Cl 204

Published May 18, 1943

Serial No. 356,108

ALIEN PROPERTY CUSTODIAN

METHOD FOR DECREASING OR PREVENTING THE ACTIONS OF PICKLING ACID ON METALS, ESPECIALLY IRON- AND METAL-ALLOYS

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No Drawing. Application filed September 9, 1940

When metallic, especially iron articles and articles consisting of metal alloys are exposed to the action of the air and particularly at higher temperatures, oxygen compounds are formed, such as layers of oxide or hydroxide and hammerscale, which layers must be removed prior to any further treatment such as for instance application of coatings, cold-drawing, fine-rolling and the like.

For removing these oxygen compounds dry-cleaning or wet-cleaning methods are generally used. The first of these methods is of a mechanical kind and effected by means of sand blast apparatus, grinding or the like. The second mentioned cleaning method is either of chemical kind and effected by treatment with diluted (aqueous) solutions of mineral acids, preferably hydrochloric acids or sulphuric acids, this proceeding being generally called "pickling", or by electrolytic method.

The dry-cleaning, as compared with the wet-cleaning, is employed only very seldom as it is difficult to carry out, expensive and cannot be used everywhere.

The cleaning of the material by means of acids ensures a complete removal of all oxides but has a number of serious inconveniences.

As the layer of oxide or hammerscale does not cover the surface of the material in uniform thickness, the core metal under the layer is strongly corroded in the course of the pickling proceeding after the thinner layers of oxidic character have been removed. This dissolution of metal is accompanied by strong development of hydrogen, whereby not only the pickling acid is squirted about in the room where the treatment takes place so that the health of people staying in the room is endangered, but the hydrogen is absorbed in atomary state by the core metal in the form of an alloy of the metal with the hydrogen gas. This proceeding, for instance on articles of iron, leads to a considerable quality decrease in the form of the feared pickling brittleness. With this pickling brittleness is connected, besides an unnecessarily strong metal dissolving which has to be considered as loss, an undesirable roughening of the metal surface and a just as undesirable loss in pickling acid.

For avoiding the inconvenience of the excessive development of hydrogen a so-called slackening medium or economical mordant is added to the pickling acids. This medium consists of organic and sometimes of inorganic substances. In the patent literature numerous propositions of this kind are described which concern very different media used all with the same object in view, that is to exert a slackening effect on the hydrogen development when the pickling acid acts upon the metal, and to practically exclude the dissolution of the core metal.

In spite of these possibilities just the well protecting economical mordants possess the inconvenience that their application, if made to sufficient extent, considerably increases the cost of the cleaning proceeding. For this reason one often renounces in practice on the application of economical mordants and puts up with the inconvenience of the hydrogen development and the loss of metal and acid. A quantity of economical mordant from 0.05 to 0.1% of the weight of the acid mordant is usually required to obtain a sufficient slackening effect on the action of the core metal of iron articles and with employment of a 10% sulphuric acid of 60° C.

When the electrolytic cleaning method is employed, the metal articles in question are treated either as cathodes or as anodes or according to the middle conductor principle with direct- and alternating current.

Either acids or lyes or also solutions of neutral salts serve as electrolyte. In alkalis as well as in the solutions of neutral salts a sufficient removing of certain metal oxides, for instance of the pertinaciously adhering hammerscale layers is obtained only with difficulty. If the material to be treated is interposed as cathode into the electrolyte consisting of acid the layer of hammerscale can be removed and partly a metal dissolution can be reduced, but it is not possible to attain a stronger reduction of the loss in metal on account of the high corroding temperatures and acid concentrations. Owing to the cathodically developed hydrogen very much pickling acid is lost by spraying at the usual high current densities from 100 to 1000 amperes per square meter cathode surface, and the danger that the pickling brittleness occurs is also considerably increased.

If the material to be treated is anodically inserted in the electrolytic proceeding, the losses in metal dissolved anodically by the current are added to the loss in metal due to the action of the acid and these losses can then no longer be supported economically.

At the application of the central conductor system in the acid electrolyte the influence of the cathode, as has been ascertained by the applicant, is stronger than that of the anode; this method is therefore technically useful. It demands, however, for the technically useful pickling period rather high current densities from 100

to 500 amperes per square meter electrode surface.

The above explained inconveniences of the wet-treatment method can however be avoided according to the invention, if a combinatoric combination of the acid treatment of the metallic, preferably iron material is carried out with addition of substances having an economical mordant character with simultaneous effect of the electric current.

The expression "substances having a character of economical mordant" means all those substances or mixtures of substances preferably of organic kind, which are capable of reducing the action of the acids on metals or to practically completely eliminate the same and which are known on the market under the designation "slackening medium", "economical mordants" or "inhibitors". To these belong further other known additions of organic kind, such as dextrin, glues, gum arabic, gelatine, turkey red oils and so on. They must, in any case, have the effect to slacken the corrosion of metals when added in sufficient quantities to the pickling acids.

