

# ALIEN PROPERTY CUSTODIAN

## PROCESS FOR PRODUCING A PROTECTING LAYER AGAINST CORROSION ON THE SURFACE OF METALS OR ALLOYS

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This invention relates to a process for producing a protecting layer against corrosion on the surface of metals or alloys, this layer being adhesive, strong and subsequently liable to undergo a strengthening, a dyeing or painting.

According to this process, the metal or alloy are treated with a solution containing such ions as to yield at least one readily hydrolysable salt at the expense of the metal or alloy. This salt is subsequently hydrolysed to leave a protecting layer on the metal or alloy, this protecting layer being made up of an oxidized compound such as a hydroxide, an oxide or a basic sub-salt.

This invention enables to treat even quite extended surfaces very economically. It makes use of baths made up of ordinary water and of smallest amounts of unexpensive salts. The machinery is very simple and may entirely be made up of steel. The obtained coatings, without being as thick and strong as those obtained by electrolysis, are, however, quite sufficient for most practical wants, and they constitute an excellent protection against corrosion, above all after having undergone an impregnation.

According to this invention no foreign compound to the metal is deposited on the latter; the metal is not directly, but indirectly oxidized.

The treatment may take place in a single bath or also in several successive baths; it is possible to vary the composition of the baths during the treatment, and the same may also be done with any other working condition.

It is also permissible to add to the aforementioned solution a certain amount of the hydrolysable salt which is to be formed at the expense of the supporting metal or alloys.

For producing a hydrolysable metallic salt, the metal is treated with an acid or with a salt and by preference with a weak acid or with a salt deriving from a weak acid. In order that the hydrolysis of the obtained metallic salt may really take place and form a protecting oxide coating on the metal, the operation is effected in such conditions as known to promote hydrolysis; this means that the dilution and the temperature are increased. In order to obtain a very diluted solution of the hydrolysable salt, the treatment is therefore effected with a diluted solution of the reagent. The reagent will then exert but a slight action upon the metal, and this action will cease as soon as the protecting layer will be formed. Briefly, the metal is treated with a hot and diluted solution of an acid or a salt, by preference with a hot and diluted solution of a weak acid or of a salt deriving from a weak

acid, the reagents being chosen in such a manner as to give a salt of the metal by direct attack (when a weak acid is used) or by displacing of a base (when a salt of a weak acid is used), which is hydrolysable.

In the case, for instance, of aluminium, magnesium and their alloys, the treatment may be effected with a solution of alkaline or earthy-alkaline cyanides or sulfides, or with any other salt deriving from a weak acid. The hydrolysis takes place as soon as the salt of the light metal is formed, and the supporting metal receives then an adhesive layer made up of an oxide, hydroxide or of a basic sub-salt.

It must be noted that the action of these reagents was hitherto considered as continuing indefinitely without producing the aforementioned effect, and it was admitted that the metal would indefinitely be dissolved. This invention just states the new fact that if the dilution of the reagents is very great in order that the hydrolysis phenomena may take place, and if the treatment is effected in such conditions as to promote the hydrolysis as far as possible, a rapid slackening and then a stopping of the ordinary dissolution of the metal occur, and the hydrolysis process produces then an oxidized protecting layer on the supporting metal.

The particular regulating of the reaction giving good results is illustrated, but not limited, by the following example:

The metal is treated with a very diluted solution (of about 1 gr. per litre) of alkaline cyanide. The operation takes place at 80-90° C. in a reflux-apparatus. The metal is first strongly attacked by reason of the hydrolysis of the alkaline cyanide itself; the formation of a cyanide of the treated light metal takes place, but this cyanide is strongly hydrolysed and instable in the conditions of the experiment and gives, at once, rise to the formation on the supporting metal of a hydroxide layer of the same metal. When aluminium is treated, there is, moreover, formation of an alkaline aluminate which partly dissolves in the bath to a limited concentration and undergoes, in its turn, a hydrolysis yielding thus a supplementary amount of hydroxide to the coating. Practice has shown that this second stage does not give rise to a good coating, and care must be taken to limit it. The volume of the bath must be sufficient in order that the aluminate concentration has no time to become troublesome before the formation of the protecting layer.

