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METHOD FOR INCREASING THE RESISTANCE TO CORROSION OF STAINLESS STEEL

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The present invention relates to a method for increasing the resistance of steel devices to acids.

It is well known that commercial stainless steels such as steels with 15 to 18% chromium, 18/8 chromium-nickel steels (18% chromium and 8% nickel), 18/8 chromium-nickel steels with molybdenum and copper do not shown an industrial resistance to certain acids, whatever the degree of dilution of the latter may be. Thus, the said steels resist sulphuric acid only when the latter is in the form of its most concentrated solutions (60 to 65° Bé.) or, on the contrary, in the form of its most diluted solutions (less than 6%) and, in both cases, only when the said solutions are cold.

The resistance to concentrated solutions is not even total; moreover, it is practically rather precarious owing to the fact that since these latter solutions are hygroscopic the concentrated liquid which creeps along the walls above the level of the solution absorbs the moistness of the air so that it is diluted and can then cause strong local corrosion.

Likewise, if the above mentioned steels show a certain passivity to sulfuric acid solutions of high dilutions the observed resistance remains at least very unstable.

Thus, an 18/8 chromium-nickel steel test-piece when immersed during 48 hours in an acid of 40 Bé. has lost 1800 grams per square meter at 30° C.; a test-piece of the same size has lost more than 1000 grams per square meter per hour in the same acid at 100° C. and more than 7000 grams per square meter per hour in boiling acid and this irrespective of its surface condition, whether sand blasted, pickled or pickled and glazed or polished. 18/8 steel with molybdenum and copper resists better in the cold but a test-piece of said steel when immersed in sulphuric acid of 40° Bé. at 30° C. during 48 hours has still lost 350 grams per square meter while it had lost only 3 grams per square metre in acid of 65° Bé.

The above mentioned steels are also seldom apt to resist long enough in other corrosive mediums such as, phosphoric acid and organic acids when used at certain concentrations.

This lack of resistance appears in a still more marked manner in the case of apparatus made of such stainless steels and comprising welded joints and parts which have been distorted or hammered in a cold or hot state. The zones adjacent the weldings always undergo a deeper attack than the rest of the metal owing to the preheating to which they have been submitted. The danger is considerably increased when a rod different from that which forms the sheet metal to be welded (case of chromium-manganese steel) is used for supplying metal for the welding.

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The foregoing results in that for many applications, the chemical industry has no other means than to resort to ceramic materials, glass, wood, lead and other like materials. Unfortunately said materials off a quite insufficient mechanical strength and a high difficulty of application.

The present invention provides for a method to increase in a very large measure the resistance of stainless steels with respect to a certain number of acids, particularly sulfuric acid, and which makes it possible to obtain with such steels vats or other apparatus showing a perfect resistance to sulfuric acid in all concentrations and at temperatures as high as in the neighborhood of 100° C. and a considerably increased resistance to nitric acid, phosphoric acid, organic acids and other corrosive mediums such as sea water, Javel water, etc.

Said method fundamentally consists in the whole of the following measures applied simultaneously or successively:

(*a*) The steel surfaces which are later to come into contact with the corrosive medium are submitted to a uniform attack by an acid, attack limited to a small loss of weight, of the order of 150 grams per square meter for instance;

(*b*) The same surfaces are submitted, simultaneously with the above mentioned corrosion treatment or after said treatment, to a passivation treatment capable of conferring to a metal an electro-positive potential with respect to the calomel electrode such as, for instance, attack by moist air, by means of an acid or, preferably, by an electrolytic anodic treatment.

The combined treatment according to the invention may be applied either to separate elements such as, for instance, sheet metal, intended to be used for the manufacture of vats or other apparatus or to already finished devices.

In case the constituent parts of an apparatus are treated before the assembly of the latter, it is necessary, after the assembly, to pickle the weldings which may have been effected.

Only the combination of the above mentioned means makes it possible to obtain for the treated apparatus a stability with respect to corrosive mediums which was never obtained hitherto. In fact, if the surfaces under consideration are submitted to one or said treatments only, no appreciable result is obtained.

