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2,844,496

FORMATION OF CORROSION RESISTANT FILMS ON ALUMINUM

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No Drawing. Application February 25, 1957
Serial No. 641,807

18 Claims. (Cl. 148—6.21)

This invention relates to the production of corrosion resistant films on the surface of aluminum and aluminum alloys.

While the corrosion resistance of pure aluminum is known to be excellent, the use of alloying elements to improve the strength and physical properties of aluminum has lowered the corrosion resistance of the metal to such an extent that protective films are necessary for commercial use. In addition it is well known that paints, enamels and other organic finishing materials have poor adhesion to metallic aluminum and aluminum alloys and it is necessary to provide adherent films compatible with organic coatings in order to have satisfactory adhesion. In the past such films have been produced by the elaborate time-consuming and expensive processes such as electrolytic anodizing. Other films have been produced in the past by treatment in alkaline oxidizing baths. However, due to the well-known corrosive attack of alkalis on aluminum parts, the surfaces have been badly etched and in some instances alkalis have been retained in pores of the metal to produce subsequent corrosion and failure.

Accordingly it is the object of our invention to improve the techniques of producing corrosion resistant films on aluminum and aluminum alloys.

In fulfilling this object we have devised novel processes which include the use of unique compositions in specially prepared baths in all of which our invention will be found to reside. This will be more fully appreciated from a reading of the following specification containing specific exemplary examples of how our invention may be employed and the particular novelty thereof pointed out in the appended claims.

We have found an acid composition for the production of corrosion resistant films on aluminum and aluminum alloys which does not have the disadvantages inherent in the former processes. It consists essentially of an acid composition containing certain oxidizing and activating agents. The acidity of our composition is produced by sulfamic acid whereas the oxidizing agents are chromic acid, chromates, dichromates and nitrates. Fluorides have been found suitable for use as the activating agent. Alkali metal salts including ammonium of the above have proven satisfactory in the composition. Sulfamic acid has been found to be most suitable in our composition. The etching on aluminum is very slight and this acid if left on the aluminum parts would not tend to produce active corrosion. All of the materials used are solids at normal temperatures. Therefore, the mixture can be packaged as a solid composition. This is an advantage over most prior aluminum-treating compositions which contain liquids, making it necessary in many cases to package them in carboys or other relatively expensive types of containers for liquids.

It is to be understood that the range of composition is very wide and large changes in the proportionate amounts of the several materials can be tolerated and still produce satisfactory results. The following examples together with details of the processes in which they are used

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are illustrative of the ranges of concentration which we have successfully employed:

Example #1

	Parts by weight
5 Sulfamic acid.....	4.7
Chromic acid.....	71.5
Sodium fluoride.....	14.3
Sodium nitrate.....	9.5
10	100.0

This mixture was dissolved in water to produce a concentration of three ounces per gallon. The pH was maintained at 1.8 by adjusting with chromic acid or caustic soda as necessary. A metal part made of Alcoa No. 3 aluminum alloy, after cleaning to remove soil, was immersed for a period of 5 minutes at a temperature of 70° F. The part was then rinsed in running cold water and dried. It showed a light yellow iridescent film. This part showed 984 hours salt spray corrosion resistance.

Example #2

	Parts by weight
Sulfamic acid.....	71.5
25 Sodium dichromate.....	21.4
Sodium fluoride.....	4.3
Potassium nitrate.....	2.8
30	100.0

This mixture was dissolved in water to produce a concentration of three ounces per gallon. The pH was maintained at 1.8 by adjusting with chromic acid or caustic soda as necessary. A metal part made of Alcoa No. 24 aluminum alloy, after cleaning to remove soil, was immersed for a period of 5 minutes at a temperature of 70° F. The part was then rinsed in running cold water and dried. It showed a light yellow iridescent film. This part showed 700 hours' salt spray corrosion resistance.

Example #3

	Parts by weight
40 Sulfamic acid.....	71.5
Potassium dichromate.....	10.7
Ammonium fluoride.....	10.7
45 Sodium nitrate.....	7.1
50	100.0

This mixture was dissolved in water to produce a concentration of three ounces per gallon. The pH was maintained at 1.8 by adjusting with chromic acid or caustic soda as necessary. A metal part made of Alcoa No. 52 aluminum alloy, after cleaning to remove soil, was immersed for a period of 5 minutes, at a temperature of 70° F. The part was then rinsed in running cold water and dried. It shows a light yellow iridescent film. This part showed 900 hours' salt spray corrosion resistance.

