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Description

This invention relates to an aluminium-coating solution, process and concentrate, as well as aluminium articles coated thereby.

The term "aluminium" is here used to embrace not only pure aluminium but also alloys of aluminium, for example those aluminium alloys which contain minor amounts of metals such as magnesium, manganese, copper and silicon.

It is known to coat aluminium surfaces by treating them with aqueous coating solutions which react with the aluminium, converting its surface into a so-called "conversion coating" thereupon, which is corrosion resistant and thus protects the underlying aluminium from corrosive attack. Such conversion coatings will also normally and desirably provide a firm foundation to which subsequently-applied overlying siccative coatings, decorative or functional in nature and formed from materials such as paints, lacquers, inks, etc., will adhere tightly and strongly.

Amongst many other, broader applications one particular use for certain conversion coating solutions is in connection with the coating of aluminium cans. However, although there are other aluminium-coating procedures in which it may be desired that the coating should impart a coloured appearance, for example a yellowish to green tint, to the aluminium surface the corrosion-resistant coatings which are to be applied to aluminium cans should be uniformly clear and colourless, so that even after they have been coated the cans will still have the natural bright shiny appearance of the underlying aluminium, which it is desired to retain in the final product even though portions of the can may be covered with overlying siccative coatings.

It is however not sufficient that the coatings should be clear and colourless when applied to the cans, it is also necessary that they should afterwards so remain. Specifically the coating must be able to resist discolouration when the coated can is subjected to moderately hot water, for example at water temperatures within the range of from about 60°C (140°F) to about 77°C (170°F), during operations usually called "Pasteurization" of the cans. Such a "Pasteurization" treatment has a tendency to cause an uncoated or an inadequately-coated aluminium surface to blacken or otherwise discolour, thereby giving the can an unattractive appearance.

Perhaps curiously, it is however also desirable that under extreme conditions coated aluminium cans should be able to undergo discolouration, since this can be the basis for a simple test designed to confirm the presence of the desired coating. One such test conventionally employed in the can industry is known as the "muffle test". By means of such a test a can manufacturer is able to sample cans randomly from the production line and to confirm that the desired clear and colourless coating although invisible is actually present on the cans.

There are nowadays already available some coating solutions which form uniformly clear and colourless coatings upon aluminium surfaces. Perhaps the most widely used of these coating solutions is one which contains chromic acid, phosphoric acid and hydrofluoric acid. In recent years there has however been an industry-wide switch away from coating solutions containing hexavalent chromium to those which do not, because the use of hexavalent chromium tends, in general, to create waste-disposal problems.

There are however chromate-free compositions said to be capable of forming coatings upon aluminium. Recent developments of this kind are exemplified by the disclosures to be found in British Published Patent Application GB 2,014,617 A, and United States of America Patents Nos. 4,017,334, 3,964,936, and 4,148,670. These all describe acidic aqueous solutions which include a fluoride-containing compound and variously either a zirconium-, titanium- or hafnium-containing compound. That however is not all—in United States Patent No. 4,148,670 a further essential constituent of the composition is said to be phosphate, while a polyhydroxy compound having six or fewer carbon atoms is described as optional ingredient; whereas in United States Patent No. 4,017,334 not only phosphate but also tannin are both described as additional essential constituents.

The presence of phosphate in the solution is said to contribute to the corrosion-resistance and paint-receptive properties of the coating, and moreover to render the coating susceptible to the so-called "muffle test" should that wish to be used in order to confirm the presence of the coating on an aluminium surface. Phosphate however is not altogether a welcome ingredient, since it has been found to cause a decrease in the adhesion of certain water-borne siccative coatings and thus it would be desirable to produce a coating in which phosphate is not an essential ingredient.

DE—A1—2,704,261 and GB—A—1,504,494 describe alkaline aqueous solutions for aluminium surfaces which include either titanium or zirconium ions and a complexing agent. The recommended pH is at least 10. The solution generally contains an alkali metal, for example, in the form of a salt with as anions hydroxides, carbonates, phosphates or borates. A surfactant is also an optional ingredient. After the alkaline treatment, the treated surface is generally rinsed with water, and in a particularly preferred embodiment, the rinsed surface is then contacted with an aqueous acidic solution containing tannin or tannic acid.

It is the fundamental purpose of this invention to provide an aqueous conversion-coating solution which, although it does not require the use of hexavalent chromium or any similarly toxic materials and moreover can if wished be phosphate-free, nevertheless is capable of forming upon an aluminium surface a clear and colourless, corrosion-resistant coating which provides an excellent foundation to which

overlying, siccative coatings can later adhere. It should moreover here be noted that as just used and as used hereinafter any reference to "corrosion resistance" is intended unless otherwise stated to imply not merely that the coated surface is resistant to corrosion in the normal sense but also that it resists blackening or other discolouration when exposed to the aforementioned "Pasteurization" or other similar hot-water or boiling-water treatment.

According to the present invention there is provided a chromate-free, acidic, aqueous coating solution of pH from 1.5 to 5, capable of forming a clear, colourless and corrosion-resistant coating upon an aluminium surface, which contains:—

(a) one or more of the Group IVa metals zirconium, hafnium and titanium in a total amount of at least 0.5×10^{-3} mole/litre;

(b) fluoride in an amount at least sufficient to combine with all of the Group IVa metal(s) present; and

(c) an additive in the form of:

(i) a surfactant present in a concentration of at least 0.01 g/litre; and/or

(ii) a polyhydroxy organic compound having up to 7 carbon atoms and present in a concentration of at least 0.025×10^{-3} mole/litre, when the additive is this polyhydroxy organic compound alone the solution being free from phosphate and boron.

The acidic, aqueous coating solution of this invention can be used to treat a bright shiny aluminium surface in such a manner that its bright shiny appearance is not impaired, yet there is formed upon the surface a uniformly colourless and clear coating, which exhibits excellent corrosion-resistance and to which overlying siccative coatings will tightly adhere.

Moreover, the coating solutions of the present invention are able to form this desirable type of coating upon aluminium even in the absence of materials which either are toxic or create waste disposal problems; thus the coating solutions of this invention can be and are free from not only hexavalent chromium but also elements such as manganese, iron, cobalt, nickel, molybdenum and tungsten, as well as toxic materials such as ferricyanide and ferrocyanide. The absence of such materials from the coating solution makes it unnecessary to subject the effluent to any special treatment before it is discharged to the environment or to a sewage-disposal plant.

Furthermore, the coatings formed by the coating solutions of this invention are especially valuable if they are to serve as the foundation for overlying siccative coatings applied in the form of water-based compositions. There has recently been a trend in the industry away from the use of coating compositions based upon organic solvents, and instead in favour of water-based coating compositions. Industrial experience has however shown that, whatever their other advantages siccative coatings formed from water-based compositions do not adhere to conversion coatings of the prior art Zr, Ti, or Hf type as well as siccative coatings formed from compositions based upon organic solvents. Specifically for example the siccative coatings formed from water-based compositions tend not to adhere so well to underlying conversion coatings formed from the phosphate-containing solutions of United States Patent No. 4,148,670 as those formed from siccative coating compositions based upon organic solvents. It is however a most advantageous fact that the conversion coating solutions of the present invention can be used to form coatings upon aluminium surfaces which provide an excellent paint-receptive foundation to which siccative coatings formed from water-based compositions will tightly adhere.

When component (c) is the polyhydroxy compound we have observed that the corrosion resistance of the coatings formed by the coating solutions may tend to vary, dependent on the type of water used in preparing such compositions. Generally speaking, it seems that the corrosion-resistance properties of the coatings are better when they are formed from solutions made up in hard water than when they are formed from solutions made up in soft water. The relatively low calcium concentration in soft water appears to be detrimental to the corrosion resistance of the resultant coatings; or perhaps one should instead say that the relatively high concentration of calcium in hard water is beneficial to the corrosion-resistance of the resultant coatings. There is however no variation in corrosion-resistance of the coating dependent upon water-hardness in the solution when component (c) is either surfactant alone or a mixture of surfactant with polyhydroxy compound.

At this point it is convenient to mention that the term "surfactant" is used herein to mean any material which when present in a small amount will markedly reduce the surface tension of water. Thus for instance the presence of as little as 2 parts per million of surfactant dissolved in water can reduce the surface tension of water by more than one-third of its normal value. The term thus embraces all the various conventional classes of surfactants, namely anionic, cationic, non-ionic and amphoteric surfactants. It should however be noted that the use of a non-ionic surfactant is preferred in accordance with the present invention.

The acidic aqueous coating solution must as stated contain one or more of the Group IVa metals titanium, zirconium and hafnium in conjunction with fluoride and with a polyhydroxy compound and/or a surfactant. Any convenient sources of these components may be employed which are soluble in the solution

As the sources of the zirconium, titanium or hafnium one can for instance use soluble fluozirconate, fluotitanate or fluohafnate compounds, such as fluozirconic, fluotitanic and fluohafnic acids and the corresponding salts such as ammonium and alkali metal fluozirconates, fluotitanates and fluohafnates.

Other suitable sources include metallic fluorides such as zirconium fluoride (ZrF_4), titanium fluoride (TiF_3, TiF_4), and hafnium fluoride (HfF_4).

The coating solutions can moreover be prepared from mixtures of soluble compounds, one of which contains the Group IVa metal(s) and the other of which contains the fluoride. Examples of such compounds are water-soluble salts comprising nitrates and sulphates of Zr, Ti or Hf (for example zirconium nitrate, zirconium sulphate, titanium (iv) sulphate and hafnium nitrate) the hydrofluoric acid and its water-soluble salts such as ammonium and alkali metal salts thereof.

It is possible to form satisfactory coatings from solutions containing as little as 0.5×10^{-3} mole/litre (M/l) of either Zn, Ti, or Hf (equivalent to 0.05 g/l of Zr, 0.02 g/l of Ti and 0.09 g/l of Hf); and when utilizing a mixture of more than one of these groups IVa metals they should together total at least 0.5×10^{-3} M/l. Dependent upon other parameters of the coating process it may however be necessary to employ greater amounts of these ingredients in order to produce satisfactory coatings, as will be explained below.

There is no upper limit upon the concentrations of dissolved zirconium, titanium or hafnium which can be used, except of course their solubility limits in the acidic aqueous coating solution, which are dependent on other parameters of the coating solution, including particularly the acidity and the fluoride content of the coating solution and the amounts of other optional ingredients which might be present. These various parameters should be so controlled as to avoid the formation of precipitates of zirconium, titanium or hafnium compounds. Any such precipitate is undesirable for several reasons. Precipitation depletes the ingredients; if any precipitate is deposited upon the coated aluminium surface it can adversely affect the properties of the coating; and the accumulation of any type of precipitate tends to interfere with the coating procedure, thus for example it can clog spray-nozzles. Supposing that in some specific situation one encounters precipitation it can be cured by lowering the pH of the coating solution and/or by increasing the concentration of fluoride.

The minimum fluoride concentration is that required to combine with all of the zirconium, titanium and/or hafnium to form a soluble complex therewith, for example a fluozirconate, fluotitanate or fluohafnate. The minimum amount of fluoride is thus dependent on the amount of zirconium, titanium and/or hafnium in the solution. We have in general found that at least about 4 moles of fluoride are needed per mole of Zr, Ti and/or Hf in order to prevent precipitation of those metals. We prefer to employ at least about six moles of fluoride per mole of Zr, Ti and/or Hf.

Furthermore it must be remembered that during prolonged operation of the coating process, thus in situations where the coating solution is recycled or a bath of the solution is used continuously, there will be a build-up in the concentration of the aluminium dissolved off the surface by the solution. Such a build-up of dissolved aluminium may adversely affect the coating process unless the coating solution contains an amount of fluoride sufficient to complex the dissolved aluminium.