The formation of the protecting layer progressively slackens the attack of the metal; it is nearly stopped after one hour of working. After rinsing for eliminating the useless or prejudicial products, the metal is coated with a thin, adhesive, resisting and smooth layer. When the volume of the bath is insufficient and the precipitation of aluminate takes place, the layer is dusty and brittle.

The composition of the baths to be used for the treatment is illustrated, but not limited, by the following examples:

*Pure aluminium*

Temperature: 75–85° C; duration of the treatment: 1 to 3 hours.

Per litre of ordinary water:

		Gr.
(1)	Alkaline cyanide .....	2 to 4
	Alkaline chlorate or perchlorate or acetate or oxalate or sulfite or fluoride or sulphide.....	3
	Alkaline cyanide.....	3
(2)	Alkaline fluoride.....	1
	Alkaline sulphide.....	1

*Duraluminium and cast alloys*

Temperature: 75–85° C; duration of the treatment: 1 to 3 hours.

		Gr.
(1)	Alkaline cyanide.....	4 to 6
	Alkaline acetate or perchlorate or chlorate or oxalate or sulfite .....	4 to 6
	Alkaline cyanide.....	4 to 6
(2)	Alkaline chlorate or oxalate or sulfite .....	6 to 18

Eventually, an alkaline sulfate (up to 30 gr. per litre) may be added for discolouring the layers, if they are liable to become coloured.

It may be also be made use of the continuous electric current without greatly modifying the process, the treated metal being at the anode. In the aforementioned example, the electric current promotes the formation of the cyanide of the treated metal and its intensity shall remain very low, because a too intense formation of this cyanide opposes to its immediate hydrolysis, and the hydroxide layer is made up of nonadhesive sheets coming easily off and constantly formed anew. It may also be made use of the alternative current and its effect seems to be favourable.

It may also be made use of chemical agents to modify the hydrolysis conditions of the dissolved salts, and the process does not then undergo any deep change. The baths may be stirred, and use may be made of vessels having shapes of any kind, diaphragms and so on. In a general manner, it is advisable to eliminate by mechanical way or by any other means, the bubbles which will remain adhesive to the metal and which are mainly produced at the beginning of the treatment; these bubbles would produce unprotected spots.

Moreover, care must be taken to avoid any defect such as straws, holes, and above all, inclusions of foreign bodies and more particularly those of metals, on the surface to be treated. Thus, it happens frequently that small iron particles, coming from roller-cylinders and more particularly from heated rollers, become incrustated in aluminium surfaces and form non-protected spots.

The bath may also be modified in order to adjust the hydrolysis reaction or to modify the characteristics of the layer or to obtain several con-

comittant reactions leading to a simultaneous layer constituted by a mixture adsorption or combination of various organic or inorganic bodies in the deposited coating. These modifications may be realised for the entire duration of the working of the bath or for a fraction of the duration.

Thus, use may be made of ordinary water to supersede, partly or in its totality, the distilled water in the composition of the bath and the progress of the treatment then undergoes a change. The use, in particular, of a water rich in lime sulfate gives tougher layers and more suitable to impregnation when light metals are treated.

Thus also, the addition of a soluble silicate at the end of the treatment may lead to an incorporation of silica into the coating. The coating then becomes suitable to be dyed in a basic dyeing bath. Additions of metallic salts such as chromium, manganese, titanium, tungsten, molybdenum salts or salts of metallic anions, chromates, manganates, titanates, tungstates, molybdates have some tendency to add to the coating layer more or less saline hydroxides in a more or less combined state.

Among the organic bodies, fatty acids and their salts such as stearic acid and stearates, when added to the bath, have some tendency to yield organic salts of the treated metals to the coating, and the coating layer becomes then water repellent.

Colloidal suspensions of resines, gum, latex, organic or inorganic matters added to the bath may be looked upon as auxiliary agents for the main treatment because these matters may be incorporated into the oxidized layer during its formation thus improving its properties.

Electrolysis and electrophoresis may be used to incorporate the improving agents into the coating layer.

Practice has shown that the physical state of the treated metal is of certain consequence for the characteristics of the protecting layer.

