

PATENT SPECIFICATION

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(54) COMPOSITIONS AND PROCESSES FOR THE COATING OF ALUMINIUM

(71) We, AMCHEM PRODUCTS, INC., a Corporation organized and existing under the Laws of the Commonwealth of Pennsylvania, United States of America, of Brookside Avenue, Ambler, Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to compositions and processes for the coating of aluminium. More particularly, it concerns the application to aluminium surfaces of coatings which are corrosion resistant, to which overlying coatings (such as those formed from paints, inks and lacquers) adhere excellently, and which may be formed using aqueous coating solutions which are free of toxic materials such as chromates and ferricyanide.

It is known to treat aluminium surfaces with aqueous coating solutions that are effective in forming on the surface coatings which are corrosion resistant (and thereby protect the surface from degradation due to attack by corrosive materials). In general, the coatings formed from such solutions are also required to have properties such that subsequently-applied decorative or functional coatings (formed from materials such as paints, lacquers and inks, and referred to hereinafter as "siccative coatings") adhere tightly and strongly to the base coating.

An example of an aluminium coating operation, and one in which the present invention has particularly good applicability, is the coating of aluminium cans. In general, the corrosion-resistant and adherent coatings which are applied to aluminium cans are in addition required to be uniformly clear and colourless, so that the coated cans have the bright, shiny natural appearance of the underlying aluminium (which is desired in the final product even though portions of the can may be covered with coloured paints or inks). Furthermore, the coated aluminium cans are

required to resist discolouration when subjected to moderately hot water — for example, water having a temperature within the range of 140° to 170°F (60° to 77°C). By way of background, it should be noted in this connection that in certain applications aluminium cans are so treated (the can industry generally refers to this process as "pasteurization"), and this treatment has a tendency to cause an uncoated — or even a coated — aluminium surface to blacken or otherwise discolour, thereby leaving the can with an unattractive appearance. In general, when the term "corrosion resistance" is used hereinafter in connection with coatings for aluminium cans, it includes within its meaning the ability of the coated surface to resist blackening or other discolouration when exposed to hot water treatment.

There are presently available coating solutions which form on aluminium surfaces uniformly clear and colourless coatings. One of the most widely used such coating solutions contains chromic acid, phosphoric acid and hydrofluoric acid. Now, while such a coating solution is indeed capable of forming coatings of the type desired, its use creates severe waste disposal problems because of the presence therein of hexavalent chromium, a very toxic material. It would be of great advantage to the can industry to have available coating solutions which do not contain hexavalent chromium (or other toxic materials — such as ferro or ferrocyanide, and salts of manganese, cobalt, iron and nickel, and any of the transition elements from vanadium to copper inclusive).

This invention seeks to provide an aqueous coating solution which is free of hexavalent chromium and other toxic materials, and which is capable of forming on an aluminium surface a uniformly clear and colourless coating which is corrosion resistant and adheres excellently to subsequently-applied siccative coatings. This invention also seeks to provide a process of coating using such a solution.

In one aspect, therefore, this invention

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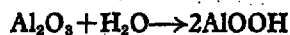
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provides a process for the formation of a coating upon an aluminium surface, in which process there is applied to the aluminium surface an acidic aqueous coating solution comprising at least 3 ppm dissolved zirconium, at least 5 ppm fluoride, and at least 10 ppm dissolved boron having a pH of from 3 to 5, and being free of ferro- and ferricyanide, any organic polymeric material, chromium, manganese, iron, cobalt, molybdenum and tungsten, the solution being applied to the aluminium surface for such a time and at such a temperature as to form thereon a uniformly clear and colourless coating so that when the coated surface is thereafter subjected to boiling water for a 2 minute period it does not blacken.

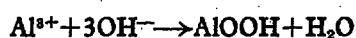
The process of the present invention can be used to coat the surface of pure aluminium or of alloys of aluminium (for example, aluminium alloys containing minor amounts of such materials as magnesium, manganese, copper and silicon). Two of the currently most popular alloys used in the aluminium can industry are aluminium alloys 3003 and 3004 (respectively Al, 1.2% Mn, rest impurities, and Al, 1.2% Mn, 1.0%, Mg, rest impurities).

As mentioned above, there are conditions under which an aluminium surface which is initially bright and shiny in appearance has a tendency to darken or turn black — typically when exposed to hot water. This may be explained as follows (though the invention is not limited thereby).