From a practical standpoint it is thus very desirable that the coating solution, when operating on an industrial scale, should contain an excess of fluoride beyond that amount complexed with aluminium and any other constituents in the solution that form complexes with the fluoride. Such excess fluoride is referred to herein as "available fluoride"; and the manner in which one calculates the amount of "available fluoride" is well-understood in the art. A coating solution which contains available fluoride is one in which fluoride is available to complex with aluminium.

Although as just indicated some excess or available fluoride is desirable care should be taken to avoid too much. It is recommended that the available fluoride concentration should be no greater than 26.3×10^{-3} mole/litre (or no greater than 500 parts per million) in order to avoid undue etching of the aluminium surface, which tends to give a dull and frosty appearance to the surface, and so as also to avoid adverse affects on the corrosion resistance and paint-receptive properties of the coating, as well as to avoid precipitation of calcium or other such ions present in the solution.

The source of fluoride for use in the coating solution can be any material which is soluble therein and provides a source of fluoride capable of complexing aluminium, provided that it does not contain anything else which adversely affects the coating process. Supposing however that fluoride is added as a complex fluoride of titanium, zirconium or hafnium, then another source of fluoride should also be added to the solution so as to serve as a source of fluoride for complexing the aluminium that builds up during continuous operation. Alternative sources of fluoride for this purpose include materials such as HF, salts thereof, NH_4F . HF, alkali metal bifluorides, H_2SiF_6 or HBF_4. The particularly preferred sources of fluoride are HF and HBF_4.

As already mentioned above, when a surfactant is present in the solutions of the present invention it will preferably be a non-ionic surfactant. Although as little as 10 parts per million (equivalent to 0.01 g/litre) of surfactant can suffice it is preferred to use the surfactant in a concentration of from 20 to 100 parts per million. Still higher amounts, for example up to about 500 parts per million, can be used without detriment, but we have found that in general little or no additional improvements are achieved at such higher concentrations.

When a polyhydroxy compound is to be present it may be any water-soluble polyhydroxy compound which has no more than seven carbon atoms. The source may obviously be the polyhydroxy compound itself, but it may also be any compound soluble in the coating solution which when dissolved therein yields the desired polyhydroxy compound and is not otherwise detrimental to the coating-ability of the solution or the corrosion-resistance and paint-adherence of the coatings. Examples of such compounds include

gluconic acid and its salts, sodium glucoheptonate, sorbitol, mannitol, dextrose, ethylene glycol, and glycerine. Particularly preferred polyhydroxy compounds are gluconic acid and its alkali metal and ammonium salts. The source of polyhydroxy compound may also be any compound soluble in the coating solution which there yields gluconate and/or gluconic acid; and examples of such compounds are stable gluconolactones such as glucono-*delta*-lactone and glucono-*gamma*-lactone.

The presence of the polyhydroxy compound in the coating solution (even when it is free from phosphate) allows the operator of the manufacturing process to conduct a simple test so as to check whether the coating has been formed on the aluminium surface. Because the coating is not visible to the eye it is very helpful to have some simple test to confirm that the coating solution is forming a coating, especially in industrial operations which can involve the treatment of vast quantities of aluminium in a relatively short time. Without some check it would be easy for some change in the operating parameters of a bath of the coating solution, occurring as a result of mechanical or human failure and which renders it ineffective, to go unnoticed and lead to much defective output before it is discovered. Improper replenishment of the coating solution can for instance easily go undetected for quite some time unless a careful check upon the quality of the product is maintained.

What we have found is that an aluminium surface coated with the solution of the present invention, containing the specified polyhydroxy compound but no phosphate, will undergo a colour change when subjected to a relatively high temperature for a relatively short period of time, for example about 482°C (900°F) for 5 minutes, changing from colourless and invisible to a visible coating coloured from light golden brown to darker shades of brown or purple. This test, referred to herein as the "muffle" test, can be used upon randomly selected samples of the treated aluminium articles to check whether or not the desired invisible coating has been formed upon the aluminium surface. If not, the uncoated aluminium surface will have a dull greyish appearance after the muffle test. It may here be noted that it has till now been generally believed that the presence of phosphate was necessary to obtain a positive result in the muffle test, so that it is rather surprising that the presence of the polyhydroxy compound enables the muffle test to work even in the absence of phosphate.

Both the polyhydroxy compound and also the surfactant have the further advantage that their presence in the coating solution improves the ability of coatings formed therefrom to withstand blackening (or other discolouration) for a period of at least 5 minutes, and often indeed up to as long as 15 minutes, when subjected to Pasteurization-type procedures in water having a temperature within the range of from say 60°C to 77°C (140°F—170°F).

Moreover other aspects of the corrosion-resistance and paint-receptive properties of the coatings seem to benefit from the use of the polyhydroxy compound, particularly in the case of coatings formed from a coating solution having a pH below about 3.5.

It has furthermore been found that overlying siccative coatings, particularly water-borne siccative coatings, will adhere especially well to coatings which have been formed from solutions which contain polyhydroxy compounds but are free from phosphate. This may be contrasted with the fact that although organic-borne siccative coatings do adhere well to coatings containing phosphates, certain water-borne coatings do not adhere thereto nearly as well.

As regards the necessary concentration levels, we have found that coated aluminium cans which have a high level of water-stain resistance and are capable of discolouring when subjected to the aforementioned muffle test can be produced from coating solutions containing as little as 0.025×10^{-3} mole/litre of the polyhydroxy compound; but the coating solutions will preferably contain from 0.3×10^{-3} mole/litre to 1.75×10^{-3} mole/litre of the polyhydroxy compound. It is indeed possible to use higher amounts, for example up to 2.5×10^{-3} mole/litre, but generally we have found that little or no additional improvements are achieved at such higher concentrations.

When the solutions of the present invention contain not only the polyhydroxy compound but also surfactant, it is recommended that at least 40 parts per million of the polyhydroxy compound should be present, but that although higher amounts can be used it is also recommended that no more than 1,000 parts per million of the polyhydroxy compound should be present. The coating solution will besides surfactant also contain preferably from 40 to 400 parts per million of the polyhydroxy compound.

The pH of the acidic aqueous coating solution can vary over the wide range from 1.5 to 5. When surfactant is present in the solutions of the present invention improvements in corrosion resistance attributable thereto are observed particularly within the pH range of from 3.5 to 4.5. When the polyhydroxy compound is present in the solutions of the present invention, improvements in corrosion resistance attributable thereto are observed, particularly within the pH range of from 3.0 to 5.0, and especially within the range of from 3.0 to 4.0.

The pH of the coating solution may conveniently be adjusted to any desired value by using appropriate amounts of any acid or base which will not interfere with the coating process. The acid employed can for example be perchloric acid or sulphuric acid, but will preferably be nitric acid; and the base employed for pH adjustment will preferably be ammonium hydroxide.

The coating solutions of the present invention should very desirably be kept free from chromium, from iron cyanides, and from any materials which in the solution will tend to form solids which precipitate.

The presence of other materials is however not excluded. Examples of other materials which optionally can be added to the coating solution are those already reported as being useful in Zr, Ti or Hf and

fluoride-containing coating solutions. Thus for instance United States of America Patent No. 3,964,936 discloses the inclusion of a source of boron in such an amount as to create a boron concentration of at least 10 parts per million and ranging up to 200 parts per million. When the acidic aqueous coating solutions of the present invention contain surfactant they may also advantageously contain such a boron compound, and in that event the source of boron will preferably be boric acid in the aforementioned amounts. Again, United States of America Patent No. 4,017,334 and British Patent Application No. GB 2,014,617 A both disclose tannin as another optional ingredient, which can be added to the solution in concentrations of from at least 25 parts per million ranging up to 10 grams per litre.

Although it is one of the major advantages of this invention that the coating solutions can be free from phosphate it is not in all circumstances necessary that they should be phosphate-free. Specifically, when the conversion coating is to serve as the foundation for siccative coating compositions based upon organic solvents it is permissible for the coating solution of the present invention except when it contains the polyhydroxy compound and is surfactant-free, optionally to include phosphate in concentrations of from 10 parts per million to 1,000 parts per million, as described in United States of America Patent No. 4,148,670.

Still other materials which optionally can be included in the coating solutions of the present invention are various other acids, such as for example glutaric, ascorbic, maleic or salicylic acids, which if present in concentrations of at least 5 parts per million and preferably within the range of from 100 to 500 parts per million may serve to improve the adhesive properties of the resultant coatings, or achieve other advantages.

Within the above-disclosed broad ranges of the concentrations of the various ingredients in the solutions of this invention the choice of any particular concentration will depend on various considerations. Thus, when the solution is to operate at a relatively high pH, then relatively smaller amounts of zirconium, titanium and/or hafnium should be present, in order to deter precipitation. Conversely, when the period of contact between the aluminium surface and the coating solution is to be relatively short, then relatively higher amounts of the aforementioned metals should be used; and similarly, when the temperature at which the coating solution is to be contacted with the aluminium surface will be relatively low, then again relatively higher amounts of all the ingredients should be used.

To assist further understanding, it may be noted that one preferred coating solution in accordance with the present invention (hereinafter identified as "Solution A") can be formulated as follows:

Solution A:

Ingredient	Approximate concentration in moles/litre
Zirconium Source (calculated as Zr)	0.5×10^{-3} to 1.75×10^{-3}
Polyhydroxy Compound	0.3×10^{-3} to 1.75×10^{-3}
Available Fluoride	0.5×10^{-3} to 2.5×10^{-3}
	pH value ≒3.4 to 4

The zirconium source in Solution A is preferably ammonium fluorzirconate, and the polyhydroxy compound is preferably gluconic acid. The source of available fluoride is preferably hydrofluoric acid, and nitric acid is preferably used if needed to adjust the pH to a value in the desired range.

When hafnium is added to Solution A, it is preferably added in a concentration in the range of from 0.5×10^{-3} mole/litre to 1.75×10^{-3} moles/litre. The preferred source of hafnium is HfF_4. If desired Solution A may also contain any of the other previously-discussed optional ingredients.

It may also be noted that another preferred coating solution in accordance with the present invention (hereinafter identified as "Solution B") can be formulated as follows:

Solution B:

Ingredient	Approximate concentration
Zirconium Source (calculated as Zr)	0.75×10^{-3} to 2×10^{-3} M/l
Surfactant	10—500 parts per million
Available Fluoride	sufficient to complex all Zr and Al
	pH value ≒3.5 to 4.5

It may further be noted that Solution B will preferably contain:
1×10^{-3} to 1.75×10^{-3} M/l Zr; and
20 to 100 parts per million of surfactant and that its pH value will preferably be in the range of from 3.7 to 4.3.

The zirconium source in Solution B will preferably be fluozirconic acid, at least in the make-up composition, since this will provide not only the Zr but also the necessary fluoride. Nitric acid is preferably used if needed to adjust the pH to a value in the desired range.

The coating solution of the present invention will most conveniently be prepared from an aqueous concentrate of the ingredients by diluting it with an appropriate amount of water.

A concentrate suitable for making up Solution A should thus for example be such that when it has been diluted down to form only from 0.5 to 10 weight percent of the resultant coating solution, the concentrations of the various ingredients in the coating solution will be:

(A) at least 0.5×10^{-3} mole/litre of zirconium and/or hafnium;

(B) at least 0.025×10^{-3} mole/litre of the polyhydroxy compound; and

(C) fluoride in an amount at least sufficient to combine with substantially all of the zirconium or hafnium to form a complex therewith;

while the pH of the coating solution is within the range of from 3 to 5.

