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PROCESS FOR THE TREATMENT OF METALS BY MEANS OF GALVANIC CURRENT IN WHICH THE METAL TO BE PROTECTED SERVES AS CATHODE

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Three methods have hitherto been employed for the protection of metals against corrosion:

(1) *Electrolytic treatment, that is to say the application of an external source of electric current.*—By this means one can either obtain an electrodeposited layer of another metal (as for instance in nickel and chromium plating); a deposit of an oxide or a salt of the metal to be protected (as for instance in the case of the anodic treatment of aluminium or the silicate treatment of magnesium); or the electrodeposition of the oxide of another metal, always more or less mixed with the oxide of the metal to be protected (as for instance in the case of the treatment of magnesium with alternating current in a solution containing chromic ions).

(2) *Chemical treatment.*—By this means one obtains on the surface of the metal to be protected, as the result of the chemical action of the medium in which it is immersed, a layer of one of its oxides or salts (as for instance in the phosphatisation of iron or in one of the chemical processes for the protection of aluminium by oxidation); the deposition of a layer of metal by ionic displacement (as for example in the deposition of copper on zinc immersed in a solution of a copper salt); or of a layer of oxides of another metal, always more or less mixed with the oxide of the metal to be protected (as for example in the deposition of oxides or molybdenum upon zinc immersed in solution containing molybdenum).

(3) *Treatment by chemical contact.*—This procedure differentiates itself from the preceding treatment by the fact that in this case the metal to be protected must be in mechanical contact with a third metal which begins to effectuate the deposit and may be considered to initiate the reaction. An example of such a process is to be found in the protection of iron by aluminium, where it is necessary to surround the iron by a thin band of zinc. The aluminium first commences to deposit on the zinc, and the iron is then coated in its turn by the aluminium; whereas there is no deposit of aluminium on the iron in the absence of zinc.

The present invention has for its object an entirely new process for the protection of metals, which has given surprisingly good results. Its basis consists in utilising an electric current produced galvanically, by which means a deposit is obtained on the metal object it is desired to protect; that is to say one operates without employing any external source of electric current, and the electric current which serves to deposit the protective coating is obtained by joining two different immersed metals, one of which functions as cathode and the other as anode, by means of an external conducting circuit.

The inventor has already described in his previous Patent No. 314,349, January 17th, 1940, lodged under the title "Improvements in protection of metallic objects by galvanic action," a process by means of which one can obtain a layer of an oxide of manganese upon metals which are immersed in solutions in which are dissolved compounds giving ions containing the element manganese. In the process set forth in the above patent the metal to be protected functions as anode, and is joined by means of an external electric circuit to a cathode, preferably composed of carbon.

Further experiments by the said inventor have enabled him to make the surprising discovery that if a galvanic treatment is employed in which the metal to be protected functions not as anode but as cathode, such a process may serve as a general means by which all metals may be protected, and that in particular such a process affords an exceedingly effective treatment against corrosion for such metals as aluminium, iron, copper, lead and their alloys.

An altogether remarkable advantage of the treatment set forth and described in the present invention is that the protective layer deposited on the metal is of uniform thickness irrespective of the form of the metal object on which it is deposited. This is so even in the event of the said metal object presenting hollows or recesses; whereas if electrolytic processes of protection are employed, the protection afforded to such hollows or recesses it always deficient.

The present invention permits moreover of depositing a film of oxides other than those of the metal to be protected, which fact is of particular importance in the case of iron whose oxides act as catalytic promoters of deep seated corrosion.

The bath may consist of any solution which permits of obtaining a galvanic current with the electrodes chosen. The inventor has found that particularly efficacious results are obtained when employing solutions containing salts, oxides, acids or bases in which figure a metal capable of two or more degrees of oxidation, whose lower valency compounds are insoluble in water, such for example as manganese, chromium, titanium, vanadium or molybdenum. As a result of the galvanic current, the solution is reduced in the neighborhood of the cathode with result that a layer of insoluble oxide is deposited and fixes itself firmly

to the cathode. As an example may be cited the reduction of $KMnO_4$ to Mn_2O_3 or Mn_3O_4.

In contradistinction to the lines of electric force produced by an electrolytic current due to an external source, the lines of electric force produced by a galvanic current, in as much as they have their origin in the metal itself, are uniform and regular, and penetrate into the most pronounced hollows and recesses.

As has previously been explained, all metals are capable of acting as cathodes when treated according to the present invention, providing always a more electropositive metal functions as anode. Thus, for instance, in highly oxidising solutions, such for instance as $KMnO_4$, the cathode may be constituted by an object in iron or aluminium which it is desired to protect, while the anode consists of magnesium or zinc. In this case, both metals become coated with adherent deposits having for basis an oxide of manganese highly resistant to corrosion.

It is in general preferable that there should be a difference in potential of at least 1 volt between the cathode and anode; but in many instances a smaller difference of potential is sufficient to ensure the deposition of an adequate protective coating.

The following is a description of the exact manner in which the present invention may be put into effect; it is however given merely by way of example, and must not be construed in any limitative spirit.

The solution consists of $KMnO_4$ and chromic acid, the anodes are composed of magnesium and the cathodes of objects in iron or aluminium which it is desired to protect. The potential difference is about 1.9 volts. The iron or aluminium becomes coated with a uniform film of Mn_2O_3 free from Al_2O_3 or Fe_2O_3. An identical film is deposited at the same time on the magnesium anodes.

In general, 15 minutes suffice to produce a coating which serves as an excellent basis for painting. If the objects are not subsequently to be painted, they should be left for about half an hour and then preferably dipped in hot paraffin after previous drying.

The present invention also covers the same treatment when applied to the degreasing of metals. It is general knowledge that nascent hydrogen serves as an excellent means of thoroughly degreasing metals. The manner in which the present invention of degreasing metals is put into effect is to immerse the metal in an appropriate solution and connect it by means of an external electric circuit to another more electropositive metal also immersed in the same solution, which more electropositive metal then functions as anode. For instance if an object in iron is thus connected to an object in aluminium, a galvanic electric current traverses the solution, and hydrogen is evolved on the iron which functions as cathode.

The inventor has moreover made the surprising discovery that this action of degreasing can be still further increased and ameliorated if the potential difference between the anode and cathode is increased by hanging upon the same metallic support to which the object to be degreased is attached, objects in another substance which have the power either of inereasing the said potential difference, or even of lowering it to such an extent that the sign of the voltage becomes reversed, thus causing the previous anode to become the cathode and vice versa. As an example, one may again cite the case of aluminium and iron referred to above. Thus for instance if objects in carbon are attached to the same bar which serves to support the aluminium objects, the aluminium becomes less electro-positive than the iron and now forms the cathode instead of the anode, with the result that hydrogen is evolved no longer on the iron, but on the aluminium which it degreases. On the other hand, if the objects in carbon are hung on the same bar as the iron objects, the original difference of potential is increased, and the degreasing action on the iron is more rapid and effective.

The present invention also covers by way of new industrial products, all metallic objects on which a protective coating has been deposited while they served as cathodes in a bath transporting a galvanic current and all metallic objects which have been degreased by similar means.

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