Aluminium is generally covered with a thin, continuous, protective film of Al_2O_3 , which is commonly known as a "barrier film". However, when aluminium is immersed in water the outer surface of the Al_2O_3 film is hydroxylated to various hydroxides. During the initial stages, a dense protonated film of $AlOOH$ is formed on the outer surface of the Al_2O_3 barrier film, which always remains strongly adhered to the aluminium metal, by the reaction



During the reaction, Al^{3+} ions from the underlying metal migrate across the Al_2O_3 film (due to the potential gradient and concentration gradient of ions), and the Al^{3+} ions take up OH^- ions at the Al_2O_3/H_2O interface, leading to the formation of more $AlOOH$ according to the reaction



(the $AlOOH$ thus formed becomes a part of the dense $AlOOH$ film). At the same time, protons (H^+ ions) in the hydrated oxide film diffuse inwardly, and are replenished with H^+ ions from the electrolyte. Therefore, an upward change of pH in the water may be observed during the reaction.

As the reaction continues, the "oxide" film grows in thickness by the ionic migration mentioned above. However, the dense protonated "oxide" film ($Al_2O_3/AlOOH$) reaches a limiting (steady-state) thickness, with the rate of diffusion of active H^+ and Al^{3+} ions through the film equaling the rate of transformation of the outer layer into $Al(OH)_3$ by the reaction



as the total thickness of the film becomes greater. Unfortunately, as more $Al(OH)_3$ is formed the continuity of the $Al(OH)_3$ with the surface film ($Al_2O_3/AlOOH$) is disturbed, and the outer $Al(OH)_3$ layer becomes colloidal and porous in nature. It is the reflection of light through this porous $Al(OH)_3$ film which gives the surface its darkened or blackened appearance.

Thus, two types of coating are produced on an aluminium surface when it is subjected to hot water. An inner coating of $Al_2O_3/AlOOH$ is continuous and dense, and this coating is resistant to corrosion, and is an excellent base for anchoring a paint or lacquer. On the other hand, the outer $Al(OH)_3$ layer is composed of randomly oriented, loosely connected platelets. This porous layer has poor corrosion resistance and poor adhesive properties.

It is believed that treatment by the process of the invention results in zirconium being introduced into the surface layers of the $Al(OH)_3$ coating as it is formed, and that the complex so formed prevents any further build up of the $Al(OH)_3$ layers primarily by blocking off ion migration (and thus stopping the further formation of $AlOOH$ and its subsequent conversion to $Al(OH)_3$). The mechanism suggests that in H_2O alone $(OH)^-$ ions become a part of the film structure, the protons of the hydrated film diffuse inwardly because of the concentration gradient and potential gradient, and the H^+ ion is immediately replenished from the electrolyte. In the solutions of the invention, however, it is believed that four such protons will be replaced by a single Zr^{4+} ion, which in turn will reduce the $(OH)^-$ ion concentration at the surface of the film. When the Zr becomes chemically bonded to the hydrated alumina film, the concentration gradient across the film of protons is reduced, and thus the formation of $Al(OH)_3$ is prevented. This in turn improves the corrosion resistance of the film overall. Auger Electron Spectrum analysis of coatings formed by the process of the invention has shown the presence of both zirconium and fluorine in the coating. As will be seen in the test results reported below, the process of the invention is capable of providing coated surfaces which are not only initially uniformly bright and shiny, but remain so even when

the coated aluminium surface is subjected to boiling water.

The zirconium in the coating solutions of the invention can be obtained from almost any water-soluble zirconium compound. Typical examples are zirconium nitrate or sulphate, zirconium fluoride, or a zirconium complex such as an ammonium or alkali-metal fluozirconate. The use of zirconium fluoride (ZrF_4) or a fluozirconate is often advantageous, since it may also act as a source of the required fluoride. Subject to the comments made hereinafter, the amount of zirconium may in general be from the lower limit of 3 ppm up to the solubility limit of the zirconium compound in the solution. In a make-up bath, however, a preferred lower limit is 50 ppm.

The fluoride in the coating solutions of the invention can also be obtained from almost any water-soluble fluorine compound. Typical examples are hydrofluoric acid and its salts (such as zirconium fluoride), and complexes such as an ammonium or alkali-metal fluozirconate. The use of zirconium fluoride or a fluozirconate is generally advantageous, in that it acts as a source of zirconium as well. Subject again to the comments made hereinafter, the amount of fluoride may in general be from the lower limit of 5 ppm up to the point at which there is so much fluoride as to cause an undesirable degree of etching of the aluminium surface (resulting in the surface losing its bright, shiny look, and becoming dull and "frosted"). In a make-up bath a preferred lower limit is 75 ppm and a preferred upper limit is 200 ppm, but in a used bath there may be as much as 1000 ppm fluoride without detriment.

