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(54) **Method of producing conversion coatings.**

(57) Conversion coatings of the hydrated metal oxide type are deposited on a substrate of Al, Mg, Sn or Zn or their alloys, from an aqueous solution of Al^{III} having a pH of 1.5 to 5.5 and containing NO_3^-. The coating produced is of hydrated aluminium oxide. Conversion coatings having further enhanced corrosion resistance are produced from solutions which include borate and have pH's in the range of 4 to 5.5

EP 0 044 171 A1

METHOD OF PRODUCING CONVERSION COATINGS

The present invention relates to the deposition of coatings on metal substrates and particularly to a method of depositing non-metallic conversion coatings containing hydrated metal oxides.

Conversion coatings are coatings of water insoluble inorganic metal salts which are deposited on metallic substrates to enhance the corrosion resistance of the substrate, to improve the adhesion of paint and/or lacquers to be applied, over the conversion coating, to the substrate or to enhance the strength of the bond between the substrate and a layer, typically of plastics material, to be laminated thereto.

The type of the conversion coating used depends inter alia on the nature of the substrate and the intended end use. For ferrous metal substrates, phosphate conversion coatings are widely used. For non-ferrous metals "chromate" conversion coatings are widely used. "Chromate" conversion coatings provide the substrate metal with a protective coating based on the hydrated oxides of chromium and contains Cr^{VI} and, usually, Cr^{III} and cationic species derived from the substrate. Anionic species, other than oxides and hydroxides, including hydrated species, may be occluded from the solution. This is in

contrast with "phosphate" coatings where the coating includes phosphate as a major anion. In the present context reference to hydrated oxides is intended to refer to water insoluble metal and oxygen containing conversion coatings in which it is believed that the metal is principally present as its hydrous metal oxide(s) and/or hydroxide(s) and it is this kind of coating that is referred to in the term "hydrated metal oxide" type of coating.

Currently conventional chromate conversion coating systems involve deposition from highly acid baths, typically based on sulphuric or nitric acids, including dissolved Cr^{VI} e.g. from CrO_3 or a chromate salt. Coatings deposited from solutions containing sulphuric acid are yellow-gold and those deposited from solutions containing nitric acid tend to be slightly blue. These solutions are highly corrosive because of their acidity and toxic because of the presence of Cr^{VI}. It has recently been suggested that Cr^{VI} may be carcinogenic. These are principally operating dangers which can be met by suitable careful design of equipment and the adoption of appropriate safety precautions by the operators. A further major problem with Cr^{VI} based systems is that effluent treatment is difficult because of the toxicity of Cr^{VI} even in very small concentrations. Present regulations set a maximum concentration of less than 1 ppm of Cr^{VI} in effluent discharges and even stricter limits are likely in the future. In view of the difficulties arising from the toxicity of Cr^{VI}, techniques avoiding the use of Cr^{VI} have been sought.

In our earlier U.K. Patent Specification No. 1531056 and West German Offenlegungsschrift No. P 28 22 463 we have described electrolytic techniques for the production of chromium-containing conversion coatings based on Cr^{III}. Such coatings can be made containing substantially no Cr^{VI} and we have referred to them as "chromite" coatings. Further, although the use of Cr^{VI} as a minor constituent in the electrolyte is described in Specification No.1531056, solutions containing no Cr^{VI} at all are described and Offenlegungsschrift No. P 28 22 463 involves no Cr^{VI}. Such Cr^{VI}- free, Cr^{III} - based systems are an improvement on Cr^{VI}- based systems especially with regard to effluent treatment, but they are not a complete answer to the problem because Cr^{III} is itself somewhat toxic, although much less so than Cr^{VI}, and the effluent concentration maximum limits are fairly stringent (ca 2 ppm).

The present invention is based on the discovery that it is possible to deposit corrosion resistant conversion coatings of the hydrated metal oxide type from solutions containing no chromium at all.

Accordingly the present invention provides a method of depositing a conversion coating of hydrated aluminium oxide on a substrate of aluminium, magnesium, tin or zinc, which method comprises contacting the substrate to be coated with an aqueous

solution of Al^{III} at a concentration of at least 0.05 g l^{-1}, the solution having a pH of from 1.5 to 5.5 and including nitrate ions as a depolarising agent for the reaction between the solution and the surface of the substrate, whereby a conversion coating is deposited on the surface of the substrate.

We refer herein to the conversion coatings being of hydrated aluminium oxide. As those skilled in the art will appreciate the coatings may initially include aluminium hydroxide or other similar species and after aging (see below) the structure of the coating may be more highly catenated. In this specification we use the term "hydrated aluminium oxide" to include aluminium oxy and hydroxy species precipitated from aqueous solution by increasing pH and the transformation products in the coating on drying.

In the method of this invention in the reaction between the solution and the substrate, the substrate behaves anodically in the reaction:

$$M \longrightarrow M^{n+} + ne^{-}$$

where M is the metal of the substrate, and n+ is the oxidation state of the metal ion released from the substrate. The reaction liberates electrons which polarize the reaction at the substrate. The nitrate ion in the solution acts as an electron receptor, being reduced in the process, and depolarizes the reaction. The reduction of the nitrate causes a rise in the pH of the film of solution adjacent the

substrate and leads to precipitation of hydrated aluminium oxide in this film and the deposition of the conversion coating on the substrate. The conversion coating contains hydrated aluminium oxide and will usually include cationic species derived from the substrate metal, probably also as hydrated oxides, and may include other species occluded from the solution. In the absence of nitrate, the low acidity of the solution causes the substrate dissolution reaction, which is a necessary pre-requisite for the formation of a conversion coating, to be choked preventing the formation of satisfactory coherent conversion coatings. In the presence of nitrate an alternative reaction path is provided which does not require high acidity to promote the dissolution reaction. The nitrate reacts according to the following equation:

$$NO_3^- + 10H^+ + 8e^- \longrightarrow NH_4^+ + 3H_2O.$$

This reaction effectively absorbs H^+ thus causing the pH to rise. Nitrate ion is exceptionally effective in depolarizing the surface reaction because its full reduction to ammonium ion is an 8 - electron reduction and reduction of 1 mole of nitrate to ammonium consumes 10 moles of hydrogen ion i.e. nitrate has a very low equivalent weight when acting as an electron accepting depolarizer.

The solutions of Al^{III} used in this invention present a very small polution hazard especially as

compared with Cr^{III} and even more so as compared with Cr^{IV}. Indeed, it is well known that aluminium is effectively non toxic in dilute solution and aluminium salts are added to waste waters, especially those containing heavy metal pollutants, in the detoxification of such wastes. Further, the other components used in the solutions do not give rise to severe pollution problems. In some cases the solutions contain fluoride, but the concentration of fluoride used in low and fluoride effluent treatment techniques are established and we do not expect any problems in the handling of this fluoride.

As indicated above, the minimum concentration of the aluminium ions in the solution to produce satisfactory conversion coatings is 0.05 gl^{-1}. At lower concentrations conversion coatings form slowly, if at all and the concentration is difficult to maintain. Preferably the concentration is not higher that 5 gl^{-1} because at higher concentrations precipitation of hydrated aluminium oxide from the bulk of the solution may occur, there is no further beneficial effect in the production or properties of the conversion coating and the solution is more expensive and dragout losses are higher. The optimum range of concentration is 1 to 3 gl^{-1}. Concentrations of the aluminium ions are quoted as gl^{-1} of the aluminium itself.