No explanation is necessary in the present instance by which proceedings in detail the presence of organic slackening media of the kind stated or which have become known from the patent literature exerts a slackening or preventing effect upon corrosion of the metallic material by the acid mordant in question, if according to the invention the material to be treated is further interposed in an electrolytic circuit. It ought to be sufficient, that applicants have ascertained that the stated effect, prevention of an excessive hydrogen development and also of the pickling brittleness of the iron and therefore of the losses in metals and acids occur, besides a considerable reduction of the usual high current densities at the electrolytic cleaning processes, if according to the invention organic substances possessing the character of economical mordant are added to the electrolyte. In any case, instead of the current densities from 100 to 1000 amp/m² surface usual up to the present, current densities below 50 amp/m² down to 1–10 amp/m² may be employed, whereby it is possible to use considerably smaller electric unities for the current supply. Further it could be ascertained, that by the simultaneous cathodic polarization in presence of organic substances having the character of economical mordant considerably less great quantities of these mordants are required than up to the present without admission of current at the treatment of the material with acid mordants.

Instead of concentrations between 0.05 to 0.1% of the slackening medium to the acid, concentrations from 0.0025 to 0.005% will be sufficient, i. e. quantities which are only $\frac{1}{10}$ or less of those which were required up to the present for obtaining a protecting effect of 90 to 95% in a 10% sulphuric acid heated to 60° C. Hereby the employment of economical mordants has been enabled economically in general. The experiments carried out have proved that with good slackening effect a low concentration of the addition with character of an economical mordant required the application of a higher current density and inversely a higher concentration makes it possible to employ a lower current density.

It has been ascertained that metal articles, which have been treated in acids with simultaneous action of the electric current and in presence of organic substances having the character of economical mordant, do not only show no pickling brittleness, but assume also a better and more brilliant appearance than, for instance, goods which have been treated merely electrically or mechanically. Similar advantages as result already from the treatment of the metal articles as cathodes can be obtained at the electrolytic pickling according to the middle conductor process, as in this instance, as already explained, the influence of the cathode is preponderant to that of the anode.

The connection of the metal articles to the current can be effected in any manner known in the technics of the electrolytic treatment of metals or in the galvanotechnics, for instance by clips, jaws or wires, bands and so on in the continuous method, by rollers, rolls or the like. For wire- and band-rings it has proved to be preferable to thread these as carriers from current conducting material such as iron, monel metal and others and to connect such carriers with the source of current. The current may however be fed alone according to the well known central conductor principle by the electrolyte.

Any desired kind of current may be employed and the polarity of the current may be reversed from time to time, intervals without current may be interposed, direct current may be overlaid with alternating current and so on.

The method according to the invention may be preferably employed also for cleaning stationary containers, steam boilers, pipe conduits and so on of heavy metals or light metals from stone-like deposits or other impurities by means of acids. Also the alloyed steels, especially rust-free steels which are difficult to clean and pickle can be treated with acid according to the present method.

Example

The action of a 10% sulphuric acid at 60° C upon a plate of soft iron sheet metal amounted to 250 g/m² calculated for a day at two hours duration of experiment. This loss was reduced to only 14 g/m² per day by addition of 0.05% of a slackening medium known in commerce and at similar experimental conditions. The slackening effect which has been ascertained amounts to about 94%. A 10% sulphuric acid containing 0.0025% of the same slackening medium resulted in an iron loss of 163 g/m² per day, which means a slackening effect of only 35%. If the plate of soft iron sheet metal was treated cathodically in pure 10% sulphuric acid at 60° C, a slackening effect of only about 70–80% could be obtained even at high current densities, for instance 10 amp/m² and above. If the same sheet metal plate was treated at 60° C in sulphuric acid of 10%, which contained 0.0025% of the slackening medium, at a current density of only 0.7 amp/m² the metal loss amounted to only 3 g/m² per day, which means a slackening effect of 98.8%. In spite of the fact that $\frac{1}{20}$ of the quantity of the slackening medium and about $\frac{1}{14}$ of the former current density were used, the slackening effect obtained was considerably greater.

On the anode, on which the capability of the iron to dissolve is always increased, the action of the iron in sulphuric acid of 10% at 60° C at a current density of 1.25 amp/m² is increased from 250 g/m² per day to 620 g/m² per day, that is to 248% of the initial value. If to the sulphuric acid 0.0025% of the slackening medium is added the action amounts under similar conditions and at similar anodic current density to only 393 g/m² per day, that is it has been increased to only about 157%.

If the middle conductor pickling method is employed, the solubility is reduced from 250 g/m² per day to 187 g/m² per day at a current density of 0.3 amp./m², because, as has been ascertained, the cathodic protection is surprisingly preponderant to the anodic solubility. The slackening effect amounts in the present instance to 25%.

In the currentless state a reduction of solubility from 250 g/m² per day to 163 g/m² per day at a slackening effect of 35% results as already mentioned with an addition of 0.0025% of the slackening medium to a sulphuric acid of 10% heated to 60° C. If however both methods are applied at the same time, i. e. 0.0025% of the slackening medium and 0.3 amp./m², only 90 g/m² per day are dissolved in two hours, which corresponds to a slackening effect of 64%.

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