The coating solutions of the invention also include dissolved boron.

The boron may conveniently be added as boric acid, boric oxide or a water-soluble salt of boric acid (for example an ammonium or alkali-metal borate). As mentioned hereinbefore, Auger Electron Spectrum analysis of coatings formed by the solutions of the invention has shown the presence of zirconium in the coating, and it is found that the amount of zirconium in the coating is greatly increased when the solution contains boron. For example, in one series of tests analyses showed relative zirconium intensity values of from 20 to 50 times greater when the solution contained boric acid than the values obtained when the solution contained no boron. The amount of boron in the solution ranges from a lower limit of 10 ppm up to the solubility limit of the boron compound in the solution. Normally, however, amounts of boron in excess of 200 ppm do not yield proportional increases in the properties desired, and for good overall results a preferred upper concentration limit is about 125 ppm.

The pH of the solutions of the invention is from 3 to 5. If the solution is too acidic, the aluminium surface exposed thereto becomes etched, and it has a grey-to-bluish haze rather than the natural bright and shiny finish that is generally desired. Furthermore, because a solution which is too acidic will cause a relatively large amount of aluminium to be dissolved, there is then formed relatively large amounts of $Al(OH)_3$ on the aluminium surface (as mentioned above, it is believed that $Al(OH)_3$ is the cause of an aluminium surface having poor adhesive properties, and blackening after it is subjected to boiling water). On the other hand, the acidity of the solution should be high enough for the zirconium to remain in the coating solution in dissolved form. In general, it has been found that the solutions of the invention should have a pH within the range of from 3 to 5 in order for the solution to form colourless and clear coatings, and in order to maintain the zirconium in dissolved form in the solution.

If it is desired to adjust the pH of the coating solution, it is much preferred to do so by adding nitric acid. Problems can be encountered if an acid such as phosphoric is used, because this acid tends to precipitate the zirconium from the solution as zirconium phosphate. Furthermore, the use of hydrofluoric acid to adjust pH can also lead to problems, because it is difficult to control pH adjustment with this material, and it can tend to pit and attack the aluminium surface. Nevertheless, it may be desirable to add hydrofluoric acid to a worked bath of the coating solution to complex aluminium that is dissolved during coating formation. Suitable amounts of HF can be added to perform this function while avoiding the use of amounts which tend to pit the aluminium surface. For example, a worked bath can contain up to 1000 ppm or more of fluoride.

Although various ranges for zirconium and fluoride amounts in the solution have been given above, in fact the effective amounts of these materials will depend on various factors such as the age of the solution, the temperature of the solution, the amount of boron present, the period of contact with the aluminium surface, and the method of application. A freshly prepared coating solution having a pH of about 4 and containing as little as 3 ppm zirconium and 5 ppm fluoride, and applied by spraying at relatively high temperatures (for example, 130° to $150^\circ F$ — 55° to $66^\circ C$) can be used effectively. For a make-up bath to be used in an industrial operation, it is preferred that the coating solution contain at least 50 ppm zirconium and at least 75 ppm fluoride. The upper limit on the amount of Zr is governed by its solubility in the solution, but the upper limit on the fluoride (including fluozirconate compounds) is governed mainly by the amount

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at which the fluoride causes etching of the aluminium surface, which in turn tends to produce a dull and frosty surface. The concentration of fluoride at which this occurs will depend on factors such as pH, temperature of application, and contact time. In general, it is recommended that the concentration of fluoride in a make-up bath be no greater than about 200 ppm.

Very preferably the solution will not contain any (or any appreciable amounts of) transition element from vanadium to copper inclusive.

The solution can be applied to the aluminium surface by any suitable method. Preferably, the solution can be applied by spraying, but the aluminium surface can also be immersed in the solution, or treated by flow-coating techniques.

The temperature of the coating solution should be such that the zirconium is chemically bonded to the aluminium hydrated oxide lattice. In general, the temperature of the solution should be in excess of 100°F (38°C) to effect this, though preferably the solution will have a temperature of from 120° to 150°F (50° to 66°C). Temperatures in excess of about 160°F (71°C) tend to produce a dull frosty surface.