Example #4

	Parts by weight
60 Sulfamic acid.....	16.0
Sodium dichromate.....	80.0
Potassium fluoride.....	2.4
Sodium nitrate.....	1.6
65	100.0

This mixture was dissolved in water to produce a concentration of three ounces per gallon. The pH was maintained at 1.6 by adjusting with chromic acid or caustic soda as necessary. A metal part made of Alcoa No. 3 aluminum alloy, after cleaning to remove soil, was immersed for a period of 3 minutes at a temperature of 70° F. The part was then rinsed in running cold water

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and dried. It showed a light yellow iridescent film. This part showed 456 hours' salt spray corrosion resistance.

Example #5

	Parts by weight
Sulfamic acid.....	53.4
Sodium dichromate.....	40.0
Sodium fluoride.....	1.3
Lithium nitrate.....	5.3
	100.0

This mixture was dissolved in water to produce a concentration of three ounces per gallon. The pH was maintained at 1.8 by adjusting with chromic acid or caustic soda as necessary. A metal part made of Alcoa No. 75 aluminum alloy, after cleaning to remove soil, was immersed for a period of 5 minutes at a temperature of 90° F. The part was then rinsed in running cold water and dried. It showed a light yellow iridescent film. This part showed 500 hours' salt spray corrosion resistance.

Example #6

	Parts by weight
Sulfamic acid.....	45.4
Sodium dichromate.....	34.2
Sodium fluoride.....	15.9
Ammonium nitrate.....	4.5
	100.0

This mixture was dissolved in water to produce a concentration of three ounces per gallon. The pH was maintained at 1.8 by adjusting with chromic acid or caustic soda as necessary. A metal part of Alcoa No. 61 aluminum alloy, after cleaning to remove soil, was immersed for a period of 10 minutes at a temperature of 100° F. The part was then rinsed in running cold water and dried. It shows a light yellow iridescent film. This part showed 600 hours' salt spray corrosion resistance.

Example #7

	Parts by weight
Sulfamic acid.....	52.4
Sodium chromate.....	39.4
Sodium fluoride.....	7.9
Potassium nitrate.....	3
	100.0

This mixture was dissolved in water to produce a concentration of one ounce per gallon. The pH was maintained at 1.8 by adjusting with chromic acid or caustic soda as necessary. A metal part made of Alcoa No. 38 aluminum alloy, after cleaning to remove soil, was immersed for a period of 3 minutes at a temperature of 80° F. The part was then rinsed in running cold water and dried. It showed a very light yellow iridescent film. This part showed 490 hours' salt spray corrosion resistance.

Example #8

	Parts by weight
Sulfamic acid.....	34.4
Sodium dichromate.....	26.0
Sodium fluoride.....	5.2
Sodium nitrate.....	34.4
	100.0

This mixture was dissolved in water to produce a concentration of three ounces per gallon. The pH was maintained at 1.8 by adjusting with chromic acid or caustic soda as necessary. A metal part of Alcoa No. 3 aluminum alloy, after cleaning to remove soil, was immersed for a period of 7 minutes at a temperature of 90° F. The part was then rinsed in running cold water and dried. It showed a light yellow iridescent film. This part showed 700 hours' salt spray corrosion resistance.

As will be seen from the foregoing examples, a large range of compositions is possible, all of which obtain

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satisfactory corrosion resistant coatings. For instance, it is not necessary to use sodium dichromate, sodium fluoride, or sodium nitrate since it has been shown that potassium, ammonium and lithium salts are satisfactory. Moreover the range of concentrations, while critical, is still quite broad. For instance in 100 parts, the sulfamic acid may range from about 5 to 72 parts by weight; the alkali metal dichromate from about 11 to 80 parts by weight; the alkali metal fluoride from about 1 to 16 parts by weight; and alkali metal nitrate from about .3 to 34 parts by weight. While satisfactory films will be produced from formulae within the range given above, we have found the following composition to be preferable to include the greatest range of aluminum alloys:

	Parts by weight
Sulfamic acid.....	50.0
Sodium dichromate.....	37.5
Sodium fluoride.....	7.5
Sodium nitrate.....	5.0
	100.0

While our examples have shown the time of immersion to be from 3 to 10 minutes at temperatures of from 70 to 100° F., we have found that immersion time may be less than 1 minute when light coatings are required for special purposes or may be longer than 15 minutes when especially heavy coatings are required. The speed of production of the coating depends somewhat on the temperatures and at low temperatures such as 50° F. somewhat longer times will be required whereas shorter times will be necessary when the temperatures are above 100° F. The uniformity of the film produced, however, is somewhat impaired at temperatures above 100° F. The concentration of the bath may also vary widely. In fact, tests made at as low as ½ ounce per gallon produced almost colorless corrosion resistant films. Concentrations made at higher than 6 ounces per gallon still produce satisfactory films but this is an economic disadvantage and not necessary.

As will be noted in all the examples, the reaction of the bath is highly acidic. The optimum pH appears to be between 1.6 and 2.0 although satisfactory films have been produced with pH as low as 1.2 and as high as 2.6.

While the composition of the film formed is not known with certainty it is believed that it consists essentially of oxides and chromates of aluminum. The sulfamic acid in the formula is useful in controlling the reaction of the bath as well as providing activation. Sulfamic acid is also believed to act as a stabilizer for the bath and to prolong its life without leaving harmful residues on or in the coating. The chromate and nitrate salts are believed to provide the oxidation of the aluminum together with formation of aluminum chromate. The fluoride salt is believed to be an activator and its use produces deeper films more rapidly.

In the examples given above, it will be noted that the corrosion resistant film was of a light yellow color. In a great range of applications of our invention the color of the film is immaterial; however, in many other applications the iridescence and the yellowness is esthetically objectionable.

We have found that, by adding 1 to 2 parts by weight of boric acid to any of the compositions set forth in the foregoing examples, the iridescence in the resulting film may be eliminated. Not only are more attractive light yellow films produced but there is no substantial reduction in the corrosion resistance of these films.

We have further found that, by adding 3 to 5 parts by weight of boric acid to any of the previously described examples, the corrosion resistant film will approach a colorless condition and that the addition of 5 to 10 parts by weight of boric acid will give a truly colorless film. By way of illustration, 5 parts by weight of boric acid were added to the composition of Example #2 and an

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aluminum part then treated in the manner described. The part had a colorless film and showed just under 400 hours' salt spray corrosion resistance. While this is somewhat less corrosion resistance than what may be obtained from compositions containing less or no boric acid, it is still a definite advancement over prior coatings of this type and finds widespread commercial utility.

Having thus described our invention what we claim as novel and desire to secure by Letters Patent of the United States is:

1. A composition of matter for use in providing corrosion resistant films on aluminum and alloys thereof consisting essentially of, in 100 parts, about 5 to 72 parts by weight of sulfamic acid; about 1 to 16 parts by weight of an alkali metal fluoride; about .3 to 34 parts by weight of an alkali metal nitrate, and about 11 to 80 parts by weight of a compound chosen from the group consisting of chromic acid, alkali metal chromates and alkali metal dichromates.

2. A composition of matter as set forth in claim 1, which additionally includes 1 to 10 parts by weight of boric acid.

3. A composition of matter as set forth in claim 1, which additionally includes 1 to 5 parts by weight of boric acid.

4. A composition of matter for use in providing corrosion resistant films on aluminum and alloys thereof consisting essentially of, in 100 parts, about 5 to 72 parts by weight of sulfamic acid; about 11 to 80 parts by weight of chromic acid; about 1 to 16 parts by weight of sodium fluoride; and about .3 to 34 parts by weight of sodium nitrate.

5. A composition of matter for use in providing corrosion resistant films on aluminum and alloys thereof consisting essentially of, in 100 parts, about 5 to 72 parts by weight of sulfamic acid; about 11 to 80 parts by weight of sodium dichromate; about 1 to 16 parts by weight of sodium fluoride; and about .3 to 34 parts by weight of sodium nitrate.