The corrosive attack and the passivation of the elements before their assembly may be applied in some simple cases of welded apparatus having a small number of weldings and the parts of which are not submitted to severe deformation in a cold state. The necessary pickling of the weldings is advantageously realized by means of a mixture having, for example, the following composition:

Sodium fluoride: 0.4 to 2% by weight
Nitric acid of 36° Bé.: 10% by volume

Said mixture may be used cold or hot. It acts much more rapidly when heated. The pickling may be realized very simply by cleaning the welded parts with a cloth impregnated with the mixture by passing said cloth repeatedly over said parts and then allowing to dry during 24 hours in a moist atmosphere. It is to be noted that this mixture constitutes, generally speaking, an excellent pickling reactive for stainless steel coming out of thermic treatment.

In most cases, however, it is necessary to effect the corrosion and the passivation on the finished apparatus; in such a case it is not necessary to proceed with a particular pickling of the weldings, said pickling being effected automatically in the course of both the above mentioned operations.

As explained above, the corrosion and the passivation may be effected simultaneously or successively.

If said operations take place successively the corrosion treatment must be effected preferably by means of a reducing acid such as a diluted sulphuric or hydrochloric solution. The duration of the attack is controlled so as to lead to a loss of weight of the steel of about 150 grams per square meter, for instance. It generally varies, according to the nature of the steel and of the acid which are used, between ten minutes and one hour in the cold. The attack may be effected with a loss of weight which is less than that which has just been indicated if the metal has already been submitted to an attack either in the course of a prior operation before the manufacture of the apparatus or, in the case of sheet metal, in the course of its pickling process at the end of its manufacture. The effect of this corrosion must not, however, have been destroyed by a later preheating or cold rolling.

The passivation treatment consecutive to this first treatment may be effected, for instance, through action, on the surfaces to be treated, of an oxidizing non-corrosive bath such as a 10% solution of nitric acid, the treatment being extended from one to 48 hours until a markedly electro-positive and preferably high potential with respect to the calomel electrode is obtained for the treated metal.

The treatment of apparatus encounters no difficulties when they are of relatively small dimensions. In this case, the said apparatus may be totally immersed in the passivation liquid, passivation thus being ensured both inside and outside.

If the dimensions of the apparatus to be treated are too great for the latter to be entirely filled up with acid, the treatment may be effected by separate immersion or filling up of various parts capable of being assembled later on by bolting, welding or any other method. But it is then absolutely necessary to provide for a passivating pickling of the joining regions of the said various parts (weldings) as well as of the parts the passivity of which may have been destroyed during

the assembly, for instance through thermic treatment, hammering, etc.

As regards resistance to sulfuric acid, the best passivation method consists in filling the vessel with sulphuric acid the concentration of which is substantially equal to that of the acid which is intended to be contained therein and in applying to said vessel during said filling operation a D. C. voltage of 1.5 to 2 volts, whereby the inner part of the vessel serves as positive pole and receives an intensity of the order of 5 amp. per square meter. This is obtained in practice by connecting the body of the vessel itself to the positive pole of the source of current and by arranging inside said vessel an 18/8 molybdenum steel cathode having its lower end located only a few millimetres short from the bottom in order that in the beginning of the filling the corrosion has no time to start in the lower part of the vessel. The current is interrupted a few moments after the filling is ended.

In case the corrosion and passivation are realised simultaneously in order to obtain a good resistance towards sulfuric acid, a first method consists in using both the passivating and corrosive action of certain mixtures such as the above mentioned mixture of sodium fluoride and nitric acid. The use of this mixture is rather delicate; due to the fact that it is no longer passivating when its content in iron and chromium salts exceeds a certain value, which requires its frequent renewal. On the other hand, certain steel grades such as the 18/8 molybdenum steel require its use in a heated state (60° C.). In this case the corrosion is comparatively small, of the order of 50 grams per square meter on previously sand blasted surfaces. For passivation, aqua regia is to be proscribed in an absolute manner.

It is also possible, and this is the most efficacious and most reliable method, to use the above mentioned electric treatment but while extending it after the filling so as to determine a loss of weight of the order of 50 to 250 grams per square meter.

For example, the apparatus is filled in the above mentioned manner but while raising the intensity of the current to a higher value up to 100 amp. per square meter in case of previously sand blasted surfaces showing, owing to this fact, a maximum aptitude to corrosion. The action of the current is extended with the same intensity during about fifteen minutes after the end of the filling; then it is reduced to a much smaller value, of the order of 3 amp. per square meter, and maintained at this value during two to four days. It is also possible to render the treatment much more rapid by maintaining the current at the initial filling intensity but the consumption of current and the loss of metal are much higher.

