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PROCESS FOR TREATMENT OF METALLIC SURFACES

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It is known that by the passage of a continuous current anodic effects are produced on metallic surfaces plunging as electrodes into an electrolytical bath. Thus it is possible to dissolve metallic surfaces or a metal deposited on a supporting metal, to produce a protecting oxidized layer or to achieve a cleansing and even an electrolytical polishing or brightening.

We have found that these effects of the electric current may be obtained without the help of the electric current by addition to a bath which can work with the electric current to produce a given anodic effect, at first of well chosen oxidizing compounds, then of stabilizing substances and at last of various matters facilitating the chemical process or improving the result. As oxidizing compounds are preferably chosen those compounds the reduction products of which are colourless and soluble and that easily undergo a reoxidation in order to secure the regeneration of the baths. If one of these oxidizing compounds to be added yields reduction products that are insoluble or coloured and if the anodic effect is to give a protecting layer, it will be possible to realize peculiar colouring effects and the strengthening of this layer.

This anodic effect may also to be cause of a redressing effect as also of a condensation effect. Electrolytes containing ferricyanides, manganicyanides and cobalticyanides and analogous complex compounds are particularly suitable to make up condensation or redressing electrolytes.

The oxidizing compounds may still be partly or wholly present in the electrolytic bath. In such a case the present invention foresees the utilisation of the same bath without current and if necessary in presence of some additional substances.

It has been observed, moreover, that the electrolytical baths modified as has been said previously in order to be capable of working without current, may in their turn act as electrolytes and simultaneously produce both electrolytical and chemical effects.

The regeneration of the exhausted baths is generally achieved by a chemical reoxidation as for instance by means of oxygen or compressed ozone applied under pression or without any pression or in some electrochemical way. Examples will be given farther.

It has been observed that in some cases it was useful to add to the bath some very small amounts of a catalytic agent such as a cerium salt or when the bath is an alkaline one the catalyst may be a halogenated salt.

Examples

1°—The detining of tin-plate which may be achieved by anodic attack in an alkaline bath will be easily completed by the action of an alkaline solution containing an oxidizing compound as for instance a ferricyanide or simply by oxygen or air dissolved under pression or without any pression. The supporting iron will remain inattacked. The same is true for the removal of zinc covering galvanised iron as also for the removal of a lead-coating the supporting metal being iron.

2°—The realization of a protecting anodic layer on aluminium and its alloys by means of electrolytical baths containing sulfuric ions or hydroxyl groups is well known. If a soluble ferricyanide as for instance an alkaline ferricyanide is added to a bath made up of sulfates and if this bath is alkalinized by means of soda in order to secure the stability of the ferricyanide compound, an excellent protecting coating is then realized by a chemical effect. If a soluble ferricyanide as for instance an alkaline ferricyanide is added to an alkaline carbonatic bath capable of producing an anodic effect, the protecting coating achieved in a chemical way will be inferior to that realized in the foregoing case. Good results may also be achieved in these baths by adding various salts other than sulfates.

With sulfates, for instance, it is probable that the process is as follows: the ferricyanide draws to itself the alkaline metal of the sulfate and sets in liberty the sulfuric ion. This sulfuric ion acts then on the metal in the same manner as in the case of the anodic effect by forming a sulfate of this metal which undergoes a hydrolisis and combines with the carbonate of the bath in order to give, on the one hand, an oxide on the metal and, on the other hand, an alkaline sulfate and carbonic acid. The practise has shown what salts act in these baths in the same way as the sulfate does. We may particularly mention acetates and nitrates. Some compounds such as fluorides and fat acids hinder the reaction and their presence in the bath must be avoided, Some other compounds such as chlorides, bromides, iodides produce localized effects and must also be avoided. Yet traces of these salts are useful and act as catalysts.

Our practise has shown that the bath must not be too alkaline and the alkalinity is regulated by means of some bicarbonate or carbonic gas.

Similarly results may be achieved by using instead of ferricyanide some oxygen or air dissolved under pression or without applying any pression. Some examples of the bath compositions are given here below:

		G.
(1)	Potassium ferricyanide	260
	Solvay soda	72
	Sodium sulfate	33
	Sodium acetate	12
	Sodium bicarbonate	1

Tap water, to make up 1 l.
Temperature: 70–80° C. Duration: 1 hour.

		G.
(2)	Potassium ferricyanide	150
	Solvay soda	40
	Sodium sulfate	18
	Sodium acetate	7
	Sodium bicarbonate	2

Tap water, to make up 1 l.
Temperature: 70–80° C. Duration: 1 hour.