The preparation of the surfaces to be treated may comprise a cleaning or a scouring by known processes. When light metals are treated with a cyanide, the bath itself is scouring, and if the metal is not excessively dirty it need not otherwise be scoured.

It may become desirable to add in advance to an alloy a compound enabling it to form, after applying the aforementioned treatment, the best possible layer. Thus, in the case of aluminium alloys, the presence of copper and of magnesium is highly favourable to the production of strong coating layers.

Briefly, it is advantageous to eliminate any impurity which would be prejudicial, in a particular or in a general manner, to the strength of the coating layer. Practice has shown that any defect in the protecting layer is nearly always caused by a local impurity to which the treatment cannot be applied. In the absence of these impurities the coating layer is perfectly continuous. Even the holes, cracks and other defects in the continuity of the surface are coated with the protecting layer if no superficial inclusion hinders its formation. However, in the case of deep cavities where the bath would be renewed but with difficulty, it may be necessary to favour the regularity of the reaction by means of suitable stirring.

The protecting layers formed according to the invention are suitable to be dyed with organic or inorganic dyes. The fixation processes of dyes

on hydroxide layers or layers of basic salts are very well known and constitute the basis of the dyeing industry on fabrics. All that is known in this branch of industry may then be applied and more particularly auxiliary fixation treatments with acetates, solubilised oils and so on. In the case of layers principally made up of alumina which is amphoteric, the coating layer may fix either acid dyes or basic dyes. Practice has shown that the fixation of acid dyes is more readily realised. The aforementioned dyes may receive any addition liable to facilitate the fixation. In the case of alumina, for instance, some acid dyes fix well only in the presence of traces of acetic acid or of lime acetate.

For the proper working of the dyeing treatment it is necessary that the protecting layer should be fresh and humid. The treated metals must be kept in a water bath until the beginning of the dyeing operation and no longer.

A coating layer having lost its dyeing power recovers it after a new treatment which is the very same as the first and which may be of a shorter duration.

The dyeing treatment must be followed by a rinsing eliminating the excess of the dye and the additional substances incorporated into the dyeing bath, and more particularly acetic acid.

The protecting layers formed in accordance with the invention may be impregnated, in their thickness, with various substances in order that they may become stronger and water repellent. This impregnation eliminates the fortuitous defects of the protecting layer, the small holes of the layer being filled with the impregnation substance. In the case of layers having been dyed, the impregnation fixes the colouring matter. As impregnation substance, any dissolved or melted substance may be used which is capable of penetrating into the coating layer, with or without combination with the layer or the supporting metal.

Any dissolved substance aforementioned as being liable to be used in the bath yielding the coating layer may be incorporated into the bath. As the penetration of the substances is secured by the

present water, it is advisable to obviate any drying of the layer between the two treatments, and the metals must be kept under water.

As example for a melted substance liable to be fixed by reaction on the coating layer, I may mention stearic acid, with or without additions of metallic stearates, which is fixed in consequence of the formation of basic aluminium stearate or of stearate of the supporting metal, and which imparts remarkable water repellent and anti-corrosive properties to the protecting coating layer.

As example for substances of this kind, I may also mention linseed oil to which metallic linoleates, turpentine and natural or synthetic resins can eventually be added.

The impregnation with the melted substances is particularly efficient when working in the following manner: the substance is heated at the highest temperature it may support, as also the metal, without becoming injured. The metal kept under water since the treatment and slightly dried but still humid, is suddenly introduced into the melted bath where it is kept as long as vapour evolves. At the end of the vapour evolving, the piece is withdrawn, and the excess of the impregnation matter is wiped.

The adding of dyes to the melted substances enables the dyeing of the protecting coating. Thus, when stearic acid is used a dye soluble in melted stearic acid is added to the fatty matter.

The protecting layers formed in accordance with the invention may receive any treatment with a paint or varnish. The operations still described may specially be adjusted with a view to obtain a particularly good coating layer for this purpose.

The protecting coatings obtained by this invention enjoy very good dielectric properties. These properties will be improved by the aid of a melted insulating matter, and this operation enables to eliminate any trace of water and to stop up the holes on the coating layer. All the operations previously described may be adjusted in such a manner as to impart the best dielectric properties.

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