In all the above described treatments the initial physical condition of the metal is of minor importance if said treatments are effected on the finished apparatus; however, the chemical treatment with a fluoride bath as well as the electric treatment—after corrosion or simultaneously with the corrosion—are facilitated when the metal which constitutes the apparatus has already been submitted to a corrosion, even if the latter has been followed by a deformation such as, for instance, a cold rolling; the chemical treatment may then be shorter and the current in the electric treatment can be reduced and maintained during less time.

On the contrary, if it is desired to avoid treatment of the finished apparatus, the sheet metal

used in its construction must have already been rendered passive to acid and said passivity must not have been destroyed during the rolling or conformation operations. Anyhow, the treatment of the finished apparatus which, by the way, is always to be recommended, cannot be avoided when the apparatus is to resist hot acid or when the sheet metal is to be submitted to conformations in a heated state or to severe conformations in a cold state or furthermore when the weldings cannot be pickled.

On the other hand, the various treatments indicated above as well for the case of the successive corrosion and passivation as for the case when both said operations are effected simultaneously have not all the same efficaciousness according to the nature of the steel constituting the walls of the apparatus and according to the concentration and the temperature of the sulphuric acid which is to come into contact with the treated surfaces.

Thus, for instance, with a steel containing 15% chromium, without nickel, a satisfactory resistance of the apparatus can be obtained only towards cold solutions of sulphuric acid and on condition that the passivating treatment is effected electrically.

On the contrary, stainless steels with 18% chromium and 8% nickel, having been submitted to one of the above mentioned chemical treatments, satisfactorily resist sulphuric acid solutions of any concentration at temperatures under 50° C.. In order to be able to resist higher temperatures the apparatus made of such steels must necessarily be submitted to an electric passivating treatment.

A chemically or electrically treated stainless chromium manganese steel containing, for example, 18% chromium, 10% manganese, 2% nickel and 0.5% titanium resists up to about 100° C. the acid concentration which is the most corrosive for this steel: 19° Bé. Under the same conditions the 18/8 molybdenum steel resists acid showing a concentration of 40° Bé. which is the most corrosive for it.

It does not seem to be possible whatever may be the treatment employed and the steel which is used, to obtain a stable passivity of stainless steels to concentrated or fairly diluted sulphuric acid at boiling temperature. However, the application of a very weak permanent anodic current of the order of 3 amp. per square meter makes it possible to maintain in a passive condition the surfaces in contact with the acid so long as the current passes while limiting the corrosion to a small value.

If, instead of essentially endeavoring to obtain the resistance to sulphuric acid it is desired to obtain a considerably better resistance to other corrosive mediums such as nitric acid, phosphoric acid, organic acids, more particularly acetic acid and oxalic acid, sea water, Javel water and the like, the corrosion operation is preferably realized by means of a uniform attack by a corrosive solution such as a reducing acid (diluted hydrochloric or sulphuric acid or their mixtures) or of mixtures of reducing and of oxidizing substances (solutions of hydrochloric and nitric acids, hydrofluoric and nitric acids or sodium fluoride and nitric acid). The passivation is then operated by means of an oxidizing non-corrosive liquid such as nitric acid.

The best results have been obtained by adopting for the corrosion treatment either a mixture of hydrofluoric and nitric acids or the above mentioned mixture of sodium fluoride and nitric acid, used between 30 and 80° C.

The duration of the treatment depends upon the temperature and the surface conditions of the metal. For usual surfaces (commercial surfaces which are pickled, brightened or not, rolled in a cold state) the attack may last 3 to 24 hours at the temperature of 30° C. and 30 minutes to two hours at the temperature of 60° C.

The nitric passivation treatment consecutive to the corrosion treatment is realized with a 10% solution of nitric acid. The operation requires two to three days if the operation is realized at 30° C. and one week if realized at 10° C. A stainless steel device which has been so treated offers a bright silver white surface of very characteristic aspect.

Results which are still appreciable though less satisfactory than those which are obtained with two consecutive operations can also be obtained, as regards resistance to various corrosive liquids, by means of a single operation combining the corrosion and passivation, for instance by means of mixture of sodium-fluoride-nitric acid.