The concentrate will preferably be such that when diluted down to form no more than from 0.5 to 10 weight percent of the resultant coating solution the latter will contain:

(A) from 0.5×10^{-3} mole/litre to 1.75×10^{-3} mole/litre of zirconium, added as a fluozirconate such as sodium, potassium or most preferably ammonium fluozirconate;

(B) from 0.3×10^{-3} mole/litre to 1.75×10^{-3} moles/litre of polyhydroxy compound, added as gluconic acid;

(C) from 0.5×10^{-3} mole/litre to 2.50×10^{-3} moles/litre of hydrofluoric acid, HF; and

(D) nitric acid in such an amount that the pH value of the coating solution is within the range of from 3.4 to 4.

A concentrate suitable for making up Solution B should, by way of further example, be such that when it has been diluted down to form only from 0.5 to 10 weight percent of the resultant coating solution, the concentrations of the various ingredients in the coating solution will be:

(A) at least 0.5×10^{-3} mole/litre of one or more of the Group IVa metals zirconium, titanium, and hafnium;

(B) at least 10 parts per million of surfactant; and

(C) fluoride in an amount at least sufficient to combine with substantially all of the Zr, Ti, or Hf so as to form a complex therewith.

In a coating process carried out more or less continuously upon a succession of aluminium surfaces it will be found that both the Group IVa metal and the fluoride are consumed by the chemical reaction which occurs between the solution and the surface; and moreover both these ingredients and the others also become depleted as a result of "drag-out" of the solution which clings onto the aluminium surface. The rate of depletion by drag-out is moreover affected by the shape of the surface being coated, as well as the means used to apply the coating solution to the surface. Besides chemical consumption and physical drag-out there will also be a loss of available fluoride as this is complexed by a build-up in the concentration of dissolved aluminium, as noted above. For all these reasons there is therefore a need, in a continuous coating operation for the ingredients to be replenished, either continuously or at least intermittently.

Replenishment may naturally be effected by monitoring the amount still present of each individual ingredient, and then adding an additional amount thereof to replace whatever has been lost; but it is obviously more convenient and therefore preferable to replenish the coating solution by adding thereto enough of an aqueous concentrate which has been formulated to contain the ingredients to be replenished in relative amounts which will be effective to maintain all said ingredients in the solution within their effective operating concentrations. Thus the replenishing composition will preferably contain a relatively high proportion of available fluoride when substantial aluminium build-up in the coating solution is

encountered. Preferred sources of available fluoride for use in replenishment are hydrofluoric acid (HF) or ammonium bifluoride (NH_4HF_2) or a mixture thereof or fluoboric acid (HBF_4).

Thus, to assist further understanding, it may be noted that one preferred replenishment concentrate (hereinafter identified as "Concentrate A"), which is recommended for replenishing the aforesaid Solution A, can be formulated as follows:—

Concentrate A:

Ingredient	Approximate concentration in moles/litre
Zr and/or Hf	31×10^{-3} to 251×10^{-3}
Polyhydroxy Compound	19×10^{-3} to 148×10^{-3}
Available Fluoride	90×10^{-3} to 695×10^{-3}

The available fluoride in Concentrate A will preferably be hydrofluoric acid (HF) or ammonium bifluoride (NH_4HF_2) or a mixture of these two sources.

It may also be noted that another preferred replenishment concentrate (hereinafter identified as "Concentrate B"), which is recommended for replenishing the aforesaid Solution B, can be formulated as follows:—

Concentrate B:

Ingredient	Approximate Concentration
Zr and/or Ti and/or Hf	0.05 to 0.5 M/l
Surfactant	1 to 100 g/l
Available Fluoride	0.2 to 10 M/l

According to another aspect of this invention there is also provided, in a process for forming a clear, colourless and corrosion-resistant coating upon an aluminium surface, the step of contacting said surface with the chromate-free, acidic aqueous coating solution of this invention as described above for a period of time sufficient at the operating temperature to form the desired coating thereon.

The coating process of the present invention can be used to coat surfaces of pure aluminium or of aluminium alloys in which aluminium is the predominant ingredient. There are for instance very many aluminium alloys containing minor amounts of alloying elements such as, for example, magnesium, manganese, copper and silicon. It is our belief that one of the widest uses of the coating process of the present invention will be in the coating of aluminium surfaces which have a bright, shiny appearance; and aluminium cans and aluminium strip are examples of such articles, which can be effectively coated by means of the process of this invention. At the present time, the most popular alloy used in the manufacture of aluminium cans is that known as Aluminium Alloy 3004. According to published information, the nominal chemical composition of Aluminium Alloy 3004 is 1.2% manganese, 1.0% magnesium and the balance aluminium and normal impurities. Certainly the process of the present invention is well able to form the desired coatings upon this important Aluminium Alloy 3004.

It will of course be appreciated that the coating process of the present invention should be carried out upon a clean aluminium surface. The process may therefore include the preliminary step of cleaning the aluminium surface by means of existing aluminium cleaning compositions such as alkaline or acidic cleaning solutions, which may be applied thereto by conventional techniques.

When the aluminium surface to be coated is that of so-called drawn-and-ironed aluminium cans, the preliminary cleaning step will preferably be carried out using a cleaning solution which consists of an acidic aqueous solution of a mixture of hydrofluoric acid (HF), sulphuric acid (H_2SO_4) and surfactant. Examples of such cleaning solutions are those described in our United States of America Patents Nos. 4,009,115, 4,116,853 and 4,124,407.

The coating solution can be brought into contact with the aluminium surface by any convenient method. Thus the solution can for example be applied to the aluminium surface by spraying it thereon, or the aluminium article can be dipped into the solution so that its surface is immersed therein, or the solution can be applied to the surface by roll- or flow-coating techniques or by misting techniques. The solution can

be contacted with discrete articles, such as for example cans; or it can be contacted with continuous forms of aluminium blank, such as aluminium strip, which will subsequently be fabricated into discrete articles.

The temperature of the coating solution when it is brought into contact with the surface is not very critical, and can vary within wide limits, just so long as the chosen temperature permits the reactive ingredients of the solution to react with the aluminium surface and form a conversion coating thereon. With a coating solution such for instance as the aforesaid Solution A, it is however very desirable to employ a temperature of at least 43°C (110°F) in order to produce the desired degree of corrosion resistance in a reasonable time. And again, with a coating solution such for instance as the aforesaid Solution B, it is very desirable to employ a temperature of at least 32°C (90°F) in order to produce the desired degree of corrosion resistance in a reasonable time.

On the other hand, if the temperature of the coating solution is too high, problems may be encountered, such as a dull and frosty appearance imparted to the aluminium surface. The temperature at which this may occur will depend on various parameters of the coating process, including for instance the period of contact between the solution and the aluminium surface and the reactivity of the solution, the latter being in turn dependent on the pH of the coating solution and the concentration of ingredients therein. In some instances there may be other temperature-related problems—with coating solutions such as Solution A if the pH value rises above 4.5 then precipitation of zirconium and/or hafnium oxides may become a problem at operating temperatures in excess of 71°C (160°F). With coating solutions such as Solution B it is preferred to avoid operating temperatures in excess of 60°C (140°F).

The operating temperature of Solution A will preferably be in the range of from 54°C (130°F) to 66°C (150°F). The operating temperature of Solution B will preferably be in the range of from 43°C (110°F) up to 54°C (130°F).

The period of contact between the coating solution and the aluminium surface will usually need to be at least 5 seconds, and preferably should be not less than 15 seconds. The lower the temperature of the coating solution, the longer should be the period of contact, whereas conversely the higher the temperature of the solution the shorter need be the period of contact. It will seldom be necessary to employ a period of contact greater than one minute.

After the conversion coating has been formed upon the aluminium surface by the process so far described, it should be water-rinsed. The rinsing procedure should very desirably include a final rinse with deionized water, since rinsing with water that contains even a small amount of dissolved solids may result in a coating to which a subsequently applied siccative coating does not adhere well. Although it is in other contexts fairly conventional to rinse conversion coated aluminium surfaces with an aqueous solution of chromium, for example one containing hexavalent chromium solution, it should be noted that no such chromium-after-rinse is needed in the process of this invention.

After the coated surface has been water-rinsed, or otherwise treated as described above, it should normally be dried, subject only to the comments made below. Drying can be carried out in any convenient manner, for instance by oven drying or forced circulation of hot air.

After the conversion coating has been applied, it can be provided with a further sanitary or decorative coating, for example by applying some kind of siccative coating material to the conversion coated surface. While such siccative coating materials will usually be applied after the conversion-coated aluminium surface has been water-rinsed and dried, it should be noted that sometimes the sanitary siccative coating material will be applied after the water-rinse but before drying, so that both the conversion coating of the present invention and the sanitary siccative coating will be dried simultaneously.

It is unnecessary here to give further details concerning the siccative coating materials which may be employed for their functional and/or aesthetic value over the conversion coatings formed by the process of the present invention, for such siccative coating materials (both the water-based and the solvent-based compositions) are of course in themselves well-known.

The process of the present invention may well form part of a still larger manufacturing procedure. Thus, in a beverage-canning factory where for instance aluminium cans are to be filled with beer, the cans will be cleaned and conversion coated by means of the coating process employing the coating solution of the present invention, then sanitary and/or decorative siccative coatings will be applied to the conversion-coated cans, thereafter these doubly-coated cans will be filled with beer and sealed, and finally, the beer-filled cans will be subjected to pasteurization.

This invention of course extends to aluminium articles whose surfaces have been provided with a conversion coating thereupon, and if desired otherwise treated, in accordance with the process of this invention. It extends also to the concentrates employed in making-up and/or replenishing the solutions used in such processes.

At this point it may also conveniently be noted that the zirconium, titanium and/or hafnium present in the coating solutions of the present invention is believed to be present in a complexed form which is both soluble in the solution and reactive with the aluminium surface to form thereon a coating which contains such metal(s) without affecting the bright shiny appearance of the aluminium surface. With that in mind, it will be understood that whatever other optional ingredients may be added the coating solution should be kept free from constituents which might combine with the aforementioned metals to form undesirable compounds and/or complexes, that is to say compounds and/or complexes which either will precipitate

from the solution and/or will not react with the aluminium surface and/or will indeed react but in such a manner than the bright shiny appearance of the underlying aluminium surface is altered.

In order that the invention may be well understood it will now be described in more detail, though only by way of illustration, in the following examples, and assessed relative to certain comparative examples outside the scope of this invention.

Unless stated otherwise, the aluminium surfaces treated with the solutions identified in the examples were drawn-and-ironed aluminium cans, which were first degreased, as necessary, in an acidic aqueous cleaner containing sulphuric acid, hydrofluoric acid and detergent. Unless stated otherwise, the coating solutions were applied by spraying for about 20 seconds at the appropriate temperatures. After treatment with the solutions described in the examples, the aluminium surfaces were rinsed firstly with tap water and then with deionized water, and thereafter dried in an oven for 3.5 minutes at about 204.4°C (400°F).

Thereafter, the aluminium cans were tested for corrosion resistance by subjecting them to a water stain resistance test designed to simulate can exposure during commercial pasteurization processes. The test consisted of immersing the cans for a period of 30 minutes in a hot solution of distilled or deionized water containing 0.22 g/l of sodium bicarbonate, 0.082 g/l of sodium chloride, and 2.18 g/l of a water-conditioner (*Dubois 915, which exhibits a total alkalinity of 5.8% Na_2O and on analysis contains sodium nitrate, carbonate, triethanolamine and dodecylphenyl polyethylene glycol). The solution was maintained at 65.6±2.8°C (150°±5°F) during the test. After immersion, the cans were rinsed with tap water, dried with a paper towel and then examined for staining. A cleaned-only aluminium surface, when subjected to this test, turns black or brown after a few minutes. It will be seen from the following examples that prior treatment of aluminium surfaces with coating solutions of the present invention can result in the provision of coated surfaces which resist blackening or other discoloration. The aluminium surfaces were rated as follows:

[*Dubois is a registered trademark of Dubois Chemical Inc.]