		G.
(3)	Potassium ferricyanide	26
	Solvay soda	8
	Sodium sulfate	25
	Sodium acetate	1
	Sodium bicarbonate	1

Tap water, to make up 1 l.
Temperature: 80–90°. Duration: 1ʰ 30′.

The bath while working becomes impoverished in ferricyanide and on the other hand it grows rich in ferrocyanide bicarbonate and dissolved alumina.

The most practical regeneration process is in this case the electrolytical treatment which may be realized in an intermittent manner or in a continuous way, in the treatment vat or in a special apparatus. The electrolysis is realized by means of an anode which may be made up of lead, graphite, iron or nickeled iron having a surface as great as possible, and by means of an iron cathode having a very small surface and which may be introduced into a porous vessel. We must take care of securing a certain stirring of the liquid. It is profitable to add some ferrocyanide to the bath and to stop the reoxidation when a suitable content in ferricyanide is attained.

In order to eliminate alumina and silica suspended or dissolved in the bath, it is convenient to cool the bath and to filter what may be done in an intermittent or in a continuous way.

We give here below some details about the composition of the baths: potassium carbonate tends to produce dull coating-layers while the tendency of sodium carbonate is to give transparent and bright coating-layers. Sulfates give rather transparent and bright coating-layers; acetates produce stronger, thinner and duller coating-layers.

The alkaline substance of these baths must not necessarily be a corbonate; it may also be, for instance, a borate.

The obtention of bright coating-layers on aluminium and its alloys in an electrolytical bath made up of sodium sulfate and alkalinized by means of soda is well known. By addition to this bath of an alkaline ferricyanide it is possible to achieve the same effect.

We give here below a formula indicative of the composition of the bath:

	G.
Potassium ferricyanide	180
Sodium sulfate	180
Sodium hydroxide	20

Temperature: 80° C. Duration: 5 minutes with stirring.

A bath of this kind may also serve for zinc, tin and their alloys. The chemical bath used as electrolytical bath yields a brighter coating-layer than that realized with the primitive electrolytical bath the current density being less high.

Instead of soda use may be made in the foregoing compositions of every strongly alkaline substance that is compatible with the oxidizing compound: alkaline phosphate, borate and so on. Instead of the sulfate use may be made of other salts: oxalate, acetate and so on.

In the foregoing examples mention has been made of ferricyanides acting as oxidizing compounds, but other oxides may also be used such as—in acid baths—peroxygenated acids, perchloric, permanganic, chromic, persulfuric, nitric, picric acids and their salts, the salts of metallic peroxides such as the salts of cerium peroxide and so on, dissolved oxygen, hydrogen peroxide.

In alkaline baths: the foregoing salts, peroxygenated hydrates such as those of sodium and potassium, complex salts such as ferricyanides, manganicyanides, cobalticyanides, sulfocyanides, the oxygenation products of organic reducting compounds and more particularly of photographic reducing substances, dissolved oxygen, hydrogen peroxide and so on.

The baths may also receive addition of auxiliary substances: coagulating electrolytes such as polyvalent ions when protecting layers are to be realized, catalysts, moderating substances and so on.

The surfaces treated by these processes in order to achieve a bright coating or protecting layer may also be followed by the complementary treatments in use in analogous cases and more particularly by a brightening, a discoloration, a treatment with mordants, a dyeing, a fixing treatment, a sealing, an impregnation achieved more particularly by fat compounds and fat acids, a precipitation achieved by the reaction with an inorganic compound and so on.

The discoloration of layers coloured by oxides will be realized, for instance, by means of cyanide baths, sulfite or sulfitocyanide baths.

The processes according to our invention may also constitute a stage of a more complex process. It may for instance be used to cleanse surfaces to be submitted to a subsequent anodic oxidation. By means of these processes it is also possible to achieve a bright or transparent oxidized layer that is liable to be dissolved in order to give a cleansed, smooth, or even a bright metal. In such a case the solvents which may also be used to dissolve unsatisfactory layers are chosen according to the nature of the oxidized layer. Thus if this layer is constituted by an aluminium oxide we may use concentrated cold sodium bisulfite or concentrated, hot, green chrome sulfate or one of the following substances: acides and more particularly concentrated acides, acid salts, neutral salts such as acetates, oxalates, tartrates, acid salts obtained by hydrolisis, complex salts such as concentrated green chrome salts, ferrocyanide, boron and sodium double tartrate, alkaline salts such as alkaline phosphate, alkaline compounds such as soda and more particularly high concentrated soda at 40°, concentrated potassium carbonate, concentrated ammonium, methylamine, methylammonium hydrate. The action of these substances upon the metal may eventually be lessened by an addition of inhibiting compounds such as silicate, chromate and so on.

The applying of such processes to goods of every kind constitutes a part of our invention.

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