The desired coatings can be formed by contacting the aluminium surface with the coating solution for at least 15 seconds. In general, the lower the temperature of the coating solution, the longer need be the contact time, and the higher the temperature of the solution, the shorter need be the contact time. It will normally be unnecessary to contact the surface with the coating solution for more than 1 minute.

Prior to applying the solution, the aluminium surface should be cleaned. Available acid or alkaline cleaners can be used. After cleaning, the surface should be water rinsed. Also, after the coating solution has been applied the aluminium surface should be water rinsed, including a deionized water rinse (rinsing with water that contains amounts of metal ions can lead to a coating which has poor adhesive properties). After the coated surface has been water rinsed, the coating should be dried. This can be done conveniently in an oven having forced circulation of hot air, though other available drying methods can be used. After the coating has been dried, it can be given a siccative finish if so desired. Finally, after the cans have been given the siccative finish they may, if so desired, be subjected to pasteurization conditions. Cans treated by the process of the invention will resist blackening under pasteurization conditions for at least 2, and generally 15, minutes.

As mentioned above, it appears that subjecting an aluminium surface to a solution of the present invention modifies the surface in such a way that zirconium is chemically

bonded to the aluminium hydrated oxides on the surface. A series of tests has shown the formation of coatings having a thickness within the range of from 200 to 750Å and a weight within the range of from 10 to 35 mg/sq.ft. (108 to 376.5 mg/m²), with the zirconium comprising from 5 to 35 wt. % of the coating. The figures are presented for illustrative purposes only.

The invention extends, of course, to an aluminium surface whenever coated by the process of the invention.

The coating solutions described above are themselves novel and inventive. In another aspect, therefore, this invention provides an acidic aqueous coating solution for coating aluminium, the solution comprising at least 3 ppm dissolved zirconium, at least 5 ppm fluoride and at least 10 ppm dissolved boron, having a pH of from 3 to 5, and being free of ferro- and ferricyanide, any organic polymeric material, chromium, manganese, iron, cobalt, nickel, molybdenum and tungsten, the solution being capable of forming on an aluminium surface a uniformly clear and colourless coating and providing a coated surface which resists blackening when it is thereafter subjected to boiling water for a 2 minute period.

The various features of these solutions of the invention are fully described hereinbefore.

The following Examples and Comparative Test Results are now given, though only by way of illustration, to show details of the process and solutions of the invention. The following points should, however, first be noted:

1) Unless stated otherwise, the aluminium surfaces treated with the solution identified in the Examples were drawn and ironed can surfaces which were first degreased, as necessary, in a mild aqueous alkaline cleaner (comprising 25 wt. % sodium tripolyphosphate, 58 wt. % borax, 4 wt. % of sodium gluconate and the remainder being other surface active agents), rinsed with tap water, cleaned by spraying in a hot aqueous sulphuric acid cleaner, and finally rinsed with tap water. The can surfaces thus cleaned were bright and shiny in appearance.

2) After treatment with the solutions identified in the Examples, the treated cans were rinsed in deionized water, then dried in an oven for two minutes at 400°F (204°C).

3) The treated, rinsed and dried cans were tested for corrosion resistance according to a test commonly used (and referred to in the can industry as the "pasteurization test"). This consisted of immersing the cans in boiling tap water for 15 minutes. A cleaned-only can surface having thereon a naturally formed Al₂O₃ film turned black in a few minutes; treatment of the can surfaces with coating solutions of the invention resulted in the provision of coated surfaces which were not

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blackened or otherwise discoloured in this test.

5 4) Aluminium cans treated with the solutions described in the Examples were also tested for paint adhesion. Thus, after the cans were dried as described above, the coated surface was painted with a white base coat [5007-L white modified acrylic, sold by Celanese (Registered Trade Mark)], and thereafter baked in an oven for one minute. 10 The painted cans were then immersed in boiling 1% detergent [Joy (Registered Trade Mark) solution] for 30 minutes. Immediately after removing the painted cans from the detergent solution, they were rinsed in water, 15 and the excess water was removed from the surface by wiping. The painted cans were then cross-hatched and taped, and tested for paint adhesion (this is a conventional test which includes applying Cellophane [Registered Trade Mark] sticky tape firmly over 20 the cross-hatched area, and then drawing the

tape back against itself with a rapid pulling motion such that the tape is pulled away from the cross-hatched area; the test is rated "excellent" when the tape does not peel any paint from the surface, otherwise it is rated "fail", "fair" or "good", depending upon the amount of paint peeled off).

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Examples 1—14.