5 — perfect, identical to a treated but untested surface;

4.5 — very slight diminishing of the bright appearance of the surface;

4.0 — very slight discolouration;

3.5 — light discolouration, but commercially acceptable;

3.0 — discolouration that is considered not commercially acceptable;

0 — total failure, characterized by severe blackening.

In some of the examples the aluminium cans, after treatment with the indicated solutions, were also tested for paint adhesion. After the treated surface was dried, as described above, a portion of the surface was painted with a water-based white base coat (No. CE3179-2 white polyester sold by PPG Industries Inc.) and the other portion of the surface was painted with a water based varnish (Purair* S145-121 sold by Inmont Corporation) to be referred to in the examples as CE3179-2 and S145-121 respectively. After the paint was cured, the painted surface was immersed in boiling water for 15 minutes. After removing the painted surface from the aforementioned, it was cross-hatched, using a sharp metal object to expose lines of aluminium which showed through the paint or lacquer, and tested for paint adhesion. This test included applying transparent adhesive tape (Scotch** transparent tape No. 610) firmly over the cross-hatched area and then drawing the tape back against itself with a rapid pulling motion such that the tape was pulled away from the cross-hatched area. The results of the test were rated as follows:

[*"Purair" is a registered trademark]
[**"Scotch" is a registered trademark of the 3M Co.]

10 — perfect, when the tape did not peel any paint from the surface;

8 — acceptable; and

0 — total failure.

Examples 1—15, and
Comparative Examples C1—C3

The following acidic aqueous concentrate was prepared for use in connection with the first group of examples:

fluozirconic acid (100%)	10.5 grams/litre
aqueous ammonia (29 wt. %)	5.9 g/l
nitric acid (70 wt. %)	9 g/l
deionized water to make	1 litre

The above composition was prepared by combining an aqueous solution of 23.4 grams of 45 wt.% fluozirconic acid with a portion of the water, and then the aqueous ammonia was added to the resulting solution. A white precipitate was formed, but it dissolved upon addition of nitric acid. The resulting clear solution was diluted to 1 litre with deionized water resulting in a concentrate that was used to prepare treatment solutions at 2.5% by volume in water comprising 2 parts deionized water and 1 part hard water. (In the examples, the term "hard water" refers to tap water from the township of Ambler, Pennzylvania, United States of America, which includes about 80 to about 100 ppm of calcium and has a conductivity of about 400 to about 600 ohms-1). To this solution, there was added, in the amounts indicated in Table 1 below, a non-ionic surfactant (Surfonic* LF-17), which is reported to be a low-foaming alkyl poly-ethoxylated ether. Solutions of varying acidity were prepared by adjusting the pH of the aforementioned composition with appropriate amounts of an aqueous solution of 15% (w/v) ammonium carbonate or dilute nitric acid.

[*Surfonic LF-17 is a registered trademark of Jefferson Chemical Co. Inc.]

The water-stain resistance of aluminium cans coated with the composition is recorded in Table I below:

TABLE I

Ex. No.	Surfactant conc. in ppm	pH of coating solution	Water-stain resistance rating
C-1	0	3.5	3.3
1	5	3.5	3.6
2	10	3.5	3.6
3	20	3.5	4.1
4	40	3.5	4.1
5	80	3.5	4.2
C-2	0	4	3.7
6	5	4	4.4
7	10	4	4.7
8	20	4	4.5
9	40	4	4.5
10	80	4	4.6
C-3	0	4.5	4.3
11	5	4.5	4.4
12	10	4.5	4.7
13	20	4.5	4.8
14	40	4.5	4.7
15	80	4.5	4.7

The improvements in corrosion resistance achieved over the pH range of 3.5 to 4.5 for the compositions evaluated in Table I are clearly shown. Other tests show that for the particular type of composition evaluated in Table I, the water-stain resistance of coatings formed from compositions with and without surfactant were about the same when the pH of the composition was about 2.5. Still other tests showed that for the particular type of composition evaluated in Table I, but prepared from deionized water only and containing 20 ppm of surfactant, improvements in water-stain resistance were achieved when the pH of the composition was in excess of 3.5, with substantial improvements being achieved at a pH of about 4.

Examples 16—39, and
Comparative Examples C4—C6

The next group of examples shows the use of compositions of the type described in Examples 1—15 and Comparative Examples C1—C3, but which also included 0.1 g/l of gluconic acid, this being effective in improving the water-stain resistance of the coated surface. Compositions of varying acidity, and containing either the surfactant used in the compositions of the first group of examples or another surfactant, were evaluated. Said other surfactant was a modified low-foaming polyethoxylated straight-chain alcohol (Triton DF-16*). The specific compositions evaluated and the results of the testing are set forth in Table II below:

*[Triton DF-16 is a registered trademark of Rohm and Haas Company]

TABLE II

Ex. No.	Surfactant	Concentration of surfactant in ppm	pH of coating solution	Water-stain resistance rating
C-4		0	3	3.5
16	LF-17	10	3	3.0
17	LF-17	50	3	3.9
18	LF-17	100	3	3.0
19	LF-17	500	3	3.9
20	DF-16	10	3	3.3
21	DF-16	50	3	4.0
22	DF-16	100	3	3.0
23	DF-16	500	3	4.3
C-5		0	3.5	3.8
24	LF-17	10	3.5	4.0
25	LF-17	50	3.5	4.5
26	LF-17	100	3.5	3.9
27	LF-17	500	3.5	4.1
28	DF-16	10	3.5	4.1
29	DF-16	50	3.5	4.3
30	DF-16	100	3.5	4.4
31	DF-16	500	3.5	4.3
C-6		0	4.0	3.5
32	LF-17	10	4.0	4.3
33	LF-17	50	4.0	4.7
34	LF-17	100	4.0	4.9
35	LF-17	500	4.0	4.8
36	DF-16	10	4.0	3.7
37	DF-16	50	4.0	4.2
38	DF-16	100	4.0	4.4
39	DF-16	500	4.0	4.6

Example 40

Table III below shows the effect of gluconic acid concentration on water-stain resistance of coatings applied at varying temperatures from 32.2°C to 65.6°C (90°F to 150°F). Zirconium was present in each solution in the form of ammonium fluozirconate ($(NH_4)_2ZrF_6$) at a concentration of 1.25×10^{-3}* M/l, and each solution was adjusted to a pH of 3.8 by the addition of concentrated nitric acid. Two cans were employed in determining the water-stain resistance rating of each solution.

[*M=Mole]

TABLE III

Effect of gluconic acid concentration on water-stain resistance at 1.25×10^{-3}M $(NH_4)_2ZrF_6$ concentration and pH of 3.8

Sample No.	Gluconic acid conc. ($M\times10^{-3}$)	Temp. °C	Temp. (°F)	Water-stain resistance
1	0	32.2	(90)	0 ; 0
2	0	43.3	(110)	0 ; 0
3	0	54.4	(130)	0.5 ; 0.5
4	0	65.6	(150)	3 ; 3
5	0.025	32.2	(90)	0 ; 0
6	0.025	43.3	(110)	0.5 ; 0.5
7	0.025	54.4	(130)	0.5 ; 0.5
8	0.025	65.6	(150)	4 ; 4
9	0.05	32.2	(90)	0 ; 0
10	0.05	43.3	(110)	0.5 ; 0.5
11	0.05	54.4	(130)	0.5 ; 1
12	0.05	65.6	(150)	4 ; 4
13	0.1	32.2	(90)	0.5 ; 0.5
14	0.1	43.3	(110)	1 ; 1
15	0.1	54.4	(130)	3 ; 4
16	0.1	65.6	(150)	4 ; 4
17	0.2	32.2	(90)	0.5 ; 0.5
18	0.2	43.3	(110)	2 ; 1
19	0.2	54.4	(130)	3.5 ; 4
20	0.2	65.6	(150)	3.5 ; 3.5
21	0.3	32.2	(90)	0.5 ; 0.5
22	0.3	43.3	(110)	3.5 ; 3.5
23	0.3	54.4	(130)	4 ; 5
24	0.3	65.6	(150)	5 ; 5
25	0.4	32.2	(90)	1 ; 1

TABLE III (continued)

Sample No.	Gluconic acid conc. ($M \times 10^{-3}$)	Temp. °C	Temp. (°F)	Water-stain resistance
26	0.4	43.3	(110)	4 ; 2
27	0.4	54.4	(130)	3 ; 3
28	0.4	65.6	(150)	4 ; 5
29	0.5	32.2	(90)	1 ; 1
30	0.5	43.3	(110)	4 ; 4
31	0.5	54.4	(130)	5 ; 5
32	0.5	65.5	(150)	4 ; 4
33	0.75	32.2	(90)	1 ; 1
34	0.75	43.3	(110)	4 ; 4
35	0.75	54.4	(130)	4 ; 4
36	0.75	65.6	(150)	3.5 ; 3.5
37	1.0	32.2	(90)	1 ; 1
38	1.0	43.3	(110)	2 ; 2
39	1.0	54.4	(130)	4 ; 3
40	1.0	65.6	(150)	4 ; 3.5
41	1.25	32.2	(90)	0 ; 0
42	1.25	43.3	(110)	1 ; 1
43	1.25	54.4	(130)	4 ; 4
44	1.25	65.6	(150)	4 ; 4
45	1.5	32.2	(90)	0 ; 0
46	1.5	43.3	(110)	1 ; 1
47	1.5	54.4	(130)	2.5 ; 2
48	1.5	65.6	(150)	5 ; 5
49	1.75	32.2	(90)	0 ; 0
50	1.75	43.3	(110)	1 ; 1
51	1.75	54.4	(130)	4 ; 4
52	1.75	65.6	(150)	5 ; 5
53	2.0	32.2	(90)	0 ; 0
54	2.0	43.3	(110)	1 ; 1
55	2.0	54.5	(130)	3 ; 2
56	2.0	65.6	(150)	5 ; 5

TABLE III (continued)

Sample No.	Gluconic acid conc. ($M\times10^{-3}$)	Temp. °C	(°F)	Water-stain resistance
57	5.0	32.2	(90)	0 ; 0
58	5.0	43.3	(110)	0 ; 0
59	5.0	54.4	(130)	0 ; 0
60	5.0	65.6	(150)	2 ; 2

Example 41

Table IV below also shows the effect of gluconic acid concentration on water-stain resistance, as well as on the adhesion of water-based siccative coatings, at two different pH and temperature levels. Zirconium was again present in each solution in the form of ammonium fluozirconate ($(NH_4)_2ZrF_6$) at a concentration of 1.25×10^{-3} mole/litre, and the pH of each solution was adjusted by the addition of concentrated nitric acid. Two cans were employed in determining each paint adhesion rating ("Adhesion") while each water-stain resistance rating ("Resistance") represents the average rating of six cans.