The source of the aluminium ions in the solution is

not itself critical provided it is of adequate purity and that the salt used is water soluble and that the anion does not interfere with the formation of a conversion coating (see below). Suitable salts include aluminium sulphate or sodium alum and aluminium halides specifically aluminium chloride.

The concentration of nitrate ion in the solution is generally in the range from 1 to 20 gl^{-1} measured as $NaNO_3$. At concentrations less than about 1 gl^{-1} the deposition reaction is slow because the dissolution reaction is insufficiently depolarized. At concentrations greater than about 20 gl^{-1} the reaction tends to be so rapid that the substrate dissolves quickly and the deposition of the conversion coating is not uniform. The optimum concentration range is from 3 to 10 gl^{-1}. The source of the nitrate ions can conveniently be sodium or potassium nitrate. Sodium nitrate is preferred on a cost basis.

The solutions used in the invention may include one or more surfactants to enhance wetting of the substrate by the solution. We have not found it essential to use surfactants, but under less carefully controlled conditions, such as on an industrial production line, their inclusion may be beneficial particularly in preventing air bubbles adhereing to and obscurring the substrate surface or in removing small particles of dirt or smears of oil or grease on the substrate from handling prior to conversion coating. The surfactants used are "compatible surfactants" by which we mean that they do not form insoluble products with other components of the solution. For example the aluminium salts of stearic and other long

chain carboxylic acids are insoluble and, therefore, simple salts of such acids are not compatible surfactants. Suitable compatible surfactants can be cationic, anionic or nonionic such as alkyl pyridinium halides,alkyl sulphonates, alkyl phenols and alkylene oxide condensation products of hydroxyl compounds such as alcohols and phenols. The skilled man would have no serious difficulty in selecting a suitable compatible surfactant.

The amount of compatible surfactant used will depend upon the particular circumstances but will typically be from 5 to 250 ppm and more usually from 10 to 100 ppm, by weight.

The substrate is of aluminium, magnesium, tin or zinc. In referring to these substrate metals we include their alloys in which they are the major constituents. Also we include articles of other metals, especially steel, clad or coated with the specified substrate metals e.g. zinc coated or plated (galvanized)steel and tin plated steel (tin plate). We have obtained the best technical results in providing conversion coatings on aluminium and this is accordingly the preferred substrate.

Where the substrate is aluminium or an aluminium alloy it is well known that it will normally have a film of oxide on it. In order to deposit a conversion coating on aluminium it is necessary to remove this oxide film. This is most conveniently done by including in the solution a material to dissolve the oxide film. Fluoride ion is the most convenient agent for carrying out this dissolution, which is accomplished by the formation of water soluble, stable fluoroaluminate species. For most cases simple fluorides such as sodium fluoride are adequate, but complete fluoro-salts which, in solution, partially dissociate liberating fluoride e.g. fluorosilicate and fluoborate, can also be used. It will be appreciated that addition of boric acid or a borate salt to a solution containing fluoride will generate fluoborate in situ. The concentration of fluoride used in solutions for providing conversion coatings on aluminium or its alloys will usually be from 1 to 20 gl^{-1}, optimally 3 to 8 gl^{-1}, (expressed as NaF) when added as a simple salt and from 3 to 15 gl^{-1} (as fluorosilicate) when added as a complex salt.

Instead of including fluoride in the solution it is possible to pre-treat the aluminium substrate to remove the oxide film by dipping it in, or otherwise contacting it with a separate fluoride-containing solution e.g. 10% aqueous NaF. Clearly when this is

done the substrate should not be significantly exposed to an oxygen containing atmosphere or environment to avoid re-formation of the oxide film. The substrate can be suitable protected by leaving a film of solution on it until contact with the conversion coating solution.

The use of aluminium(including aluminium alloys) as substrates in this invention is important because aluminium is finding increasingly wider applications in which the surface of the metal is to be subsequently painted, lacquered or laminated to plastics. In such applications it has been found that the oxide film on the aluminium surface generally does not allow paint or lacquer to adhere strongly. Contrary to this the aluminium oxide conversion coatings produced according to the present invention do enhance the adherion of paint or lacquer films and laminated layers. Furthermore, coating aluminium with a conversion coating is a generally quicker and cheaper process than the usual anodizing process.

The temperature of the solution will usually and preferably be ambient temperature, which, in working plating and coating plant, is typically from 20 to 25°C. If ambient temperature is below 20°C especially if it is below 15°C it is preferable to warm the solution to maintain a temperature of at least 20°C. Ambient temperatures higher than 25°C will not necessitate cooling of the solution. We have not found any advantage in heating the solution to temperatures above 25°C, but the invention will generally work satisfactorily at moderately elevated temperature. The use of temperatures over 40°C and especially 60°C is disadvantageous, economically because of the cost of

heating the solution and technically because the solution is less stable to precipitation of aluminium hydroxide from the bulk of the solution at elevated temperatures and because the reaction with the substrate may be so rapid as to prevent the deposition of uniform coherent conversion coatings.

A partial exception to this is in no-rinse techniques (described further below) where the substrate is contacted with the solution under the temperature conditions set out above and is subsequently dried without rinsing the treatment solution from it. Drying is typically at temperatures somewhat above 100°C and the reaction with the substrate continues until the water is evaporated or boiled off (or the solution is exhausted) at the elevated temperatures reached during drying.

The pH of the solution as used in the method is moderately acid in the range 1.5 to 5.5. Where the solution is as described as above the optimum pH depends on the substrate metal. For zinc and magnesium substrates the pH is preferably from 2.5 to 3.5 and optimally about 3. For aluminium substrates the pH is preferably from 3 to 4 and optimally about 3.5. For tin substrates the pH is preferably from 1.5 to 3 and optimally about 2. Where, as is described below, the solution includes borate the pH will be somewhat higher in the range 4 to 5.5, the optimum pH depending on the particular conditions (see below). Any necessary adjustments of pH can be carried out using hydrochloric or sulphuric acids or sodium or potassium hydroxides as necessary.

Where it is desired to maximise the corrosion resistance of the conversion coating we have found that it can be advantageous to include borate in the solution and to form the conversion coating under controlled pH condition. The benefits of using borate in this way are that coatings can be deposited more rapidly, enabling thicker coatings to be produced in a given treatment time, and that the corrosion resistance of the coatings is enhanced particularly for coatings on zinc including the commercially important zinc galvanized steel.

Accordingly, in a further aspect, the present invention provides a method of depositing a conversion coating of hydrated aluminium oxide on a substrate of aluminium, magnesium, tin or zinc which method comprises contacting the substrate to be coated with an aqueous solution of Al^{III} at a concentration of at least 0.05 gl^{-1}, the solution having a pH of 4 to 5.5 and including nitrate ions, as a depolarizing agent for the reaction between the solution and the surface of the substrate, and borate whereby a conversion coating is deposited on the surface of the substrate.

The mechanism by which borate, as borate ions or boric acid enhances the deposition of conversion coatings is not known. However, the presence of borate appears to encourage the flocculation of the

the hydrated aluminium oxide precipitated onto the surface of the substrate. Additionally, in aqueous solution the first ionization reaction of boric acid acts to buffer the solution in the pH range used. This pH range is higher than that indicated above as the optimum in the absence of borate.