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In this first group of Examples, the cans were treated with various acidic aqueous solutions containing potassium fluozirconate (K_2ZrF_6), and having a pH as indicated in Table I below. Boric acid was added to some of the solutions (as indicated in the Table).

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Each of the cans was sprayed with the appropriate coating solution for a period of 45 seconds; the temperatures of the coating solutions are also given in the Table.

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The coating solutions contained HNO_3 (also) in amounts which imparted to the solutions the pHs indicated.

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TABLE 1

Ex. No.	K_2ZrF_6 (g/l)	Zr (ppm)	F (ppm)	Boric Acid (g/l)	Boron (ppm)	pH	Temp. of Solution °F/°C	Pasteurization Blackening	Paint Adhesion Test
1	0.1	32	40	None	—	3.7	110/44	Slight	Fair
2	0.1	32	40	None	—	„	130/55	Very slight	Good
3	0.1	32	40	None	—	„	150/66	Very slight	Good
4	0.1	32	40	1.0	180	3.8	110/44	None	Excellent
5	0.1	32	40	1.0	180	„	130/55	„	„
6	0.1	32	40	1.0	180	„	150/66	„	„
7	0.2	64	80	None	—	„	110/44	„	„
8	0.2	64	80	None	—	„	130/55	„	„
9	0.4	128	160	None	—	3.9	110/44	„	„
10	0.4	128	160	None	—	„	130/55	„	„
11	0.2	64	80	1.0	180	3.7	110/44	„	„
12	0.2	64	80	1.0	180	„	130/55	„	„
13	0.4	128	160	3.0	540	3.8	110/44	„	„
14	0.4	128	160	3.0	540	„	130/55	„	„

The coatings formed from the coating solutions identified in Table 1 were uniformly clear and colourless, and the coated surfaces were bright and shiny in appearance. Thus, the coatings were formed without changing the bright and shiny appearance of the aluminium surface. From Table 1 it can be seen that the use of potassium fluozirconate in the amount of 0.1 g/l (Zr=32 ppm; F=40 ppm) at the conditions stated forms coatings which tend to blacken slightly when subjected to the pasteurization test (Example Nos. 1—3). On the other hand, Example Nos. 4—6 show that the use of boric acid along with 0.1 g/l of potassium fluozirconate gives coatings which do not blacken and which have improved paint adhesive properties. Examples 7—10 show that the use of amounts of potassium fluozirconate in excess of 0.1 g/l gives, under the conditions stated, coatings which have excellent corrosion resistance and paint adhesion. Example Nos. 11—14 show that the use of higher concentrations of potassium fluozirconate masks the effect of the boric acid.

Example 15.

This Example shows the effect of the con-

tinued use of a coating solution of the invention on the pH of the solution. Four litres of coating solution containing the ingredients set forth below were used in this series of tests.

Ingredients

K_2ZrF_6	0.4 g/l (Zr=128 ppm; F=160 ppm)	
H_3BO_3	5.0 g/l (B=900 ppm)	35
KNO_3	10.0 g/l	
$HNO_3(4N)$	0.4 ml/l	

Aluminium cans were each sprayed for 45 seconds with the above coating solution which was heated to and maintained at a temperature of 130°F (55°C). Excess coating solution which did not remain on the cans was collected and recycled to the coating bath, from which the solution was drawn during the spray operation. A pH monitor was set up in the bath to record the pH. Table 2 below shows the pH of the bath after the stated number of cans had been treated, and also shows the results of subjecting the cans to the pasteurization test.

TABLE 2

Can Number	pH	Pasteurization Blackening
1	4.20	None
6	4.70	"
10	4.90	Slight
12	4.99	"
16	5.01	"
22	5.20	"
28	5.30	"

From the Table it can be seen that, as the bath of coating solution is used, hydrogen ion is consumed and the pH of the solution rises (thus indicating that hydrogen ion is consumed during the reaction of the coating solution with the aluminium surface). As the pH rises, potassium fluozirconate begins to precipitate, and the coating solution becomes cloudy. Precipitation of the potassium fluozirconate decreases the activity of the coating solution, which then tends to produce coated surfaces which tend to blacken when subjected to the pasteurization test. This can be avoided by replenishing the solution with fluozirconate and/or an acid (such as nitric acid) in

amounts which lower the pH to within the aforementioned range.

Example 16.