TABLE IV

Effect of gluconic acid concentration on water-stain resistance and adhesion of water-based siccative coatings at 1.25×10^{-3}M $(NH_4)_2ZrF_6$ concentration

Sample No.	Gluconic acid conc. ($M\times10^{-3}$)	pH	Temp. °C	(°F)	Water-stain resistance	Adhesion CE3179-2	S145-121
1	0	3.5	51.7	(125)	1	10 ; 10	10 ; 7
2	0	3.5	57.2	(135)	2.67	10 ; 10	10 ; 8
3	0	4.25	51.7	(125)	4	10 ; 10	10 ; 10
4	0	4.25	57.2	(135)	2.67	10 ; 8	10 ; 8
5	0.5	3.5	51.7	(125)	5	10 ; 10	10 ; 10
6	0.5	3.5	57.2	(135)	5	10 ; 10	10 ; 10
7	0.5	4.25	51.7	(125)	4.67	10 ; 10	10 ; 10
8	0.5	4.25	57.2	(135)	4.67	10 ; 9	10 ; 10
9	1.25	3.5	51.7	(125)	4.17	10 ; 10	10 ; 10
10	1.25	3.5	57.2	(135)	5	10 ; 10	10 ; 10
11	1.25	4.25	51.7	(125)	5	10 ; 10	10 ; 10
12	1.25	4.25	57.2	(135)	5	10 ; 10	10 ; 10
13	2.5	3.5	51.7	(125)	1.17	10 ; 10	10 ; 10
14	2.5	3.5	57.2	(135)	2.67	10 ; 8	10 ; 10
15	2.5	4.25	51.7	(125)	1.67	10 ; 10	10 ; 10
16	2.5	4.25	57.2	(135)	4.67	9 ; 9	10 ; 10

Examples 42—45

An aqueous concentrate of the type used to formulate the compositions of Examples 1—15 was diluted with a sufficient amount of water (two parts deionized water and one part hard water) to yield a coating solution containing 2.5% by volume of the concentrate, to which was added 20 ppm of Surfonic LF-17. Four solutions were thus prepared, to each of which was added 0.1 g/l of one of the following ingredients:

glutaric acid, ascorbic acid, maleic acid or salicylic acid. The pH of each of the compositions was 3.5 and each was used in treating aluminium cans in the manner described above in connection with the preceding Examples. For all of the cans treated in this way, water-stain resistance ratings were above 3.5 and improved adhesion was exhibited when the cans were painted with either PPG CE3179-2 or Inmont S145-121 water-based coating compositions, or with Clements P1099-7A or Clements P550-G organic solvent-based coating compositions.

Examples 46—49

Other compositions were formulated by including 0.5×10^{-3}M/l of gluconic acid in each of the compositions of Examples 42—45 above. Coatings formed from such compositions exhibited improved adhesion with respect to top coats formed from various water-based resin coating compositions.

Example 50

Table V below shows the effect of ammonium fluozirconate concentration on water-stain resistance of coatings applied at varying temperatures from 32.2°C to 65.6°C (90°F to 150°F). Gluconic acid was present in each solution at a concentration of 0.5×10^{-3} mole/litre, and each solution was adjusted to a pH of 3.8 by the addition of concentrated nitric acid. Two cans were employed in determining the water-stain resistance rating of each solution.

TABLE V

Effect of $(NH_4)_2ZrF_6$ concentration on water-stain resistance at 0.5×10^{-3}M gluconic acid concentration and pH of 3.8

Sample No.	$(NH_4)_2ZrF_6$ conc.	Temp. °C	Temp. (°F)	Water-stain resistance.
1	0	32.2	(90)	0 ; 0
2	0	43.3	(110)	0 ; 0
3	0	54.4	(130)	0 ; 0
4	0	65.6	(150)	0 ; 0
5	0.1	32.2	(90)	0 ; 0
6	0.1	43.3	(110)	0 ; 0
7	0.1	54.4	(130)	0 ; 0
8	0.1	65.6	(150)	0 ; 0
9	0.25	32.2	(90)	0 ; 0
10	0.25	43.3	(110)	0 ; 0
11	0.25	54.4	(130)	3 ; 3
12	0.25	65.6	(150)	3 ; 3
13	0.50	32.2	(90)	0 ; 0
14	0.50	43.3	(110)	2 ; 2
15	0.50	54.4	(130)	3 ; 3
16	0.50	65.6	(150)	4 ; 4
17	0.75	32.2	(90)	2 ; 2
18	0.75	43.3	(110)	2 ; 2
19	0.75	54.4	(130)	3 ; 3
20	0.75	65.6	(150)	4 ; 4

TABLE V (contd.)

Sample No.	$(NH_4)_2ZrF_6$ conc.	Temp. °C	Temp. (°F)	Water-stain resistance.
21	1.25	32.2	(90)	1 ; 1
22	1.25	43.3	(110)	2 ; 2
23	1.25	54.4	(130)	3 ; 3
24	1.25	65.6	(150)	4 ; 4
25	1.75	32.2	(90)	1 ; 1
26	1.75	43.3	(110)	2 ; 2
27	1.75	54.4	(130)	4 ; 4
28	1.75	65.6	(150)	5 ; 5
29	2.25	32.2	(90)	1 ; 1
30	2.25	43.3	(110)	2 ; 2
31	2.25	54.4	(130)	4 ; 4
32	2.25	65.6	(150)	5 ; 5
33	5.0	32.2	(90)	2 ; 2
34	5.0	43.3	(110)	2 ; 2
35	5.0	54.4	(130)	4 ; 4
36	5.0	65.6	(150)	4 ; 4

Example 51

Table VI below shows the effect of ammonium fluozirconate concentration on water-stain resistance, as well as on the adhesion of water-based siccative coatings, at three different pH and two different temperature levels. Again, gluconic acid was present in each solution at a concentration of 0.5×10^{-3} mole/litre, and the pH of each solution was adjusted by the addition of concentrated nitric acid. Two cans were employed in determining each paint adhesion rating while each water-stain resistance rating represents the average of six cans.

TABLE VI

Effect of $(NH_4)_2ZrF_6$ concentration on water-stain resistance and adhesion of water-based siccative coatings at 0.5×10^{-3}M gluconic acid concentration

Example No.	$(NH_4)_2ZrF_6$ conc. ($M\times10^{-3}$)	pH	Temp. °C	Temp. (°F)	Water-stain resistance	Adhesion CE3179-2	Adhesion S145-121
1	0.75	3.5	51.7	(125)	4.67	10 ; 8	10 ; 10
2	0.75	3.5	57.2	(135)	5	10 ; 10	10 ; 10
3	0.75	4.0	51.7	(125)	4.83	9 ; 9	10 ; 10
4	0.75	4.0	57.2	(135)	4.67	10 ; 8	10 ; 10
5	0.75	4.25	51.7	(125)	4	10 ; 10	10 ; 8
6	0.75	4.25	57.2	(135)	4	10 ; 8	9 ; 9
7	1.25	3.5	51.7	(125)	5	10 ; 10	10 ; 10
8	1.25	3.5	57.2	(135)	5	10 ; 10	10 ; 10
9	1.25	4.0	51.7	(125)	5	10 ; 10	10 ; 10
10	1.25	4.0	57.2	(135)	5	10 ; 8	10 ; 9
11	1.25	4.25	51.7	(125)	4.67	10 ; 10	10 ; 10
12	1.25	4.25	57.2	(135)	4.34	10 ; 9	10 ; 10
13	1.75	3.5	51.7	(125)	4	10 ; 10	10 ; 8
14	1.75	3.5	57.2	(135)	4	10 ; 8	9 ; 9
15	1.75	4.0	51.7	(125)	4	10 ; 10	10 ; 10
16	1.75	4.0	57.2	(135)	4	10 ; 10	10 ; 10
17	1.75	4.25	51.7	(125)	4	10 ; 10	10 ; 10
18	1.75	4.25	57.2	(135)	4	10 ; 10	10 ; 10
19	cleaned only				0	10 ; 9	10 ; 10

Example 52

Table VII below illustrates the water-stain resistance of coatings formed from a solution of hafnium tetrafluoride, hydrofluoric acid and gluconic acid at varying temperatures from 32.2° to 65.6°C (90°F to 150°F). The solution contained 1.25×10^{-3} mole/litre of hafnium tetrafluoride, 2.5×10^{-3} mole/litre of hydrofluoric acid and 0.5×10^{-3} mole/litre of gluconic acid. For comparative purposes, coatings, were also formed from a similar solution free of gluconic acid. The pH of both solutions was adjusted to 3.8 by the addition of concentrated nitric acid. Two cans were employed in determining the water-stain resistance rating of the solutions.

TABLE VII

Water-stain resistance of coatings formed from a solution of hafnium tetrafluoride, hydrofluoric acid and gluconic acid

Sample No.	HfF_4 conc. ($M\times10^{-3}$)	HF conc. ($M\times10^{-3}$)	Gluconic acid conc. ($M\times10^{-3}$)	pH	Temp. °C	Temp. (°F)	Water-stain resistance
1	1.25	2.5	0	3.8	32.2	(90)	0
2	1.25	2.5	0	3.8	43.3	(110)	1
3	1.25	2.5	0	3.8	54.4	(130)	1
4	1.25	2.5	0	3.8	65.6	(150)	2
5	1.25	2.5	0.5	3.8	32.2	(90)	1
6	1.25	2.5	0.5	3.8	43.3	(110)	1
7	1.25	2.5	0.5	3.8	54.4	(130)	5
8	1.25	2.5	0.5	3.8	65.6	(150)	5

Examples 53—56

Tables VIII, IX, X and XI illustrate the effect of pH and temperature on the water-stain resistance of coatings formed from a solution of ammonium fluozirconate and gluconic acid, as well as on the adhesion of further water-based siccative coatings to such coatings. The solution employed contained 1.25×10^{-3} mole/litre of the ammonium fluorzirconate and 0.5×10^{-3} mole/litre of the gluconic acid. For comparative purposes, coatings were also formed from a similar solution free of gluconic acid. The pH of both solutions was adjusted to the values shown in the tables by the addition of concentrated nitric acid. Such solutions were then applied at varying temperatures from 32.2°C to 71.1°C (90°F to 160°F). Two cans were employed in determining each water-stain resistance rating and one can was employed in determining each paint adhesion rating at each pH and temperature value. The condition of each solution (clear or cloudy) at each pH and temperature level employed was also recorded. As can be seen from Tables X and XI, the presence of gluconic acid is important at pH 4.5 and 5.0 in maintaining a clear solution and preventing precipitation.