The following are examples of some forms of execution of the invention:

Example I.—Cylindrical vat of stainless steel with 18% chromium, 8% nickel intended for containing cold sulphuric acid of 40° Bé.; the body of the vat is welded along a generatrix; the bottom is formed of a disc the edges of which are hammered back at a right angle and which is welded onto the cylindrical body a few centimetres above the lower part of the vat. The sheet metal used for the constitution of the apparatus was commercial sheet metal having been submitted to a pickling operation at the end of the manufacture. It was attackable by sulphuric acid of 40° Bé.

The corrosive attack treatment was effected chemically on the finished apparatus. To this end, the vat was filled up to the edge with cold sulphuric acid of 40° Bé.; the attack was allowed to go on during one hour whereafter the vat was emptied and the apparatus left in a moist place during several days.

At the end of this time the inside of the vat had become perfectly resisting to cold sulphuric acid of 40° Bé., which is the most corrosive concentration.

Example II.—Pickling vat made of steel with 18% of chromium, 10% of manganese, 2% of nickel and 0.5% of titanium, intended for containing hot sulphuric solutions of 20° Bé. Measuring 1 m. x 2 m. and 1 m. height; containing a coil of wound and welded pipe of the same metal as the vat helically wound in a heated state and secured to the vat by rolled up supports. The sheet metal used for the construction of the apparatus and the coil was commercial sheet metal which had been submitted to a pickling operation at the end of the manufacture.

The finished apparatus was submitted to the electric passivating treatment. To this end, a vertical sheet metal band measuring about 20 x 100 cm. extending down to a few millimetres from the bottom was arranged inside the vat. A potential difference of 1.5 to 2 volts was established between the vat and the sheet metal by means of a source of electric energy capable of yielding 3 amp. during three days. The vat was then filled with sulphuric acid of 20° Bè. while causing a current of 3 amp. to pass and said current was maintained during three days.

The vat was then emptied. After said treat-

ment, it was able to contain sulphuric solutions up to temperatures nearing 100° C. without any attack of its walls.

Example III.—Cylindrical vat similar to that of Example I but made of nickel-chromium-molybdenum steel intended for containing cold commercial sulphuric acid. The apparatus being comparatively simple and the corrosion resistance requirements less high it was possible to form the vat of assembled commercial sheet metal of nickel-chromium-molybdenum steel previously passivated by a chemical treatment, thus avoiding a treatment of the finished apparatus. The inner weldings were merely pickled by means of a cloth impregnated with the above mentioned fluonitric mixture once the apparatus was finished. The vat was then rinsed and it was found able to resist the attack of cold commercial sulfuric acid.

A similar result could have been obtained by pickling the weldings with a cloth impregnated with aqua regia.

What I claim is:

1. The method for increasing the resistance to corrosion of stainless steel, which comprises treating at least the part of said stainless steel which is to be contacted with the corroding medium by the following steps: (1) an attack treatment with a solution of sodium fluoride and nitric acid until there is a loss of weight amounting to about 150 grams per square meter, (2) a non-corrosive passivation treatment with solution of nitric acid until said part has a high electro-positive potential with respect to a calomel electrode.

2. The method for increasing the resistance to corrosion of stainless steel, which comprises treating at least the part of said stainless steel which is to be contacted with the corroding medium by the following steps: (1) an attack treatment with a solution of sodium fluoride and nitric acid until there is a loss of weight amounting to about 150 grams per square meter, (2) a non-corrosive passivation treatment with an approximately 10% solution of nitric acid at 30° C., for at least 48 hours and until said part has a high electro-positive potential with respect to a calomel electrode.

3. The method for increasing the resistance to corrosion of stainless steel apparatus, which comprises treating stainless steel sheets by the following steps: (1) an attack treatment with a solution of sodium fluoride and nitric acid until there is a loss of weight amounting to about 150 grams per square meter, (2) a non-corrosive passivation treatment with a solution of nitric acid until said part has a high electro-positive potential with respect to a calomel electrode, fabricating the sheets into an apparatus by welding such as to destroy at least partially the effects of the passivation treatment, thereafter pickling the welds there produced with a solution of sodium fluoride and nitric acid, and allowing said parts to dry during at least twenty-four hours in a moist atmosphere.

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