The following coating solution was used to coat aluminium surfaces in accordance with the invention

Ingredients

K_2ZrF_6	0.4 g/l (Zr=128 ppm; F=160 ppm)	
boric acid	5.0 g/l (B=900 ppm)	75
Potassium nitrate	10.0 g/l	

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The above coating solution, which had a pH of 4, was sprayed onto an aluminium can surface for a period of 45 seconds at a temperature of 120°F (49°C). The Auger Electron Spectrum of the coated surface showed that the coating formed from the above coating solution contained mainly Zr, F and Al₂O₃ — and some Ca, apparently from the tap water from which the solution was prepared, with some superficial carbon peak.

a 45 second, 120°F (49°C) spray application with a treatment solution containing boric acid and sodium nitrate, but no zirconium or fluoride (and thus not of the invention), in treating aluminium cans which were subjected subsequently to the pasteurization and paint adhesion tests. The amount of treatment solution prepared was 1 litre, and it contained 0.1 M boric acid and 0.1 M sodium nitrate. The solution was evaluated at different pHs, identified in Table 3 below. The pH of the originally made-up solution was 7.2. It was thereafter varied by the addition thereto of nitric acid in an amount to give the pH values set forth in the Table.

Comparison Test Data 1—7.

As has been noted, boric acid can be used to advantage in the coating solutions of the invention. For comparative purposes, the comparative tests reported below show results of

TABLE 3

	pH	Pasteurization Test	Paint Adhesion Test
1 (Control)	(No Treatment)	Dark brown or black	Fail
2	7.2	Slightly yellow	Fail
3	7.2	„	Fail
4	6.2	„	Fail
5	6.2	„	Fail
6	3.2	„	Fail
7	3.2	„	Fail

With respect to the use of a treatment solution containing boric acid and sodium nitrate, it has been known heretofore that a boric acid solution can be used to form a barrier type anodic oxide film on aluminium by electrochemical reactions. Also, it has been reported heretofore that a solution containing borate and nitrate is effective in increasing the corrosion resistance of such a film in that it contributes to surface area decrease in the compact region of the oxide film. (See "Some Physical and Dielectric Properties of Hydrous Alumina Films", by Alwitt, R. S., *J. Electrochem. Soc.*, Volume 118, page no. 1730, 1971). However, it can be seen from the test results reported in Table 3 that such treatment solutions are not capable of imparting to an aluminium surface coatings which have the corrosion resistance and paint adhesion of the type provided by the use of coating solutions of the invention.

It is also to be noted that treatment solutions of the type described in Table 3 were modified by the addition thereto of fluoride the source of which was ammonium bifluoride

sodium fluoride, or sodium bifluoride (the modified solutions, like the solutions of Table 3, contained no zirconium). Coatings formed on aluminium surfaces from the modified solutions were translucent or even milky in appearance, and the coated surfaces did not have the bright appearance that was originally possessed by the uncoated metallic aluminium surfaces. In addition, the coated surfaces turned yellow when subjected to the pasteurization test, and gave very poor results when subjected to the paint adhesion test.

Examples 17 and 18;

Comparison Test Data 8—16.

This group of results shows the use of treatment solutions containing fluoride but no zirconium, zirconium but no fluoride, or neither, as well as coating solutions containing both zirconium and fluoride. In addition to the ingredients set forth in Table 4 below, each solution contained nitric acid in an amount sufficient to impart to each of the solutions a pH of 4. Each solution was sprayed at a temperature of 130°F (55°C) onto an alum-

inium surface for a 40 second period. The results of subjecting the aluminium surfaces to the pasteurization test are also reported in the Table.

TABLE 4

	Ingredient	Amount (g/l)	Boric Acid (g/l)	Pasteurization Blackening
Comparisons				
8	K_2TiF_6	0.4	None	Very slight
9	K_2TiF_6	0.4	5.0	Very slight
10	K_2SiF_6	0.4	None	Very slight
11	K_2SiF_6	0.4	5.0	Very slight
12	K_3SbF_6	0.4	None	Slight
13	K_3SbF_6	0.4	5.0	Slight
14	KBF_4	1.0	None	Almost none
15	KBF_4	1.0	5.0	Almost none
16	$Zr(NO_3)_4$	0.4	None	Severe
Examples				
17	ZrF_4	0.4	None	None
18	$Zr(NO_3)_4$ (Zr = 108 ppm) and HF, 25 ppm (F = 24 ppm)	0.4	None	None

With respect to the solutions identified in Table 4 above, it is noted that the use of each of the solutions resulted in a treated surface which was bright and shiny like the untreated surface (except for the solutions containing potassium titanium fluoride, which resulted in the treated surfaces having a light bluish tinge). From the results reported in the Table, it can be seen that, although all of the solutions improved the corrosion resistance of the aluminium surface, the coating solutions containing both zirconium and fluoride gave the most significant improvement.