The absolute value of pH is not the only factor and we have found that the most marked beneficial results are obtained when the pH is close to that at which hydrated aluminium oxide spontaneously precipitates from the bulk of the solution. For brevity we refer to this value of pH as the "pH of precipitation" in any particular case. The absolute value of the pH of precipitation is a property of the aluminium containing species in the solution, rather than simply of aluminium itself, and the species present depend on the ligands in the solution. Additionally, the solution may contain non-equilibrium species, typically hydrated aluminium-anion complex ions which are not thermodynamically stable but which persist for times comparable with the practical useful life of any particular sample of solution. The nature and composition of such species depend on the history of the particular sample of the aluminium salt used in making up the solution. We have noticed that there can be substantial differences in the behaviour of successive batches of ostensibly identical aluminium

salts in this respect. It is for this reason that we prefer to establish the desired pH of operation in this aspect of the invention in relation to the pH of operation in this aspect of the invention in relation to the pH of precipitation rather than solely in absolute values of pH. It is most desirable that the solution is not more than 1 pH unit and preferably not more than 0.5 pH units, more acid than the pH of precipitation. The pH will not be significantly more alkaline than the pH of precipitation because the concentration of the dissolved aluminium rapidly becomes too small to be of practical use with such increasing pH. The actual pH of the solution will not normally be more than 0.5 and more usually not more than 0.1 pH units more alkaline than the pH of precipitation. Preferably, the pH is substantially the same as or, within the limits set out above, more acid than the pH of precipitation.

In making up solutions for use in this aspect of the invention we have found that it is particularly convenient to make the solution up at a pH more acid than that desired for use and to add alkali e.g. as ca. 10% aqueous NaOH or KOH, to the solution until a slight persistent turbidity arising from precipitation of hydrated aluminium oxide is induced in the solution. If excess alkali is added then mineral acid e.g. HCl or H_2SO_4, until the precipitate is just or not quite redissolved can be added. This technique has obvious

practical advantages over attempting to adjust the pH to a predetermined pH value because of the variability of the pH of precipitation.

In this aspect of the invention the amount of borate included in the solution will usually be at least 1 gl^{-1} as H_3BO_3. The maximum amount is limited by solubility but will not usually be more than 40 gl^{-1} and preferably not more than 20 gl^{-1} as H_3BO_3. The borate can be added as boric acid or as alkali metal, especially sodium, borate.

Where the substrate is aluminium the solution may contain fluoride and the addition of simple borate ions would result in the formation of fluoborates thus consuming both fluoride and borate. To offset this it is desirable to add fluoborate to the solution thus increasing the equilibrium concentration of the active species, fluoride and borate. If both borate and fluoborate are added to the solution the equilibrium established in solution will normally provide sufficient fluoride to ensure dissolution of the oxide film on the aluminium. The amount of fluoborate added will typically be about twice the weight of the borate e.g. for 10 gl^{-1} borate about 20 gl^{-1} fluoborate will be used. However, it will be noted that addition of fluoborate to a solution does not, of itself, provide sufficient borate to be effective in this aspect of the invention. If the aluminium substrate is pre-treated by contact with fluoride containing

solution as described above, the addition of fluoborate can be obviated.

This aspect of the invention can be used to produce conversion coatings on any of the substrates indicated previously. However, it is particularly applicable where the substrate is aluminium or zinc, especially zinc galvanised steel. Corrosion resistance for such zinc surfaces is currently obtained by anodizing in a complex, obnoxious, highly acid and fluoride-containing electrolyte. The solution used in this aspect of the present invention is much less obnoxious and therefore substantially advantageous. The provision of corrosion resistant coatings on zinc galvanised steel is particularly important for marine applications. These coatings can be used as corrosion resistant coatings on their own or with the addition of paint or lacquer layers on top. It is unlikely that they will be used solely to provide a "key" coating for subsequent lacquering.

The coatings produced in this aspect of the invention are typically not clear but cloudly or opalescent in appearance. Thus, they are not usually suitable for coating on decorative substrates. Where it is desired to maximise corrosion resistance the appearance is of minor significance. Coatings deposited from solutions containing borate build up more rapidly and can be made more thick than those deposited without borate in the solution. We believe that the increased thickness is partly because the pH is higher and partly that the borate acts to aid flocculation as mentioned above. The coatings produced using solutions containing borate typically have

better corrosion resistance properties than those produced according to the invention but from solutions not containing borate. We do not fully understand why this is so. The increased thickness is clearly a contributory factor but the effect is more marked than can readily be accounted for solely on this basis. We think that it is probable that some borate is occluded in and incorporated into the conversion coating. In the coating after aging (see below) we believe that the boron may be present as crosslinked alumino-borate complexes which enhance the corrosion resistance of the coating. Further, the presence of boron-containing species in the coating may buffer the coating and thus the environment of the substrate thus making it less susceptible to corrosive attack. We do not know which, if either, of these effects is the more important.

The solutions used in the method of invention can be made up simply by dissolving the constituents in water followed by adjustment of the pH if necessary. Replacement of solution constituents consumed during use can be effected by adding them as solids or, preferably, as a concentrated made up solution. Where the substrate is aluminium, dissolution of the substrate will mitigate slightly the loss of aluminium from the solution in the formation of the coating. The ultimate equilibrium concentration of a solution "replenished"with Al only by dissolution of the substrate appears to be between 0.05 and 0.1 gl^{-1} at which concentration conversion coatings are deposited but not to give optimum performance.

Reference is made above to anions which interfere

with the formation of the conversion soating. Anions which interfere include those whose salts with the metals in solution are insoluble either in the bulk solution or in the film of solution adjacent to the substrate from which the conversion coating is deposited. Thus, phosphorous oxyanions, especially phosphate, PO_4^{3-}, are preferably substantially absent. The amounts present are impurities in tap and process water (typically not more than 20ppm as phosphate) can be tolerated and at such levels phosphate is regarded, for present purposes, as being substantially absent. However, higher levels of phosphate either as impurities or as added phosphate should be avoided. The presence of phosphate can cause precipitation of the metal from solution either by premature precipitation in the film of solution adjacent to the substrate or in extreme cases by precipitation from the bulk of the solution. Additionally, we have found that the presence of phosphate in the conversion coating has a deleterious effect on the properties of the coating. As well as phosphate other anions, especially the highly oxidizing, high oxidation state metal oxyanions interfere with the deposition of the desired conversion coatings. Examples of such anions and manganate, permanganate chromate and dichromate. These materials are not deliberately added to the solutions used in this invention and care will generally be taken to ensure their absence.

Apart from aluminium and alkali metal cations (which latter are water soluble at all pHs) we have found that there is no advantage in including any other metal cations in the solution. The presence of such other metals either

reduces the beneficial properties of the conversion coating or gives rise to pollution problems or both. Specifically metals,other than aluminium, having insoluble hydroxides or hydrated oxides such as Ca, Cr, Co, Fe, Mg, Mn, Ti and Zn are desirably absent from the solution. In the case of Mg and Zn trace qualities may be present from substrate dissolution.