TABLE VIII

Effect of temperature on water-stain resistance of coatings formed from a solution of 1.25×10^{-3}M $(NH_4)_2ZrF_6$ and 0.5×10^{-3}M gluconic acid at a pH of 3.0, and on the adhesion of water-based siccative coatings to such conversion coatings

Sample No.	Gluconic acid con. ($M\times10^{-3}$)	Temp. °C	Temp. (°F)	Water-stain resistance	Adhesion CE3179-2	Solution condition
1	0	32.2	(90)	2 ; 2	10	Clear
2	0	37.8	(100)	2 ; 2	10	Clear
3	0	43.3	(110)	1 ; 1	10	Clear
4	0	48.9	(120)	1 ; 1	10	Clear
5	0	54.4	(130)	1 ; 1	10	Clear
6	0	60.0	(140)	2 ; 2	10	Clear
7	0	65.6	(150)	3 ; 3	10	Clear
8	0	71.1	(160)	3 ; 3	10	Clear
9	0.5	32.2	(90)	3 ; 3	10	Clear
10	0.5	37.8	(100)	3 ; 3	10	Clear
11	0.5	43.3	(110)	3 ; 3	10	Clear
12	0.5	48.9	(120)	4 ; 4	10	Clear
13	0.5	54.4	(130)	4 ; 4	10	Clear
14	0.5	60.0	(140)	5 ; 5	10	Clear
15	0.5	65.6	(150)	5 ; 5	—	Clear
16	0.5	71.1	(160)	5 ; 5	7 (heavy paint)	Clear

TABLE IX

Effect of temperature on water-stain resistance of coatings formed from a solution of 1.25×10^{-3}M $(NH_4)_2ZrF_6$ and 0.5×10^{-3}M gluconic acid at a pH of 3.5, and on the adhesion of water-based siccative coatings to such conversion coatings

Sample No.	Gluconic acid conc. ($M\times10^{-3}$)	Temp. °C	Temp. (°F)	Water-stain resistance	Adhesion CE3179-2	Solution condition
1	0	32.2	(90)	0 ; 0	10	Clear
2	0	37.8	(100)	0 ; 0	10	Clear
3	0	43.3	(110)	0 ; 0	10	Clear
4	0	48.9	(120)	0 ; 0	10	Clear
5	0	54.4	(130)	1 ; 1	10	Klear
6	0	60.0	(140)	2 ; 3	10	Clear
7	0	65.6	(150)	2 ; 3	10	Clear
8	0	71.1	(160)	2 ; 3	10	Clear
9	0.5	32.2	(90)	2 ; 2	10	Clear
10	0.5	37.8	(100)	2 ; 2	10	Clear
11	0.5	43.3	(110)	3 ; 3	10	Clear
12	0.5	48.9	(120)	3 ; 4	10	Clear
13	0.5	54.4	(130)	4 ; 4	10	Clear
14	0.5	60.0	(140)	5 ; 5	10	Clear
15	0.5	65.6	(150)	5 ; 5	10	Clear
16	0.5	71.1	(160)	5 ; 5	10	Clear

TABLE X

Effect of temperature on water-stain resistance of coatings formed from a solution of 1.25×10^{-3}M $(NH_4)_2ZrF_6$ and 0.5×10^{-3}M gluconic acid at a pH of 4.5, and on the adhesion of water-based siccative coatings to such conversion coatings

Sample No.	Gluconic acid conc. ($M\times10^{-3}$)	Temp. °C	Temp. (°F)	Water-stain resistance	Adhesion CE3179-2	Solution condition
1	0	32.2	(90)	0 ; 0	10	Clear
2	0	37.8	(100)	0 ; 0	10	Slight haze
3	0	43.3	(110)	0 ; 0	10	Faint haze
4	0	48.9	(120)	3 ; 1	10	Cloudy
5	0	54.4	(130)	2 ; 1	10	Cloudy
6	0	60.0	(140)	2 ; 2	10	Cloudy
7	0	65.6	(150)	2 ; 2	10	Cloudy
8	0	71.1	(160)	2 ; 3	10	Very Cloudy
9	0.5	32.2	(90)	0 ; 0	10	Clear
10	0.5	37.8	(100)	0 ; 1	10	Clear
11	0.5	43.3	(110)	2 ; 1	10	Clear
12	0.5	48.9	(120)	3 ; 1	10	Clear
13	0.5	54.4	(130)	4 ; 4	10	Clear
14	0.5	60.0	(140)	4 ; 4	10	Clear
15	0.5	65.6	(150)	4 ; 4	10	Clear
16	0.5	71.1	(160)	4 ; 4	10	Clear

TABLE XI

Effect of temperature on water-stain resistance of coatings formed from a solution of 1.25×10^{-3}M $(NH_4)_2ZrF_6$ and 0.5×10^{-3}M gluconic acid at a pH of 5.0, and on the adhesion of water-based siccative coatings to such coatings

Sample No.	Gluconic acid conc. ($M\times10^{-3}$)	Temp. °C	Temp. (°F)	Water-stain resistance	Adhesion CE3179-2	Solution condition
1	0	32.2	(90)	2 ; 2	10	Cloudy
2	0	37.8	(100)	2 ; 2	10	Cloudy
3	0	43.3	(110)	3 ; 3	10	Cloudy
4	0	48.9	(120)	4 ; 3	10	Cloudy
5	0	54.4	(130)	4 ; 3	10	Cloudy
6	0	71.1	(160)	4 ; 3	10	Cloudy
7	0.5	32.2	(90)	3 ; 2	10	Clear
8	0.5	37.8	(100)	3 ; 3	10	Clear
9	0.5	43.3	(110)	3 ; 3	10	Clear
10	0.5	48.9	(120)	4 ; 3	10	Clear
11	0.5	54.4	(130)	4 ; 3	10	Clear
12	0.5	60.0	(140)	4 ; 3	10	Clear
13	0.5	65.6	(150)	4 ; 3	10	Clear
14	0.5	71.1	(160)	4 ; 2	10	Clear initially, cloudy after standing for 1 hour.

Example 57

Table XII below shows how the addition of phosphate to an ammonium fluozirconate solution adversely affects the adhesion of water-based siccative coatings to coatings formed from such solutions. The concentration of phosphate and ammonium fluozirconate in each of the solutions prepared is shown in the table. The phosphate was added as phosphoric acid. The pH of the solutions was varied as shown in the table, and again concentrated nitric acid was employed to adjust the pH. The solutions were applied as a temperature of 54.4°C (130°F). Two cans were employed in determining each paint adhesion rating of each solution.

TABLE XII

Effect of phosphate concentration on adhesion of water-based siccative coatings to coatings formed from fluozirconate solutions

Sample No.	$(NH_4)_2ZrF_6$ conc. ($M\times10^{-3}$)	Phosphate conc. ($M\times10^{-3}$)	pH	Adhesion CE3179-2	Adhesion S145-121
1	0.5	0	3.5	10 ; 9	9 ; 6
2	0.5	0	4.0	10 ; 10	8 ; 7
3	0.5	0.1	3.5	10 ; 5	8 ; 6
4	0.5	0.1	4.0	10 ; 5	7 ; 0
5	0.5	0.25	3.5	0 ; 0	9 ; 6
6	0.5	0.25	4.0	0 ; 0	8 ; 7
7	1.25	0	3.5	10 ; 10	9 ; 6
8	1.25	0	4.0	10 ; 9	8 ; 7
9	1.25	0.1	3.5	7 ; 0	8 ; 7
10	1.25	0.1	4.0	6 ; 5	10 ; 0
11	1.25	0.25	3.5	0 ; 0	7 ; 7
12	1.25	0.25	4.0	0 ; 0	8 ; 0
13	2.5	0	3.5	10 ; 10	10 ; 8
14	2.5	0	4.5	10 ; 9	9 ; 6
15	2.5	0.1	3.5	0 ; 0	10 ; 9
16	2.5	0.1	4.0	9 ; 8	8 ; 8
17	2.5	0.25	3.5	7 ; 5	8 ; 5
18	2.5	0.25	4.0	0 ; 0	9 ; 5
19	cleaned only			0 ; 10	10 ; 8

Example 58

Table XIII below shows how the addition of phosphate and gluconic acid to ammonium fluozirconate solutions affects the adhesion of water-based siccative coatings to coatings formed from such solutions. The concentration of each of these materials in each of the solutions prepared is shown in the Table. The phosphate was added as phosphoric acid. The pH of the solutions was varied as shown in the Table and concentrated nitric acid was employed to adjust the pH. The solutions were applied at the temperatures indicated. Two cans were employed in determining each paint adhesion rating of each solution.

TABLE XIII

Effect of phosphate and gluconic acid concentration on adhesion of water-based siccative coatings to coatings formed from fluozirconate solutions

Sample No.	$(NH_4)_2ZrF_6$ conc. ($M\times10^{-3}$)	Phosphate conc. ($M\times10^{-3}$)	Gluconic acid conc. ($M\times10^{-3}$)	pH	Temp. °C	Temp. (°F)	Adhesion CE3179-2	Adhesion S145-121
1	0.25	0	0	4.0	43.3	(110)	10 ; 10	10 ; 8
2	0.25	0	0	4.0	54.4	(130)	10 ; 10	8 ; 8
3	0.25	0.1	0	4.0	43.3	(110)	10 ; 8	10 ; 10
4	0.25	0.1	0	4.0	54.4	(130)	7 ; 7	10 ; 8
5	0.25	0	0.5	4.0	43.3	(110)	10 ; 10	10 ; 10
6	0.25	0	0.5	4.0	54.4	(130)	10 ; 10	10 ; 10
7	0.25	0.1	0.5	4.0	43.3	(110)	8 ; 6	10 ; 10
8	0.25	0.1	0.5	4.0	54.4	(130)	0 ; 0	10 ; 7
9	0.25	0	0	3.5	43.3	(110)	10 ; 10	10 ; 10
10	0.25	0	0	3.5	54.4	(130)	10 ; 10	10 ; 10
11	0.25	0.1	0	3.5	43.3	(110)	5 ; 5	10 ; 7
12	0.25	0.1	0	3.5	54.4	(130)	0 ; 5	0 ; 0
13	0.25	0	0.5	3.5	43.3	(110)	10 ; 10	10 ; 10
14	0.25	0	0.5	3.5	54.4	(130)	10 ; 10	10 ; 10
15	0.25	0.1	0.5	3.5	43.3	(110)	10 ; 7	7 ; 6
16	0.25	0.1	0.5	3.5	54.4	(130)	7 ; 7	7 ; 7
17	1.25	0	0	3.5	43.3	(110)	10 ; 10	10 ; 7
18	1.25	0	0	3.5	54.4	(130)	10 ; 10	9 ; 7
19	1.25	0.1	0	3.5	43.3	(110)	10 ; 10	10 ; 10
20	1.25	0.1	0	3.5	54.4	(130)	0 ; 0	7 ; 5
21	1.25	0	0.5	3.5	43.3	(110)	10 ; 10	10 ; 8
22	1.25	0	0.5	3.5	54.4	(130)	10 ; 8	10 ; 8
23	1.25	0.1	0.5	3.5	43.3	(110)	10 ; 7	5 ; 5
24	1.25	0.1	0.5	3.5	54.4	(130)	10 ; 8	7 ; 0
25	cleaned only						10 ; 10	10 ; 10

Example 59

In order to demonstrate that aluminium surfaces coated with a coating solution containing gluconic acid, zirconium and fluoride undergo satisfactorily the so-called "muffle test", while aluminium surfaces coated with a like coating solution free of gluconic acid do not, a number of aluminium cans were coated with solutions having the compositions and applied at the temperatures shown in Table XIV below, each solution having a pH of 4.25 obtained by addition of concentrated nitric acid. The coated cans were then

heated at a temperature of 482.2°C (900°F) for 5 minutes and the colour of the cans was observed. The results observed are set forth below in Table XIV.

TABLE XIV
Muffle test results of coated aluminium surfaces

Sample No.	$(NH_4)_2ZrF_6$ conc. ($M\times10^{-3}$)	Gluconic acid conc. ($M\times10^{-3}$)	Temp. °C	Temp. (°F)	Surface colour after heating at 482.2°C (900°F) for 5 minutes
1	1.25	0	51.7	(125)	silver
2	1.25	0	57.2	(135)	silver
3	1.25	0.5	51.7	(125)	light-golden-brown
4	1.25	0.5	57.2	(135)	light-golden-brown
5	cleaned only				silver

In summary, it can be said that the present invention provides the means for forming on an aluminium surface a non-chromate coating which is colourless and clear without modifying the appearance of the aluminium surface. The coated surface exhibits improved corrosion resistance, as exemplified by the test results reported above, and exhibits excellent adhesion to overlying siccative coatings formed from either water-based or organic-solvent based coating compositions.

Claims

1. A chromate-free, acidic, aqueous coating solution of pH from 1.5 to 5, capable of forming a clear, colourless and corrosion-resistant conversion coating upon an aluminium surface, which contains:—
(a) one or more of the Group IVa metals zirconium, hafnium and titanium in a total concentration of at least 0.5×10^{-3} mole/litre;
(b) fluoride in an amount at least sufficient to combine and form a soluble complex with all of the Group IVa metal(s) present; and
(c) an additive in the form of:

(i) a surfactant present in a concentration of at least 0.01 g/litre; and/or
(ii) a polyhydroxy organic compound having up to 7 carbon atoms and present in a concentration of at least 0.025×10^{-3} mole/litre, when the additive is this polyhydroxy organic compound alone the solution being free from phosphate und boron.