Comparison Test Data 16—18.
Coating solutions having the following ingredients were also used to treat aluminium cans:

25	$NaBF_4$	1.5 g/l
	$NaNO_3$	4.0 g/l
	sodium <i>m</i> -nitrobenzene sulphonate	4.5 g/l
	$Zn(NO_3)_2 \cdot 6H_2O$	0.2 g/l

(the pH of the solution was adjusted to 6.6, and the solution, was sprayed at a temperature of 35°C onto an aluminium can for a 2 minute period; the coated can surface blackened when subjected to the pasteurization test).

$(NH_4)_2ZrF_6$	1.5 g/l
$NaNO_3$	26.0 g/l
$Co(NO_3)_2 \cdot 6H_2O$	0.5 g/l
sodium <i>m</i> -nitrobenzene sulphonate	1.0 g/l

(this solution — which contains cobalt, and has a pH of 5.2, and is therefore not a solution of the invention — was sprayed onto an aluminium surface at a temperature of 70°C for a 30 second period; the coating formed from the solution was colourless and clear, and the bright and shiny coated surface did not blacken when subjected to the pasteurization test).

19) A solution as 18) above, but without any ammonium zirconium fluoride, resulted in

a coated aluminium surface which blackened heavily when subjected to the pasteurization test.

Example 19.

Clear and colourless coatings were obtained by spraying for 30 seconds at 130°F (55°C) bright and shiny aluminium can surfaces with the coating solution described below:

(NH ₄) ₂ ZrF ₆	0.3 g/l (Zr=113 ppm; F=142.5 ppm)
H ₃ BO ₃	0.062 g/l (B=11 ppm)
HNO ₃	to impart a pH of 4.2
water	to make up to 1 litre

Electron Probe Analysis of a coated surface produced as described above showed a relative zirconium intensity value of about 1000 as compared to a value of about 50 for a coated surface produced in the same way except that the coating solution used did not contain boric acid.

WHAT WE CLAIM IS:—

1. A process for the formation of a coating upon an aluminium surface, in which process there is applied to the aluminium surface an acidic aqueous coating solution comprising at least 3 ppm dissolved zirconium, at least 5 ppm fluoride, and at least 10 ppm dissolved boron, having a pH of from 3 to 5, and being free of ferro- and ferricyanide, any organic polymeric material, chromium, manganese, iron, cobalt, nickel, molybdenum and tungsten, the solution being applied to the aluminium surface for such a time and at such a temperature as to form thereon a uniformly clear and colourless coating so that when the coated surface is thereafter subjected to boiling water for a 2 minute period it does not blacken.

2. A process as claimed in claim 1, in which the source of the zirconium in the coating solution is zirconium nitrate, zirconium sulphate, zirconium fluoride, or an ammonium or alkali-metal fluozirconate.

3. A process as claimed in either of the preceding claims, in which the amount of zirconium is at least 50 ppm.

4. A process as claimed in any of the preceding claims, in which the source of the fluoride in the coating solution is hydrofluoric acid, zirconium fluoride, or an ammonium or alkali-metal fluozirconate.

5. A process as claimed in any of the preceding claims, in which the amount of fluoride is from 75 to 200 ppm.

6. A process as claimed in any of the preceding claims, in which the source of the boron is boric acid, boric oxide or an ammonium or alkali-metal borate.

7. A process as claimed in any of the preceding claims, in which the amount of boron is not more than 125 ppm.

8. A process as claimed in any of the preceding claims, in which if it is desired to adjust the pH of the coating solution, this is done by adding nitric acid.

9. A process as claimed in any of the preceding claims, in which the solution is applied to the aluminium surface by spraying.

10. A process as claimed in any of the preceding claims, in which the coating solution is applied at a temperature of at least 100°F (38°C).

11. A process as claimed in claim 10, in which the temperature is from 120° to 150°F (50° to 66°C).

12. A process as claimed in any of the preceding claims, in which the aluminium surface is contacted with the coating solution for from 15 seconds to 1 minute.