As has been indicated above the invention is particularly applicable to the coating of aluminium substrates. Accordingly, the invention provides a method of depositing a conversion coating of a hydrated aluminium which method comprises contacting the substrate with an aqueous solution containing from 1 to 2 gl^{-1} of Al^{III}, preferably as chloride or sulphate; from 3 to 10gl^{-1} of NO_3^-, measured as, and preferably in the form of, $NaNO_3$; and from 1 to 5 gl^{-1} of F^-, measured as, and preferably in the form of; NaF; the solution having a pH of from 3 to 5 and,apart from impurities,containing no materials other than water, compatible surfactant, Al^{III}, NO_3^- (and its reducting products principally NH_4^+), halide, preferably not Br^- or I^-, sulphate and alkali metal, preferably sodium, cations; whereby a conversion coating of hydrated aluminium oxide is deposited on the substrate.

Where it is desired to maximise corrosion resistance this method may be modified to adjust the pH of the solution, in the range from 4 to 5.5, to within + 0.1 and-0.5 pH units from the pH precipitation and including in the solution from 1 to 20 gl^{-1} of borate, preferably as sodium borate and, optionally from 5 to 40 gl^{-1} of

fluoborate, preferably as sodium fluoborate, the weight ratio of borate to fluoborate preferably being about 1:2. The substrate in this case can be either aluminium or zinc and if it is the latter the solution may contain trace amounts of zinc from substrate dissolution.

Using the conditions described above, contact of the substrate with the reaction solution for a period of only a few seconds will generally be sufficient to give a coherent conversion coating on the substrate. The period of time of contact will be selected depending on the thickness of the conversion coating desired which, in turn, will depend on how the coated substrate will be used. Typically, the period of time for which the substrate is in contact with the solution (the "contact time") will be from 5 seconds to 2 minutes. The contact time will be chosen to suit the intended use of the treated substrate. For "key" coatings (further described below) the contact time will typically be from 5 to 15 seconds. For corrosion resistant coatings the contact time will typically be from 10 seconds to 2 minutes. The contact time will usually be longer than time for which the substrate is immersed in the solution (the "immersion time"). This will be especially true of continuous systems especially no-rinse systems. In such systems the immersion time may be as little as 2 seconds. Since the reaction continues after removal of the substrate from the solution (up to rinsing, dewatering or drying) the effective contact time can be substantially longer than the immersion time. In systems where the solution is sprayed or rolled onto the substrate the term "immersion time" has no definite meaning and the "contact time" is the real measure of the treatment time.

The typical short time of contact of the substrate with the reaction solution allows the method of the present invention to be carried out on a continuous or semi-continuous as well as a batch-wise, basis. For example, a continuous tape or strip of the substrate metal may be drawn through a vat containing a reaction solution according to the present invention at a speed such that the desired thickness of coating is formed on the tape or strip, or a sequence of plates or sheets may be automatically dipped into, moved through and removed from a (relatively long) bath of solution.

The thickness of the conversion coating deposited depends mainly upon the concentration of the solution and the time of treatment. The conditions employed in the method of the present invention are such that, in general, conversion coatings having a thickness of from 0.01 to 5μm are obtained. Of course, the thickness of the coating will be determined according to the intended purpose of the deposited coating and the intended use of the coated substrate. Thus, for most industrial applications where the coating is intended to protect the surface of the substrate from corrosion, generally a thickness of from 1 to 5 μm will be desired, corresponding to a contact time of from about 20 seconds to about 2 minutes. Where the conversion coatings are produced using solutions containing borate (see described above) the thickness will generally be from 20 to 20 μm although the treatment time will generally be within the range set out above.

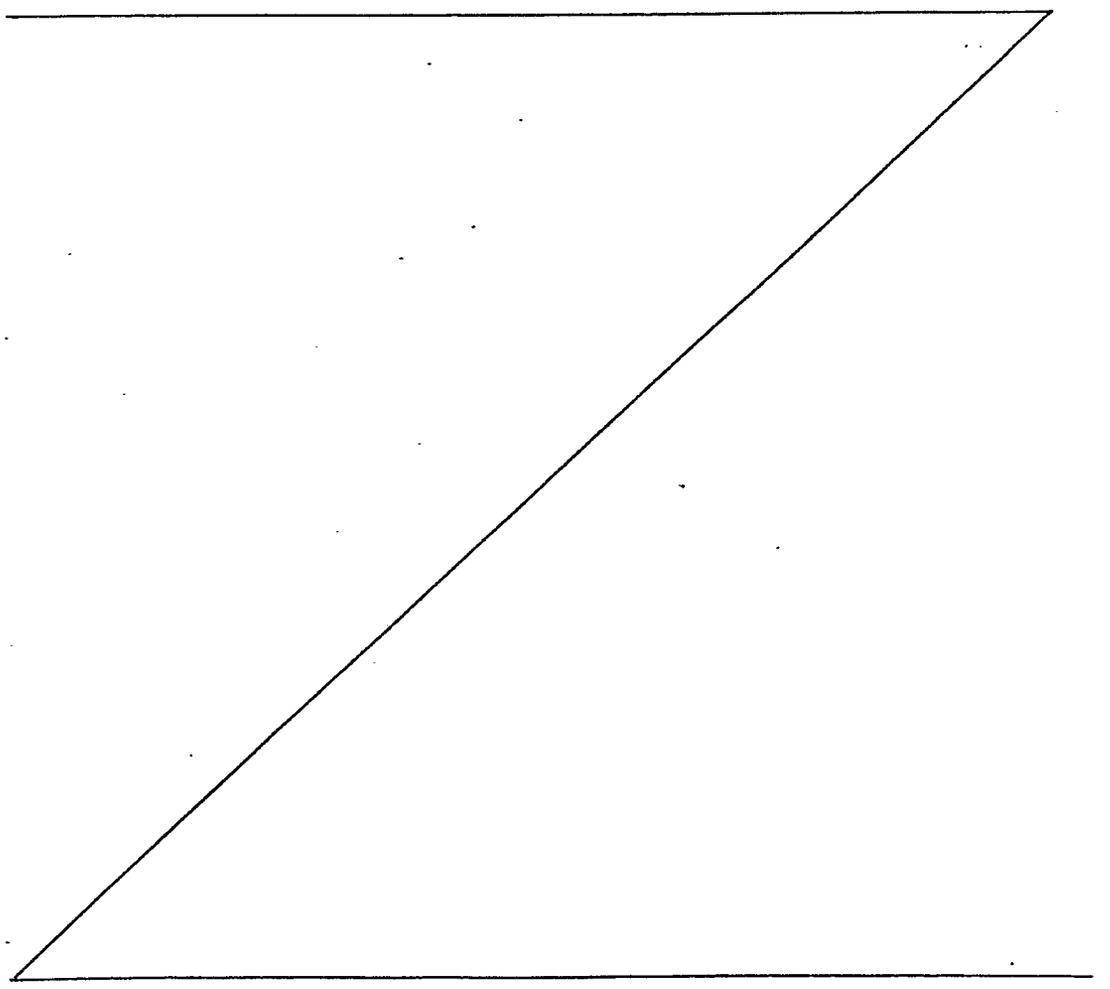
If the conversion coating is to be deposited as a "key" layer onto a substrate in order to enhance the adhesion of subsequent paint or lacquer films, a coating thickness of

from 01 to 1.0 μm is acceptable for most applications, corresponding to a contact time of from 5 to about 15 seconds. Coatings having a thickness at the upper end of this range can be produced using no-rinse systems.