6. A composition of matter for use in providing corrosion resistant films on aluminum and alloys thereof consisting essentially of; in 100 parts, about 5 to 72 parts by weight of sulfamic acid; about 11 to 80 parts by weight of potassium dichromate; about 1 to 16 parts by weight of potassium fluoride; and about .3 to 34 parts by weight of potassium nitrate.

7. A composition of matter for use in providing corrosion resistant films on aluminum and alloys thereof consisting essentially of, in 100 parts, about 5 to 72 parts by weight of sulfamic acid; about 11 to 80 parts by weight of ammonium dichromate; about 1 to 16 parts by weight of ammonium fluoride; and about .3 to 34 parts by weight of ammonium nitrate.

8. A composition of matter for use in providing corrosion resistant films on aluminum and alloys thereof consisting essentially of, in 100 parts, about 5 to 72 parts by weight of sulfamic acid; about 11 to 80 parts by weight of lithium dichromate; about 1 to 16 parts by weight of lithium fluoride; and about .3 to 34 parts by weight of lithium nitrate.

9. A composition of matter for use in providing corrosion resistant films on aluminum and alloys thereof consisting essentially of, in 100 parts, 50 parts by weight of sulfamic acid; 37.5 parts by weight of sodium dichromate; 7.5 parts by weight of sodium fluoride; and 5 parts by weight of sodium nitrate.

10. A composition of matter as set forth in claim 9, which additionally includes 1 to 2 parts by weight of boric acid.

11. A composition of matter as set forth in claim 9,

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which additionally includes 3 to 10 parts by weight of boric acid.

12. An aqueous bath for improving the corrosion resistance of aluminum and alloys thereof, said bath having a pH of 1.2 to 2.6 and comprising a water solution containing $\frac{1}{2}$ ounce to 6 ounces per gallon of a mixture comprising, in 100 parts, about 5 to 72 parts by weight of sulfamic acid; about 1 to 16 parts by weight of an alkali metal fluoride; about .3 to 34 parts by weight of an alkali metal nitrate, and about 11 to 80 parts by weight of a compound chosen from the group consisting of chromic acid, alkali metal chromates and alkali metal dichromates.

13. An aqueous bath as set forth in claim 12 wherein the said mixture additionally includes 1 to 10 parts by weight of boric acid.

14. An aqueous bath for improving the corrosion resistance of aluminum and alloys thereof, said bath having a pH of 1.2 to 2.6 and comprising a water solution containing $\frac{1}{2}$ ounce to 6 ounces per gallon of a mixture comprising, in 100 parts, 50 parts by weight of sulfamic acid; 37.5 parts by weight of sodium dichromate; 7.5 parts by weight of sodium fluoride; and 5 parts by weight of sodium nitrate.

15. A process for improving the corrosion resistance of aluminum and alloys thereof consisting of the immersion of the metal in a water solution containing $\frac{1}{2}$ ounce to 6 ounces per gallon of a mixture comprising, in 100 parts, about 5 to 72 parts by weight of sulfamic acid; about 1 to 16 parts by weight of an alkali metal fluoride; about .3 to 34 parts by weight of an alkali metal nitrate, and about 11 to 80 parts by weight of a compound chosen from the group consisting of chromic acid, alkali metal chromates and alkali metal dichromates, for a sufficient length of time to produce a desired film thickness; maintaining the pH of the bath at 1.2 to 2.6 and the temperature of the bath between 50° F. and 100° F; rinsing said metal in water and then drying same.

16. A process as set forth in claim 15, wherein the said mixture additionally includes 1 to 5 parts by weight of boric acid.

17. A process as set forth in claim 15, wherein the said mixture additionally includes 3 to 10 parts by weight of boric acid.

18. A process for improving the corrosion resistance of aluminum and alloys thereof consisting of the immersion of the metal in a water solution containing $\frac{1}{2}$ ounce to 6 ounces per gallon of a mixture comprising, in 100 parts, 50 parts by weight of sulfamic acid; 37.5 parts by weight of sodium dichromate; 7.5 parts by weight of sodium fluoride; and 5 parts by weight of sodium nitrate, for a sufficient length of time to produce a desired film thickness; maintaining the pH of the bath at 1.2 to 2.6 and the temperature of the bath between 50° F. and 100° F; rinsing said metal in water and then drying same.

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