13. A process as claimed in any of the preceding claims, and substantially as described hereinbefore.

14. An aluminium surface whenever coated by a process as claimed in any of the preceding claims.

15. An acidic aqueous coating solution for coating aluminium, the solution comprising at least 3 ppm dissolved zirconium, at least 5 ppm fluoride and at least 10 ppm dissolved boron, having a pH of from 3 to 5, and being free of ferro- and ferricyanide, any organic polymeric material, chromium, manganese, iron, cobalt, nickel, molybdenum and tungsten, the solution being capable of forming on an aluminium surface a uniformly clear and colourless coating and providing a coated surface which resists blackening when it is thereafter subjected to boiling water for a 2 minute period.

16. A solution as claimed in claim 15, and as defined in any of claims 2 to 7.

17. A solution as claimed in either of claims 15 and 16, and substantially as described hereinbefore.

SANDERSON & CO.,
For the Applicants,
Chartered Patent Agents,
97 High Street,
Colchester, Essex.

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a coated aluminium surface which blackened heavily when subjected to the pasteurization test.

Example 19.

- 5 Clear and colourless coatings were obtained by spraying for 30 seconds at 130°F (55°C) bright and shiny aluminium can surfaces with the coating solution described below:

(NH ₄) ₂ ZrF ₆	0.3 g/l (Zr=113 ppm; F=142.5 ppm)
H ₃ BO ₃	0.062 g/l (B=11 ppm)
HNO ₃	to impart a pH of 4.2
water	to make up to 1 litre

- 15 Electron Probe Analysis of a coated surface produced as described above showed a relative zirconium intensity value of about 1000 as compared to a value of about 50 for a coated surface produced in the same way except that the coating solution used did not contain boric acid.

WHAT WE CLAIM IS:—

- 20 1. A process for the formation of a coating upon an aluminium surface, in which process there is applied to the aluminium surface an acidic aqueous coating solution comprising at least 3 ppm dissolved zirconium, at least 5 ppm fluoride, and at least 10 ppm dissolved boron, having a pH of from 3 to 5, and being free of ferro- and ferricyanide, any organic polymeric material, chromium, manganese, iron, cobalt, nickel, molybdenum and tungsten, the solution being applied to the aluminium surface for such a time and at such a temperature as to form thereon a uniformly clear and colourless coating so that when the coated surface is thereafter subjected to boiling water for a 2 minute period it does not blacken.

- 25 2. A process as claimed in claim 1, in which the source of the zirconium in the coating solution is zirconium nitrate, zirconium sulphate, zirconium fluoride, or an ammonium or alkali-metal fluozirconate.

- 30 3. A process as claimed in either of the preceding claims, in which the amount of zirconium is at least 50 ppm.

- 35 4. A process as claimed in any of the preceding claims, in which the source of the fluoride in the coating solution is hydrofluoric acid, zirconium fluoride, or an ammonium or alkali-metal fluozirconate.

- 40 5. A process as claimed in any of the preceding claims, in which the amount of fluoride is from 75 to 200 ppm.

6. A process as claimed in any of the preceding claims, in which the source of the boron is boric acid, boric oxide or an ammonium or alkali-metal borate.

7. A process as claimed in any of the preceding claims, in which the amount of boron is not more than 125 ppm.

8. A process as claimed in any of the preceding claims, in which if it is desired to adjust the pH of the coating solution, this is done by adding nitric acid.

9. A process as claimed in any of the preceding claims, in which the solution is applied to the aluminium surface by spraying.

10. A process as claimed in any of the preceding claims, in which the coating solution is applied at a temperature of at least 100°F (38°C).

11. A process as claimed in claim 10, in which the temperature is from 120° to 150°F (50° to 66°C).

12. A process as claimed in any of the preceding claims, in which the aluminium surface is contacted with the coating solution for from 15 seconds to 1 minute.

13. A process as claimed in any of the preceding claims, and substantially as described hereinbefore.

14. An aluminium surface whenever coated by a process as claimed in any of the preceding claims.

15. An acidic aqueous coating solution for coating aluminium, the solution comprising at least 3 ppm dissolved zirconium, at least 5 ppm fluoride and at least 10 ppm dissolved boron, having a pH of from 3 to 5, and being free of ferro- and ferricyanide, any organic polymeric material, chromium, manganese, iron, cobalt, nickel, molybdenum and tungsten, the solution being capable of forming on an aluminium surface a uniformly clear and colourless coating and providing a coated surface which resists blackening when it is thereafter subjected to boiling water for a 2 minute period.

16. A solution as claimed in claim 15, and as defined in any of claims 2 to 7.

17. A solution as claimed in either of claims 15 and 16, and substantially as described hereinbefore.

SANDERSON & CO.,
For the Applicants,
Chartered Patent Agents,
97 High Street,
Colchester, Essex.