Conventionally conversion coatings are applied by dipping the substrate into the treatment solution for a time sufficient to develop a conversion coating of the desired thickness as briefly mentioned above. Such techniques can be used in the method of the present invention. However, the relatively mild nature of the solution used in the present invention in particular by comparison with the highly acid and oxidizing solutions used in depositing chromate conversion coatings, opens up the possibility of using other techniques which can increase throughput, decrease capitcal cost and /or increase operational flexibility. Thus, the conversion coating solution can be sprayed onto the substrate rather than applied by dripping. As described above, the treatment time is effectively the immersion time, but this need not be the case since the treatment solution can be left as a surface film on the substrate after removal from the treatment bath or as deposited on the substrate by spraying. This extends the treatment time until the solution is rinsed off or otherwise removed (assuming it is not previously exhausted). Indeed, it is possible to dry the treatment solution onto the substrate thus making it possible to operate a no-rinse system. (The substrate will usually be deliberately dried to speed aging, as described below). In the present invention no-rinse techniques enable relatively thick coatings to be

produced using short immersion or contact times, because the formation of the coating is enhanced by the elevated drying temperature. Other possibilities will be apparent to those skilled in the art.

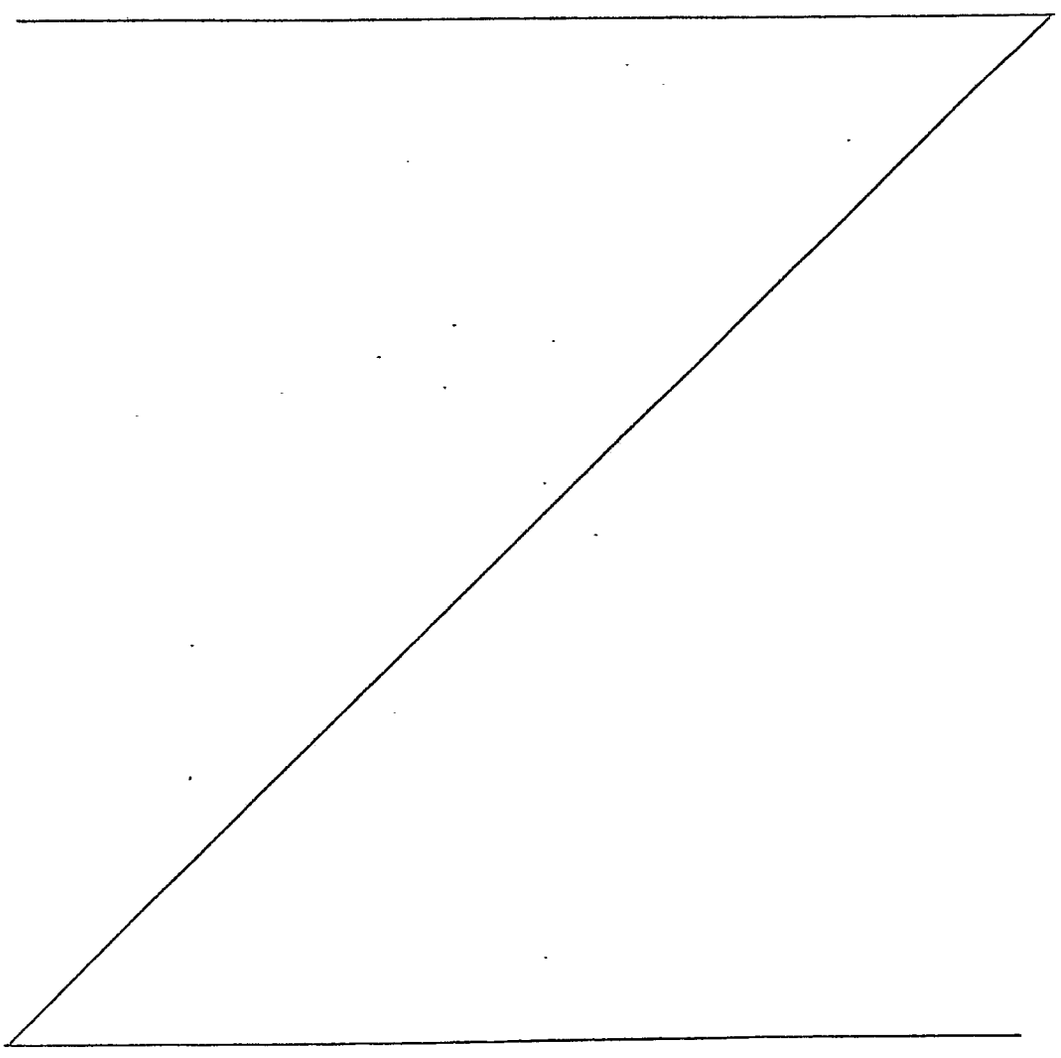
One particular technique which is not open to operators of Chromate conversion coating systems is the use of dewatering techniques such as are commonly used in less corrosive situations. In dewatering, the wet substrate is immersed in or otherwise contacted with a water immiscible liquid which readily wets the substrate. On contact, this liquid displaces the water from the surface of the substrate and the substrate can subsequently



readily be dried by evaporation of the liquid. The treatment solution can subsequently be separated from the water immiscible liquid and reused. This technique can significantly reduce effluent treatment problems and permit efficient reuse of excess solution, as compared with rinsing and subsequent drying techniques. Typically, dewatering fluids are medium boiling point hydrocarbons especially petroleum fractions such as "white spirit", kerosene and light mineral oil, containing a surfactant and a carrier solvent for the surfactant. They may also include corrosion inhibitors appropriate to the substrate. Suitable inhibitors for zinc include 2,5- dimercapto-thiadiazole and dithio-oxamide. Other compounds and inhibitors for other substances are known in the art of using dewatering fluids. Some dewatering fluids include waxes e.g. high molecular weight hydrocarbon waxes, which form a thin film over the conversion coating after evaporation of the solvent. The use of corrosion inhibitors and / or waxes can further improve the corrosion resistance of substrates treated according to this invention, although the use of waxes may not be appropriate when the substrate is subsequently lacquered or painted.

Freshly deposited coatings are soft and can be removed from the substrate by mild abrasion. The coatings can, however, be hardened and made more resistant to mechanical abrasion by air drying, e.g. at ambient temperature preferably for not less than 24 hours. The beneficial effects of drying can be accelerated by placing the coated substrates in an oven, preferably at temperatures in the range 60 to 120°C for periods of from 1 to 2 hours.

As is indicated above conversion coatings may serve as primer coatings for subsequent coatings of paint or lacquer. The conversion coating enables enhanced adhesion of the paint or lacquer coating to be achieved and provides additional protection against corrosion by suppressing under-film (i.e. under paint or lacquer) corrosion of substrate metal. The conversion coatings may also be used to "key" layers of plastics materials to the metal substrates in the productions of laminates, to improve the strength of the metal-plastic bond.



The invention is illustrated by the following Examples. Neutral salt spray testing, referred to in the Examples, is carried out according to the method set out in ASTM Method No. B - 117 .

EXAMPLE 1

An aqueous solution having the following composition was made up:

Al^{III}	1.5 gl^{-1}	(present as the sulphate)
$NaNO_3$	5 gl^{-1}	
NaF	3 gl^{-1}	
pH	adjusted to 4.0 with dilute sulphuric acid or dilute caustic soda as necessary.	

