqueous blackening composition. When the pieces are withdrawn from the protective coating solutions the coatings dry quite rapidly in the form of very thin protective films or shields.

The phrase "blackening composition" as used herein and in the appended claims is intended to include compositions useful for applying jet black or off-black coatings including those in which the deposit is rather light or thin and which appear to have a gray color due partly to the show-through of the underlying aluminum.

While the compositions of the present invention have been discussed primarily in connection with their use in the blackening of aluminum and aluminum alloy metals, it should be understood that the present compositions are also useful for the blackening of other metals such as iron, stainless steel, brass, copper, zinc, titanium, magnesium and the like. The present compositions are particularly adapted for the coloration of aluminum in view of the many problems encountered in connection with the coloration of aluminum and the provision of aluminum with a coating receptive to protective outer coatings of oil or wax.

Variations and modifications may be made within the scope of the claims and portions of the improvements may be used without others.

We claim:

1. The method of blackening aluminum which comprises the steps of preparing a blackening composition by dissolving in water from about 1 ounce to about 3 pounds per gallon of a mixture of compounds which are reactive with aluminum to render it receptive to the deposit of blackening compounds comprising up to 80% by weight of a water-ionizable chloride and from 3% to 40% by weight of water-soluble salt of a metal falling below aluminum in the electromotive series, and a mixture of blackening compounds comprising from 0.5% to 20% by weight of water-soluble sulfur-bearing compound capable of forming a black metal-sulfur reaction product upon reaction with the said metal falling below aluminum in the electromotive series and from 2% to 25% by weight of water-soluble molybdate, maintaining the pH of the solution below about 6.5, maintaining the temperature of the solution within the range of from about 50° F. to about 212° F., immersing the aluminum into the blackening composition for a period of from 1 to 30 minutes, and removing the blackened aluminum.

2. The method according to claim 1 in which the temperature of the solution is maintained within the range of from about 120° F. to about 180° F.

3. The method according to claim 1 in which the water-ionizable chloride is selected from the group consisting of alkali metal chlorides, ammonium chloride and hydrogen chloride.

4. The method according to claim 1 in which the sulfur-bearing compound is selected from the group consisting of a sulfide, thiosulfate, thiocyanate, thiourea, 2-mercaptobenzothiazole, benzothiazyl disulfide and 2-mercaptoimidazoline.

5. A blackening composition useful for the blackening of aluminum surfaces when dissolved in an aqueous solution in an amount ranging from about 1 ounce to about 3 pounds per gallon, said composition comprising a mixture of compounds which are reactive with aluminum to render it receptive to the deposit of blackening compounds and which comprise up to about 80% by weight of a water ionizable chloride and from 3% to 40% by weight of water-soluble salt of a metal falling below aluminum in the electromotive series, and a mixture of blackening compounds comprising from 0.5% to 20% by weight of water-soluble sulfur-bearing compound capable of form-

ing a black metal-sulfur reaction product upon reaction with the said metal falling below aluminum in the electromotive series and from 2% to 25% by weight of water-soluble molybdate.

6. A blackening composition according to claim 1 in which the water-ionizable chloride is selected from the group consisting of alkali metal chlorides, ammonium chloride and hydrogen chloride.

7. A blackening composition according to claim 1 in which the sulfur-bearing compound is selected from the group consisting of a sulfide, thiosulfate, thiocyanate, thiourea, 2-mercaptobenzothiazole, benzothiazyl disulfide and 2-mercaptoimidazoline.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, lines 40,43,46,74 and 75, before "water-soluble," each occurrence, insert -- a --; column 5, line 3, before "water-" insert -- a --; lines 5 and 9, for the claim reference numeral "1", each occurrence, read -- 5 --.

Signed and sealed this 2nd day of January 1968.

(SEAL)
Attest:

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EDWARD J. BRENNER
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