2. A conversion-coating solution for aluminium as claimed in claim 1, in which fluoride is present in an amount corresponding to at least 4 moles per mole of said Group IVa metal(s).

3. A conversion-coating solution for aluminium as claimed in claim 1 or claim 2, in which said Group IVa metal is or includes zirconium.

4. A conversion-coating solution for aluminium as claimed in any of the preceding claims, in which the (c) additive is or includes surfactant and the pH value of the solution is in the range of from 3.5 to 4.5.

5. A conversion-coating solution for aluminium as claimed in claim 4, in which zirconium is present in a concentration of from 0.75×10^{-3} to 2×10^{-3} mole/litre and surfactant is present in a concentration of from 0.01 to 0.5 g/litre.

6. A conversion-coating solution for aluminium as claimed in claim 5, in which zirconium is present in a concentration of from 1×10^{-3} to 1.75×10^{-3} mole/litre, surfactant is present in a concentration of from 0.02 to 0.1 g/litre, and the solution has a pH value in the range of from 3.7 to 4.3.

7. A conversion-coating solution for aluminum as claimed in any of the preceding claims, which contains surfactant in the form of a non-ionic surfactant.

8. A conversion-coating solution for aluminium as claimed in any of the preceding claims, which when the additive is not the polyhydroxy organic compound alone, also includes at least 10 parts per million of a boron compound.

9. A conversion-coating solution for aluminium as claimed in any of the preceding claims, which besides at least 0.01 g/litre of surfactant also includes at least 0.025×10^{-3} mole/litre of said polyhydroxy compound.

10. A conversion-coating solution for aluminium as claimed in any of claims 1 to 3, in which the (c) additive is or includes the polyhydroxy compound.

11. A conversion-coating solution for aluminium as claimed in claim 10, the pH value of the solution being in the range of from 3 to 5.

12. A conversion-coating solution for aluminium as claimed in claim 11, which contains from 0.5×10^{-3} to 1.75×10^{-3} mole/litre of zirconium and from 0.3×10^{-3} to 1.75×10^{-3} mole/litre of said polyhydroxy compound.

13. A conversion-coating solution for aluminium as claimed in any of claims 1—8, in which the (c) additive is the surfactant alone.

14. A conversion-coating solution for aluminium as claimed in any of the preceding claims, which also includes tannin.

15. A process for forming a clear, colourless corrosion-resistant coating upon an aluminium surface, comprising the step of contacting said surface with the chromate-free, acidic, aqueous conversion-coating solution claimed in any of the preceding claims for a period of time sufficient at the operating temperature to form the desired coating thereon.

16. A process as claimed in claim 15, in which a succession of aluminium surfaces are treated with a conversion-coating solution wherein the (c) additive is surfactant and the coating solution is intermittently or continuously replenished as necessary with an aqueous replenishing concentrate so as to maintain the concentrations of the ingredients in the coating solution within the specified limits using a replenishing concentrate containing from 0.05 to 0.5 mole/litre of zirconium, from 0.2 to 10 mole/litre of fluoride and from 1 to 100 grams/litre of surfactant.

17. A process as claimed in claim 15, in which a succession of aluminium surfaces are treated with a conversion-coating solution wherein the (c) additive is polyhydroxy compound and the coating solution is intermittently or continuously replenished as necessary with an aqueous replenishing concentrate so as to maintain the concentrations of the ingredients in the coating solution within the specified limits using a replenishing concentrate containing from 31×10^{-3} to 251×10^{-3} moles/litre of zirconium, a source material which provides from 90×10^{-3} to 695×10^{-3} moles/litre of uncomplexed available fluoride and from 19×10^{-3} to 148×10^{-3} moles/litre of polyhydroxy compound.

18. A process as claimed in any of claims 15 to 17, which after formation of said conversion coating upon the aluminium surface also includes the subsequent step of applying thereto an overlying water-borne siccative coating.

19. An aqueous concentrate for dilution with water to form the conversion-coating solution used in the process of claim 16, such that an aqueous solution containing from 0.5 to 10 weight percent of said concentrate is sufficiently acidic to form a conversion coating upon aluminium and contains (A) at least 0.5×10^{-3} mole/litre of one or more of the group IVa metals zirconium, titanium and hafnium; (B) fluoride in an amount at least sufficient to combine and form a soluble complex with substantially all of the Zr, Ti and/or Hf; and also (C) at least 0.01 g/litre of surfactant.

20. An aqueous concentrate for use in replenishment of the conversion-coating solution in the process claimed in claim 16, which comprises from 0.05 to 0.5 mole/litre of zirconium, from 0.2 to 10 mole/litre of fluoride and from 1 to 100 grams/litre of surfactant.

21. An aqueous concentrate for dilution with water to form the conversion-coating solution used in the process of claim 17, such that an aqueous solution containing from 0.5 to 10 weight percent of said concentrate, being free from phosphate and from boron, has a pH value within the range of from 3 to 5 and contains (A) at least 0.5×10^{-3} mole/litre of zirconium or hafnium or a mixture thereof, (B) at least 0.025×10^{-3} mole/litre of a water-soluble polyhydroxy compound having no more than 7 carbon atoms, and (C) at least sufficient fluoride to combine and form a soluble complex with all of the zirconium and/or hafnium present in the solution.

22. An aqueous concentrate for use in replenishment of the conversion-coating solution in the process claimed in claim 17, which comprises from 31×10^{-3} to 251×10^{-3} moles/litre of zirconium, a source material which provides from 90×10^{-3} to 695×10^{-3} moles/litre of uncomplexed available fluoride and from 19×10^{-3} to 148×10^{-3} moles/litre of polyhydroxy compound.

Revendications

1. Une solution de revêtement aqueuse acide, libre de chromate, de pH 1,5 à 5, susceptible de former un revêtement de conversion résistant à la corrosion, clair et incolore sur une surface d'aluminium, qui contient:

(a) un ou plusieurs métaux du groupe IV choisis parmi le zirconium, l'hafnium et le titane, à une concentration totale d'au moins $0,5\times10^{-3}$ mole/l;

(b) du fluorure en quantité au moins suffisante pour se combiner et former un complexe soluble avec tous le (les) métal (métaux) du groupe IV présent(s); et

(c) un additif sous la forme:

(i) d'un agent tensio-actif présent en concentration d'au moins 0,01 g/l; et/ou

(ii) un composé polyhydroxy organique ayant jusqu'à 7 atomes de carbone et présent à la concentration d'au moins $0,025\times10^{-3}$ mole/l, lorsque l'additif est ce composé polyhydroxy organique seul, la solution étant libre de phosphate et de bore.

2. Une solution de revêtement de conversion pour l'aluminium selon la revendication 1, dans laquelle le fluorure est présent en quantité correspondant à au moins 4 moles par mole du (des) susdit(s) métal (métaux) du groupe IV.

3. Une solution de revêtement de conversion pour l'aluminium selon la revendication 1 ou 2, dans laquelle ledit métal du groupe IV est ou inclut le zirconium.

4. Une solution de revêtement de conversion pour l'aluminium selon les revendications précédentes, dans laquelle l'additif (c) est ou inclut un agent tensio-actif et la valeur du pH de la solution est dans le domaine de 3,5 à 4,5.

5. Une solution de revêtement de conversion pour l'aluminium selon la revendication 4, dans laquelle le zirconium est présent en concentration de $0{,}75\times10^{-3}$ à 2×10^{-3} mole/l et l'agent tensio-actif est présent en quantité de 0,01 à 0,5 g/l.

6. Une solution de revêtement de conversion pour l'aluminium selon la revendication 5, dans laquelle le zirconium est présent en concentration de $1{,}10\times10^{-3}$ à $1{,}75\times10^{-3}$ mole/l et l'agent tensio-actif est présent en une concentration de 0,02 à 0,1 g/l et cette solution a une valeur de pH dans le domaine de 3,7 à 4,3.

7. Une solution de revêtement de conversion pour l'aluminium selon les revendications précédentes, qui contient un agent tensio-actif sous la forme d'un agent tensio-actif non ionique.

8. Une solution de revêtement de conversion pour l'aluminium selon les revendications précédentes, qui, lorsque l'additif n'est pas le composé polyhydroxy organique seul, contient également au moins 10 parties par million d'un composé de bore.

9. Une solution de revêtement de conversion pour l'aluminium selon les revendications précédentes, qui, outre au moins 0,01 g/l d'agent tensio-actif, contient également au moins $0{,}025\times10^{-3}$ mole/l du susdit composé polyhydroxy.

10. Une solution de revêtement de conversion pour l'aluminium selon les revendications 1 à 3, dans laquelle l'additif (c) est ou inclut le composé polyhydroxy.

11. Une solution de revêtement de conversion pour l'aluminium selon la revendication 10, la valeur du pH de la solution étant dans le domaine de 3 à 5.

12. Une solution de revêtement de conversion pour l'aluminium selon la revendication 11, qui contient de $0{,}5\times10^{-3}$ à $1{,}75\times10^{-3}$ mole/l de zirconium et de $0{,}3\times10^{-3}$ à $1{,}75\times10^{-3}$ mole/l dudit composé polyhydroxy.

13. Une solution de revêtement de conversion pour l'aluminium selon les revendications 1 à 8, dans laquelle l'additif (c) est l'agent tensio-actif seul.

14. Une solution de revêtement de conversion pour l'aluminium selon les revendications précédentes, qui comprend également du tanin.

15. Un procédé de formation d'un revêtement résistant à la corrosion, clair, incolore, sur une surface d'aluminium, comprenant l'étape de mise en contact de ladite surface avec la solution de revêtement de conversion aqueuse, acide, libre de chromate, selon l'une quelconque des revendications précédentes, pendant une période de temps suffisante, à la température opérationnelle pour y former le revêtement désiré.

16. Un procédé selon la revendication 15, dans lequel une succession de surfaces d'aluminium est traitée avec une solution de revêtement de conversion dans laquelle l'additif (c) est l'agent tensio-actif et la solution de revêtement est renouvelée de façon intermittente ou continue, si nécessaire avec un concentré de renouvellement aqueux, afin de maintenir les concentrations des ingrédients dans la solution de revêtement à l'intérieur des limites spécifiques utilisant un concentré de renouvellement de 0,05 à 0,5 mole/l de zirconium, de 0,2 à 10 moles/l de fluorure et de 1 à 100 g/l d'agent tensio-actif.

17. Un procédé selon la revendication 15, dans lequel une succession de surfaces d'aluminium est traitée avec une solution de revêtement de conversion dans laquelle l'additif (c) est un composé polyhydroxy et la solution de revêtement est renouvelée de façon intermittente ou continue, si nécessaire avec un concentré de renouvellement aqueux, afin de maintenir les concentrations en ingrédients dans la solution de revêtement à l'intérieure des limites spécifiques en utilisant un concentré de renouvellement contenant de 31×10^{-3} à 251×10^{-3} mole/l de zirconium, un matériau de source qui fournit de 90×10^{-3} à 695×10^{-3} mole/l de fluorure disponible non complexé et de 19×10^{-3} à 148×10^{-3} mole/l de composé polyhydroxy.

18. Un procédé selon les revendications 15 à 17, qui, après la formation dudit revêtement de conversion sur la surface d'aluminium comprend également l'étape subséquente d'application d'un revêtement siccatif hydrique.