Aluminium panels were treated by dipping them in the solution at ambient temperature (ca. 22°C) for periods of time of from 10 seconds to 2 minutes. The dipped panels were subsequently dried and tested by subjecting them to neutral salt spray testing. All the panels treated had salt spray resistance of greater than 1000 hours. An untreated (control) panel showed corrosion after only 24 hours.

EXAMPLE 2

Example 1 was repeated varying the concentrations of the solution constituents, solution pH and dipping time within the limits set out below

Al^{III}	1 to 2 gl^{-1}	(present as sulphate, sodium alum or chloride)
$NaNO_3$	3 to 8 gl^{-1}	
NaF	1 to 5 gl^{-1}	
pH	1.5 to 4	
time	10 seconds to 2 mins.	

Panels treated at ambient temperature (20 to 25°C) throughout these ranges had salt spray resistances of up to 1000 hours.

EXAMPLE 3

An aqeous solution having the following composition was made up:

Al^{III} 1.5 gl^{-1} (present as sulphate)

$NaNO_3$ 5 gl^{-1}

pH adjusted to 3

Zinc plated steel panels were treated by dipping in this solution at ambient temperature for from 10 seconds to 2 minutes. The dipped panels were subsequently dried and neutral salt spray tests showed resistance for up to 24 hours. Untreated control panels failed almost immediately.

This Example was repeated several times varying the Al^{III} concentration from 1 to 2 gl^{-}, the $NaNO_3$ concentration from 3 to 8 gl^{-1} and the pH from 2 to 4 and gave comparable results throughout the ranges.

EXAMPLE 4

A steel panel was electroplated with 5 μm tin, dried and immersed for 30 seconds in a solution of the following composition

$Al_2(SO_4)_3$ 18 gl^{-1}

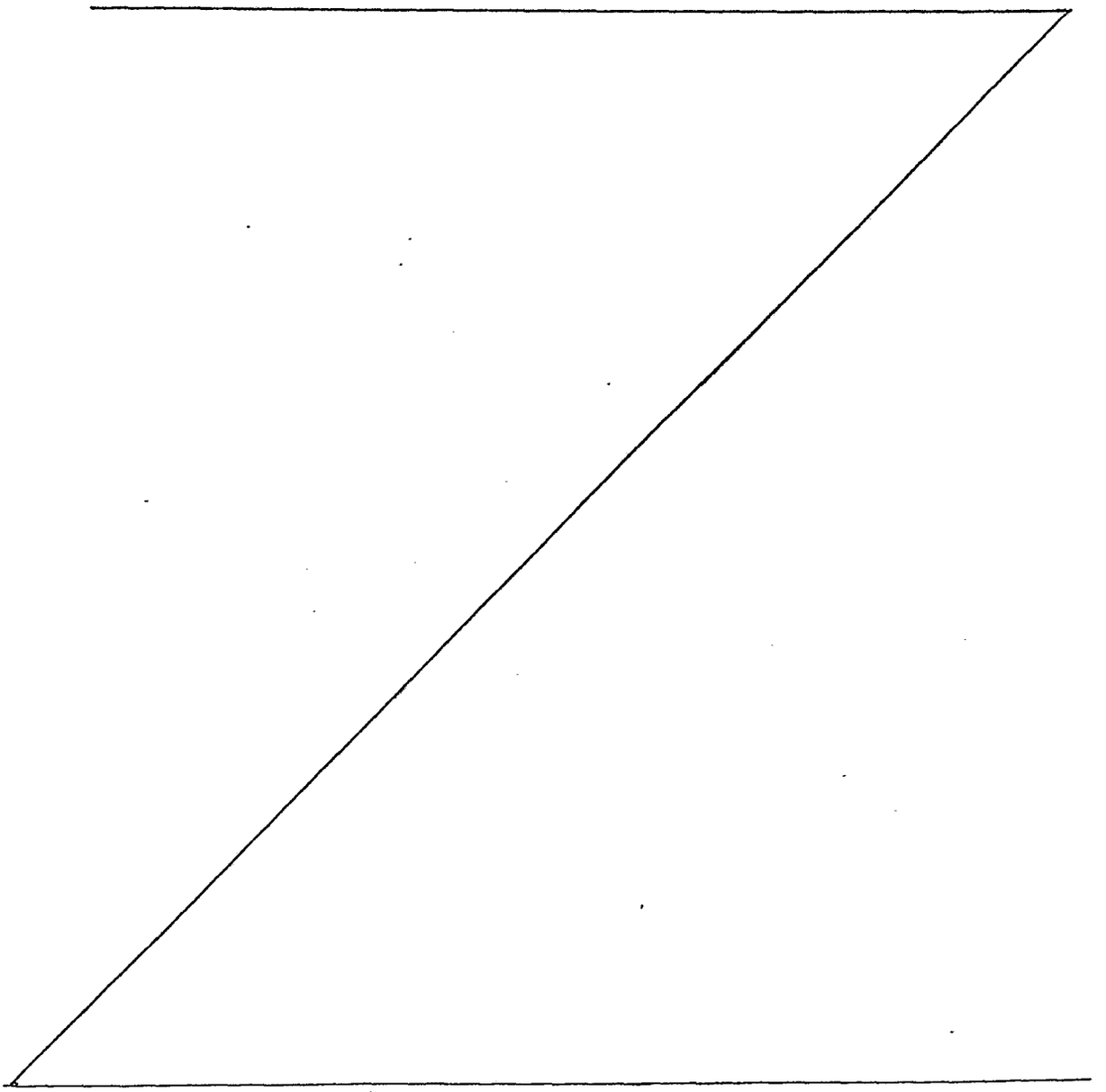
$NaNO_3$ 7 gl^{-1}

pH adjusted to 4.0

Temperature 25°C.

After drying a pale blue film was visible on the surface. The solution was modified by adding 10 gl^{-1} of sodium borate and the pH was adjusted(increased)until a slight precipitate of hydrated aluminium oxide was present. A second similar tin plate panel was immersed for 30 seconds in the solution and after drying a blue-yellow film was visible on the

surface. These two panels together with a third similar but untreated tin plate panel were exposed to neutral salt spray testing. After 24 hours of testing the untreated panel had tin corrosion products on its surface but no corrosion of either of the coated panels had occurred.



Example 5

An aqueous solution having the following composition was made up:

Al^{III} 2 gl^{-1} (as sulphate)
$NaNO_3$ 6 gl^{-1}
$NaBF_4$ 20 gl^{-1}
pH adjusted to 4.0.

Aluminium panels were degreased, etched and desmutted by conventional techniques and after rinsing were immersed in the solution for 30 seconds at ambient temperature. The panels were then dried and a faint iridescence was visible on the surface of the panels indicating that a conversion coating had been deposited.

A solution identical to that above was made up except that

H_3BO_3 10 gl^{-1}

was added. The pH was adjusted by adding NaOH solution until a faint cloudiness due to aluminium hydroxide was observed. The pH at this point was 4.5. A further series of aluminium panels prepared as above were treated by immersion in the modified solution for 30 seconds at ambient temperature.

Both sets of panels were subjected to neutral salt spray testing. The first set of panels showed corrosion of the substrate after 300 hours of testing; the second set showed the same effects after 500 hours of testing.

Example 6.

Example 5 was repeated using two sets of aluminium panels except that the sodium fluoborate was omitted and the aluminium panels, after desmutting and rinsing, were dipped in an aqueous solution containing 10 gl^{-1} sodium fluoride for 10 seconds at ambient temperature and transferred without rinsing to the conversion coating solutions. The two sets of panels were subjected to neutral salt spray testing. The first set survived 250 hours testing whereas the second set survived 500 hours testing.

Example 7

An aqueous solution having the following composition was made up:

$Al_2(SO_4)_3$	15 gl^{-1}
$NaNO_3$	10 gl^{-1}
NaF	1.5 gl^{-1}
pH	adjusted to 4.0.

A first set of aluminium panels were degreased, etched, desmutted and rinsed and dipped in the solution at ambient temperature for 30 seconds and then rinsed and dried.

A second set of aluminium panels were treated in the same way as the first set except that the temperature of the solution was 60°C and the immersion time 2 seconds.

A third set of aluminium panels were treated in the same way as the second set except that after the 2 seconds immersion they were dried without rinsing.

All three sets of panels were subjected to neutral salt spray testing. The first set survived 900 hours of testing; the second set survived only 200 hours testing;

and the third set survived 800 hours testing

Example 8

Two aluminium panels and two electrogalvanized steel panels (10 μm Zn) were conventionally cleaned and pretreated for conversion coating. A conversion coating solution was made up containing:

$Al_2(SO_4)_3$	12 gl^{-1}
NaF	5 gl^{-1}
$NaNO_3$	7 gl^{-1}
pH	adjusted to 4.0
Temperature	25°C.

The four panels were immersed in the solution for 60 seconds to conversion coat them, rinsed in water, air dried for 48 hours at ambient temperature and electrostatically powder painted. Each panel was scribed in a cross hatch pattern through the coating to the substrate metal. All the panels were subjected to 500 hours neutral salt spray testing followed by 300 hours of humidity testing (also according to ASTM test No. B-117). Examination of the panels showed that they all passed according to the standard because they showed no sign of underfilm corrosion or loss of paint adhesion.

Example 9

An aqueous solution having the following composition was made up:

$Al_2(SO_3)_4$ 12 gl^{-1}

NaF 4.5gl^{-1}

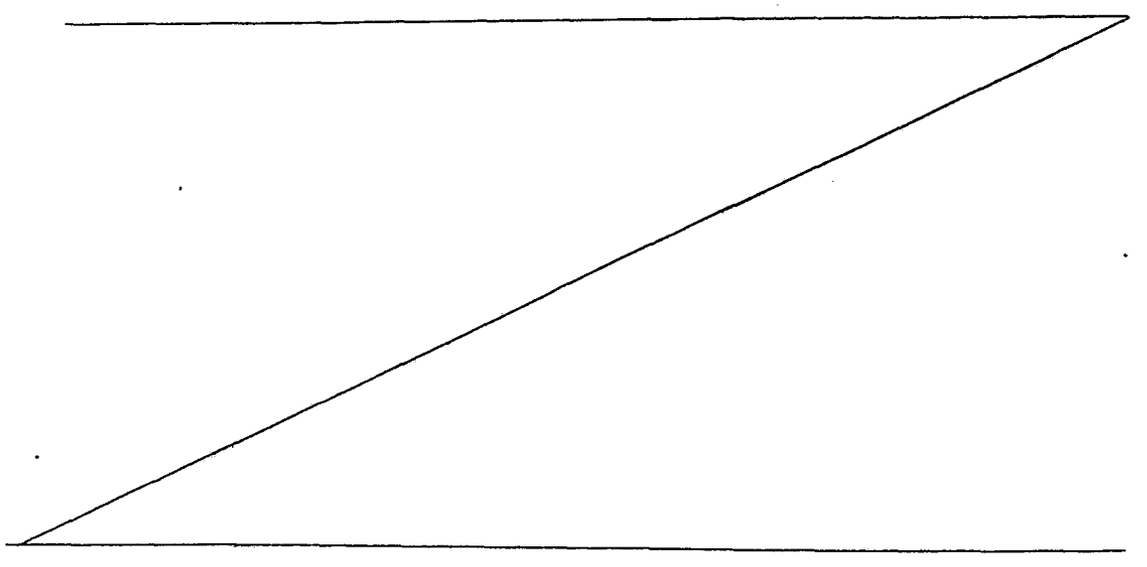
$NaNO_3$ 7 gl^{-1}

pH adjusted to 4.0

Temperature 25°C.

An aluminium panel was degreased, etched and desmutted and after rinsing and drying immersed in the above solution for 1 minute to deposit a conversion coating on it. The panel was removed from the solution and, without intermediate rinsing or drying, immersed in a commercially available dewatering fluid, IL 968 obtained from Esso Ltd., for 2 minutes. The conversion coating solution was completely removed by this treatment and the panel had a film of dewatering fluid on its surface.

The treated panel was dried in air at ambient temperature for 24 hours and then subjected to neutral salt spray testing. It survived 600 hours of testing satisfactorily.



EXAMPLE 10

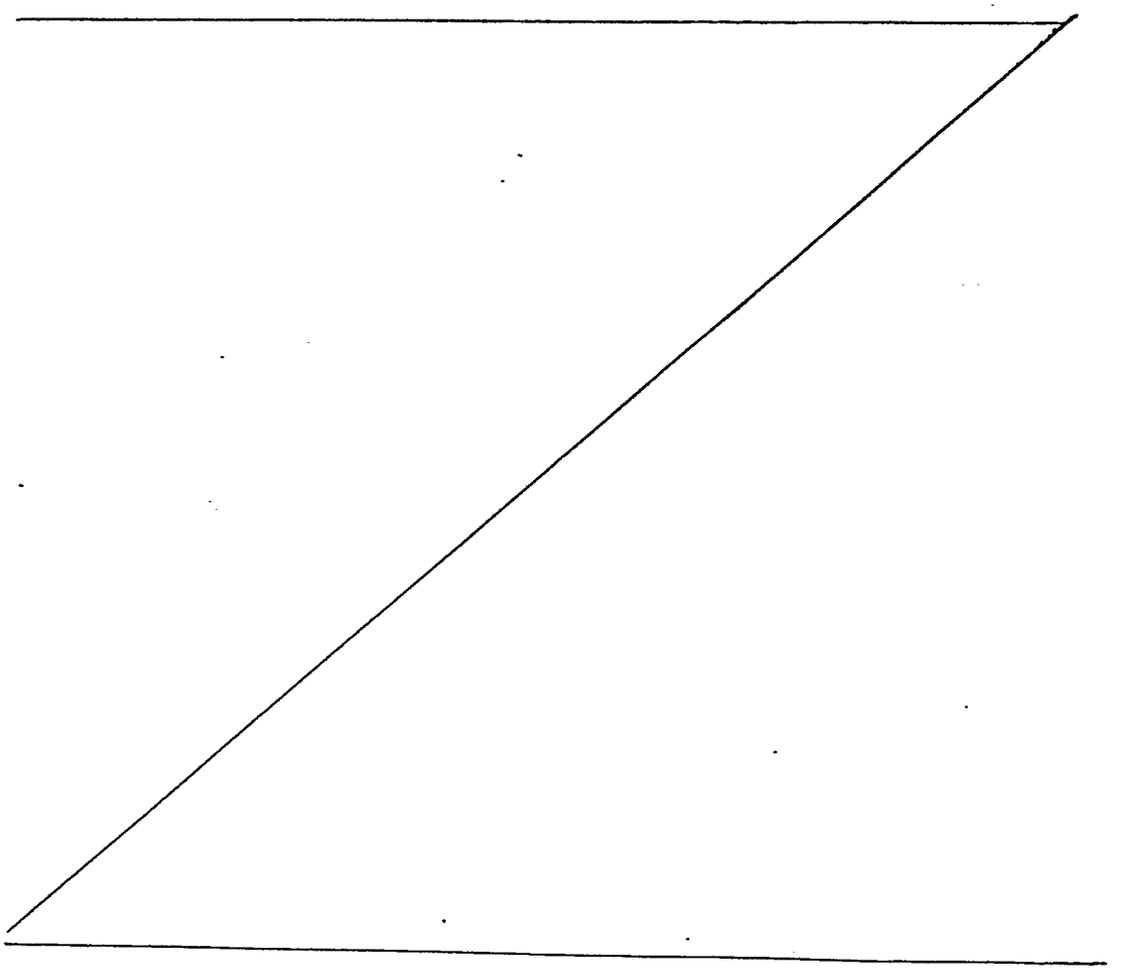
A solution having the following composition was made up:

$Al_2(SO_4)_3$	15 gl^{-1}
$NaNO_3$	10 gl^{-1}
NaF	5 gl^{-1}

pH adjusted to 4.5

Aluminium panels were degreased, etched and desmutted by standard procedures and a conversion coating was deposited on them by immersion in the above solution for 1 minute at 25°C. After rinsing in water and drying for 1 hour at 110°C, the panels were divided into two sets; one set was spray painted and the other set was spray lacquered. Further sets of panels which had been degreased etc., but not conversion coated were spray painted and lacquered under the same conditions. The organic coatings on all the panels were cured according to manufacturers' instructions. The adhesion of the organic coatings was assessed by the cross hatch adhesion test and resistance to under-film corrosion was assessed by scribing two diagonal lines across the specimen, through the conversion coating and then subjecting the specimens to 200 hours neutral salt spray testing. Both tests are according to ASTM Test No. B.117. The results are set out in the table below.

Sample	Coating	Adhesion	Corrosion Resistance
Conversion Coated	Paint	Good	Excellent
	Lacquer	Good	Excellent
Not Conversion Coated	Paint	Very Poor	None
	Lacquer	Poor	None



CLAIMS

1. A method of depositing a conversion coating of hydrated aluminium oxide on a substrate of aluminium, magnesium, tin or zinc, which method comprises contacting the substrate to be coated with an aqueous solution of Al^{III} at a concentration of at least 0.05 gl^{-1}, the solution, having a pH of from 1.5 to 5.5 and including nitrate ions as a depolarizing agent for the reaction between the solution and the surface of the substrate, whereby a conversion coating is deposited on the surface of the substrate.

2. A method as claimed in claim 1 wherein the Al^{III} is present as aluminium chloride, aluminium sulphate or sodium alum at a concentration of from 1 to 3 gl^{-1} as Al^{III} and the nitrate is present as sodium or potassium nitrate at a concentration of from 3 to 10 gl^{-1} calculated as $NaNO_3$.

3. A method as claimed in either claim 1 or claim 2 wherein the substrate is aluminium, the pH is from 3 to 5 and either the solution contains fluoride or the substrate is pre-treated with an aqueous fluoride solution to remove the surface layer of aluminium oxide on the substrate to enable deposition of the conversion coating.

4. A method as claimed in claim 3 wherein the fluoride is present as sodium fluoride at a concentration of from 3 to 8 gl^{-1} as Na F.

5. A method as claimed in claim 1 for depositing a conversion coating on a substrate of aluminium, wherein the solution contains from 1 to 2 gl^{-1} of

Al^{III} as chloride or sulphate; from 3 to 10 gl^{-1} of $NaNO_3$; from 1 to 5 gl^{-1} of Na F; the solution having a pH of from 3 to 5 and, apart from impurities, containing no materials other than water, compatible surfactant, Al^{III}, nitrate and its reduction products (principally NH_4^+), fluoride, chloride or sulphate and sodium.

6. A method as claimed in claim 1 wherein the solution has a pH of from 4 to 5.5 and includes borate in addition to Al^{III} and NO_3^-.

7. A method as claimed in claim 6 wherein the Al^{III} is present as aluminium chloride, sulphate or sodium alum at a concentration of from 1 to 3 gl^{-1} as Al^{III}; the nitrate is present as sodium or potassium nitrate at a concentration of from 3 to 10 gl^{-1} calculated as $NaNO_3$; and the borate is present as boric acid or sodium borate at a concentration of from 1 to 20 gl^{-1} calculated as H_3BO_3.

8. A method as claimed in either claim 6 or claim 7 wherein the substrate is aluminium and either the solution contains fluoride or the substrate is pre-treated with an aqueous fluoride solution to remove the surface layer of aluminium oxide on the substrate to enable deposition of the conversion coating.

9. A method as claimed in claim 8 wherein the fluoride is present as sodium fluoride at a concentration of from 3 to 8 gl^{-1} as NaF.

10. A method as claimed in any one of claims 6 to 9 where in the pH of the solution is from 0.5 pH units less than 0.1 pH units more than the pH of precipitation.

11. A method as claimed in claim 6 for depositing a conversion coating on a substrate of aluminium or zinc,

wherein the solution contains from 1 to 2 gl^{-1} of Al^{III} as chloride or sulphate; from 3 to 10gl^{-1} of $NaNO_3$; from 1 to 5 gl^{-1} of NaF; from 1 to 20 gl^{-1} of Na_3BO_3 calculated as H_3BO_3; the solution having a pH in the range 4 to 5.5 and being from 0.5 pH units less than to 0.1 pH units more than the pH of precipitation and, apart from impurities, containing no materials other than water, compatible surfactant, Al^{III}, nitrate (and its reduction products (principally NH_4^+), fluoride, chloride or sulphate, sodium, borate, where the substrate is zinc, trace quantities of zinc from substrate dissolution, and where the substrate is aluminium optionally fluorborate.

12. A method as claimed in any one of claims 1 to 11 wherein the substrate is dried and the conversion coating is aged.

13. A method as claimed in claim 12, wherein the substrate is subsequently painted, lacquered or laminated to a plastics material.

0044171

European Patent Office

EUROPEAN SEARCH REPORT

Application number
EP 81 30 2990

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	US - A - 2 327 002 (J.S. THOMPSON) * Example 5, page 1; claim 1 *	1
	FR - A - 2 219 245 (SOC. CONT. PARKER) * Example 2, page 4; claims 1-3; page 3, lines 4-6 *	1,2, 13
P/X	GB - A - 2 059 445 (RICHARDSON CHEMICAL COMPANY) * Example 2, page 5; page 4, lines 104-110 * & DE - A - 3 031 270 & FR - A - 2 465 008	1,6
A	FR - A - 794 904 (SOC. CONT. PARKER)	
A	US - A - 2 032 897 (R.R. TANNER)	
A	US - A - 3 964 936 (N. DAS)	
A	GB - A - 625 041 (RENEGIDE)	

CLASSIFICATION OF THE APPLICATION (Int. Cl.³)

C 23 F 7/00

TECHNICAL FIELDS SEARCHED (Int. Cl.³)

C 23 F 7/00

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	26.09.1981	TORFS