19. Un concentré aqueux destiné à être dilué avec de l'eau pour former la solution de revêtement de conversion utilisée dans le procédé selon la revendication 16, de sorte qu'une solution aqueuse contenant de 0,5 à 10% en poids de concentré est suffisament acide pour former un revêtement de conversion sur l'aluminium et contient:

(A) au moins 0,5 à 10^{-3} mole/l d'un ou plusieurs des métaux du groupe IV choisis parmi le zirconium, le titane et l'hafnium;

(B) du fluorure en quantité au moins suffisante pour combiner et former un complexe soluble avec essentiellement tous les composès Zr, Ti et/ou Hf; et également

(C) au moins 0,01 g/l d'agent tensio-actif.

20. Un concentré aqueux destiné à renouveler la solution de revêtement de conversion dans le procédé selon la revendication 16, qui comprend de 0,05 à 0,5 mole/l de zirconium, de 0,2 à 10 moles/l de fluorure et de 1 à 100 g/l d'agent tensio-actif.

21. Un concentré aqueux destiné à être dilué par l'eau pour former la solution de revêtement de conversion utilisée dans le procédé selon la revendication 17, de sorte qu'une solution aqueuse contenant de 0,5 à 10% en poids du susdit concentré étant libre de phosphore, de bore, présente une valeur de pH dans la gamme de 3 à 5 et contient:

(A) au moins $0{,}5\times10^{-3}$ mole/l de zirconium ou d'hafnium ou un mélange de ceux-ci;

(B) au moins $0{,}025\times10^{-3}$ mole/l d'un composé polyhydroxy soluble dans l'eau ne présentant pas plus de 7 atoms de carbone;

(C) au moins suffisamment de fluorure pour combiner et former un complexe soluble avec tout le zirconium et/ou l'hafnium présents dans la solution.

22. Un concentré aqueux destiné à renouveler la solution de revêtement de conversion dans le procédé selon la revendication 17, qui comprend de 31×10^{-3} à 251×10^{-3} mole/l de zirconium un matériau de source qui fournit de 90×10^{-3} à 695×10^{-3} mole/l de fluorure disponible non complexé et de 19×10^{-3} à 148×10^{-3} mole/l de composé polyhydroxy.

Patentansprüche

1. Chromatfreie, saure, wässrige Überzugslösung mit einem pH-Wert von 1,5 bis 5, die fähig ist einen klaren, farblosen und korrosionsbeständigen Umwandlungsüberzug auf einer Aluminiumoberfläche zu bilden, enthaltend:

(a) eines oder mehrere der Gruppe IVa Metalle Zirkonium, Hafnium und Titanium in einer Gesamtkonzentration von mindestens $0{,}5\times10^{-3}$ Mol/Liter;

(b) Fluorid in einer Menge von zumindest ausreichend zur Umsetzung und Bildung eines löslichen Komplexes mit allen anwesenden Gruppe IVa Metallen; und

(c) einen Zusatz in Form von:

(i) einem oberflächenaktiven Stoff anwesend in einer Konzentration von mindestens 0,01 g/l; und/oder

(ii) einer organischen Polyhydroxyverbindung mit bis zu 7 Kohlenstoffatomen, anwesend in einer Konzentration von mindestens $0{,}025\times10^{-3}$ Mol/Liter, wenn der Zusatz diese organische Polyhydroxyverbindung allein ist, wobei die Lösung frei von Phosphat und Bor ist.

2. Umwandlungsüberzugslösung für Aluminium gemäß Anspruch 1, in welcher Fluorid anwesend ist in einer Menge entsprechend mindestens 4 Molen je Mol der genannten Gruppe VIa Metalle.

3. Umwandlungsüberzugslösung für Aluminium gemäß Anspruch 1 oder 2, worin das Gruppe IVa Metall Zirkonium ist oder enthält.

4. Umwandlungsüberzugslösung für Aluminium gemäß einem der vorgehenden Ansprüche, in welcher der (c) Zusatz ein oberflächenaktiver Stoff ist oder einen solchen enthält und der pH-Wert der Lösung im Bereich von 3,5 bis 4,5 liegt.

5. Umwandlungsüberzugslösung für Aluminium gemäß Anspruch 4, in welcher Zirkon anwesend ist in einer Konzentration von $0{,}75\times10^{-3}$ bis 2×10^{-3} Mol/Liter und eine oberflächenaktive Substanz anwesend ist in einer Konzentration von 0,01 bis 0,5 g/l.

6. Umwandlungsüberzugslösung für Aluminium gemäß Anspruch 5, in welcher Zirkon anwesend ist in einer Konzentration von 1×10^{-3} bis $1{,}75\times10^{-3}$ Mol/Liter, ein oberflächenaktiver Stoff anwesend ist in einer Konzentration von 0,02 bis 0,1 g/l und die Lösung einen pH-Wert im Bereich von 3,7 bis 4,3 aufweist.

7. Umwandlungsüberzugslösung für Aluminium gemäß einem der vorgehenden Ansprüche, welche einen oberflächenaktiven Stoff enthält in Form eines nichtionischen oberflächenaktiven Stoffes.

8. Umwandlungsüberzugslösung für Aluminium gemäß einem der vorgehenden Ansprüche, welche, wenn der Zusatz nicht die organische Polyhydroxyverbindung allein ist, auch mindestens 10 ppm einer Borverbindung enthält.

9. Umwandlungsüberzugslösung für Aluminium gemäß einem der vorgehenden Ansprüche, die neben mindestens 0,01 g/l eines oberflächenaktiven Stoffes auch mindestens $0{,}025\times10^{-3}$ Mol/Liter der genannten Polyhydroxyverbindung enthält.

10. Umwandlungsüberzugslösung für Aluminium gemäß einem der Ansprüche 1 bis 3, in welcher der (c) Zusatz die Polyhydroxyverbindung ist oder diese enthält.

11. Umwandlungsüberzugslösung für Aluminium gemäß Anspruch 10, deren pH-Wert im Bereich von 3 bis 5 liegt.

12. Umwandlungsüberzugslösung für Aluminium gemäß Anspruch 11, die $0{,}5\times10^{-3}$ bis $1{,}75\times10^{-3}$ Mol/Liter Zirkonium und $0{,}3\times10^{-3}$ bis $1{,}75\times10^{-3}$ Mol/Liter der Polyhydroxyverbindung enthält.

13. Umwandlungsüberzugslösung für Aluminium gemäß einem der Ansprüche 1 bis 8, in welcher der (c) Zusatz der oberflächenaktive Stoff allein ist.

14. Umwandlungsüberzugslösung für Aluminium gemäß einem der vorgehenden Ansprüche, die auch Tannin enthält.

15. Verfahren zur Bildung eines klaren, farblosen, korrosionsbeständigen Überzuges auf einer

Aluminiumoberfläche, wobei die Oberfläche mit einer chromatfreien, sauren, wässrigen Überzugslösung gemäß einem der vorgehenden Ansprüche während einer ausreichenden Zeitdauer bei der Arbeitstemperatur in Berührung gebracht wird zur Ausbildung des gewünschten Überzuges.

16. Verfahren gemäß Anspruch 15, in welchem eines Folge von Aluminiumoberflächen behandelt werden mit einer Umwandlungsüberzugslösung, in welcher der (c) Zusatz ein oberflächenaktiver Stoff ist und die Überzugslösung gelegentlich oder kontinuierlich nach Bedarf aufgefrischt wird mit einem wässrigen Auffrischungs-Konzentrat, so daß die Konzentration der Zusätze in der Überzugslösung innerhalb der angegebenen Bereiche bleiben, unter Verwendung eines Auffrischungs-Konzentrates enthaltend 0,05 bis 0,5 Mol/Liter Zirkonium, 0,2 bis 10 Mol/Liter Fluorid und 1 bis 100 g/l eines oberflächenaktiven Stoffes.

17. Verfahren gemäß Anspruch 15, in welchem eine Folge von Aluminiumoberflächen behandelt wird mit einer Umwandlungsüberzugslösung, in welcher der (c) Zusatz eine Polyhydroxyverbindung ist und die Überzugslösung gelegentlich oder kontinuierlich aufgefrischt wird nach Bedarf mit einem wässrigen Auffrischungs-Konzentrat um die Konzentrationen der Zusätze in der Überzugslösung innerhalb der angegebenen Bereiche zu halten, unter Verwendung eines Auffrischungs-Konzentrates enthaltend 31×10^{-3} bis 251×10^{-3} Mole/Liter Zirkonium, ein Ausgangsmaterial, welches 90×10^{-3} bis 695×10^{-3} Mole/Liter eines nichtkomplexierten verfügbaren Fluorids liefert und 19×10^{-3} bis 148×10^{-3} Mole/Liter einer Polyhydroxyverbindung.

18. Verfahren gemäß einem der Ansprüche 15 bis 17, bei welchem nach der Bildung des Umwandlungsüberzuges auf der Aluminiumoberfläche in einer nachfolgenden Stufe ein darüberliegender Sikkativüberzug aus Wasser aufgebracht wird.

19. Wässriges Konzentrat zur Verdünnung mit Wasser unter Bildung einer Umwandlungsüberzugslösung zur Verwendung in dem Verfahren gemäß Anspruch 16, derart, daß eine wässrige Lösung enthaltend 0,5 bis 10 Gew.-% dieses Konzentrates ausreichend sauer ist zur Bildung eines Umwandlungsüberzuges auf Aluminium und die (A) mindestens $0,5\times10^{-3}$ Mol/Litre eines oder mehrere der Gruppe IVa Metalle Zirkonium, Titanium und Hafnium enthält; (B) Fluorid in einer Menge zumindest ausreichend zur Verbindung und Ausbildung eines löslichen Komplexes mit im wesentlichen dem gesamten Zr, Ti und/oder Hf; und auch (C) mindestens 0,01 g/l eines oberflächenaktiven Stoffes.

20. Wässriges Konzentrat zur Verwendung bei der Auffrischung einer Umwandlungsüberzugslösung in dem Verfahren gemäß Anspruch 16, enthaltend 0,05 bis 0,5 Mol/Liter Zirkonium, 0,2 bis 10 Mol/Liter Fluorid und 1 bis 100 g/l eines oberflächenaktiven Stoffes.

21. Wässriges Konzentrat zur Verdünnung mit Wasser zur Bildung einer Umwandlungsüberzugslösung zwecks Verwendung in dem Verfahren gemäß Anspruch 17, derart, daß eine wässrige Lösung enthaltend 0,5 bis 10 Gew.-% des Konzentrates frei von Phosphat und Bor ist, einen pH-Wert im Bereich von 3 bis 5 aufweist und (A) mindestens $0,5\times10^{-3}$ Mol/Liter Zirkonium oder Hafnium oder eine Mischung der beiden, (B) mindestens $0,025\times10^{-3}$ Mol/Liter einer wasserlöslichen Polyhydroxyverbindung mit nicht mehr also 7 Kohlenstoffatomen und (C) zumindest genügend Fluorid zur Verbindung mit allem Zirkonium und/oder Hafnium, welches in der Lösung anwesend ist, und Ausbildung eines löslichen Komplexes, enthält.

22. Wässriges Konzentrat zur Verwendung bei der Auffrischung einer Umwandlungsüberzugslösung in dem Verfahren gemäß Anspruch 17 enthaltend 31×10^{-3} bis 251×10^{-3} Mole/Liter Zirkonium, ein Ausgangsmaterial, welches 90×10^{-3} bis 695×10^{-3} Mole/Liter eines nichtkomplexierten verfügbaren Fluorids liefert und 19×10^{-3} bis 148×10^{-3} Mole/Liter einer Polyhydroxyverbindung.