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CORROSION PROTECTION OF KANSITE COATED STEEL ARTICLES

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The present invention relates to the protection of materials subject to the action of a corrosive medium and is more particularly concerned with the protection of steel and other ferrous metals which are exposed, under the conditions of service, to the action of a corrosive medium containing acidic gases, particularly hydrogen sulphide.

It has been proposed to protect installations for the treatment of petroleum products, which are formed of steel or other ferrous metals, against the infiltration of hydrogen which can lead, if there is a sufficient accumulation of hydrogen, to the formation of pustules and fissures in the installations, by the application of an aqueous solution of an alkali metal or ammonium polysulphide under specified conditions of concentration and pH. However this process only enables protection of very short duration to be obtained so that application of the inhibiting agent must be carried out continuously. In addition, this process is ineffective in providing protection against corrosion.

It is known that in a number of cases, corrosion of a metal leads to the formation of a crystallized or semi-crystallized layer of a corrosion product which is permeable to the corrosive medium so that corrosion can continue indefinitely.

In particular we have found that the natural gas of Lacq which contains about 15% of hydrogen sulphide and 9% of carbon dioxide, causes the formation in transport conduits formed of ordinary or alloy steel, of a corrosion product consisting of a homogeneous iron sulphide composed principally of kansite (Fe_9S_8) which crystallizes in the quadratic system and is permeable to the corrosive gas so that the corrosion of such conduits can continue indefinitely.

We have found that the presence of pyrite (FES_2), as well as that of pyrrhotine (Fe_7S_8) has a protective action on steel in the absence of kansite. Steel or other ferrous metals can, therefore, be protected from the action of a corrosive medium containing, in particular, hydrogen sulphide as the corrosive agent, by converting the kansite which is formed and which is permeable on an atomic scale to the corrosive medium, into pyrite or pyrrhotine which are impermeable to the medium. Such a conversion of a corrosion layer permeable to the corrosive medium into a protective layer impermeable to this same medium can also be effected in other cases of corrosion.

The present invention broadly comprises, therefore, a process for the protection of materials subject to the action of a corrosive medium which forms with said materials a corrosion product in the form of crystallized or semi-crystallized layer which is permeable to the corrosive medium, in which the corrosion product is converted into a crystallized or semi-crystallized protective layer which is impermeable to the corrosive medium.

In a particular embodiment of the process according to the invention, the conversion is effected by saturation or supersaturation of the crystal lattice of the corrosion product with one of the elements present in the composition of the said corrosion product.

By means of this process, a layer which protects the material against the corrosive medium is obtained in the same manner as a skin of iron oxide or of aluminium oxide protects iron or aluminium respectively against the corrosive action of an oxidizing medium.

In order to carry out the process according to the invention, saturation or supersaturation of the permeable crystal lattice of the corroded layer which forms after a certain service time, is effected with a product in the atomic state, for example, a vaporized product; the free atoms of the vaporized product then occupy the places left free in the permeable crystal lattice in order to convert it into a compact impermeable lattice having the desired protective effect.

Alternatively the process according to the invention can be carried out so as to prevent corrosion taking place. To this end, the new material to be protected is contacted with the corrosive medium under conditions of accelerated corrosion so that the whole of the surface of the material to be protected is corroded and the permeable corroded layer which has been formed is then subjected to the action of a vapour or gas which effects atomic saturation or supersaturation of the corroded layer.

In another method of carrying out the process according to the invention, the conversion of the crystallized or semi-crystallized layer permeable to the corrosive medium into a crystallized or semi-crystallized protective layer impermeable to the medium is effected by a thermal treatment of the corroded material in an inert atmosphere.

According to a variant of this latter procedure, a corrosion layer is first formed on new material to be protected by placing this material in contact with the corrosive medium under conditions of accelerated corrosion and the corroded layer permeable to the corrosive medium which is formed is then subjected to a thermal treatment in an inert atmosphere in order to convert it into a layer impermeable to the corrosive medium.

The present invention also comprises the protected materials produced by the present process.

In the particular case of the protection of ordinary or alloyed steels corroded by hydrogen sulphide or a medium containing it, such as the natural gas of Lacq, the process according to the invention consists of converting the initial layer of iron sulphide (kansite) having a crystal lattice permeable to the corrosive medium into another type of iron sulphide having a crystal lattice impermeable to the same corrosive medium and consisting, for example, of pyrrhotine or pyrite or of a combination of these impermeable sulphides.

According to a first specific method of carrying out the latter process, applicable to the treatment of corroded materials at a relatively low temperature, the corroded layer consisting essentially of kansite is converted into pyrrhotine with iron carbonyl in the vapour state.

Iron pentacarbonyl ($Fe(CO)_5$) can, in particular, be used. In this case it is preferred to operate in an inert atmosphere at a temperature above 130° C., and advantageously equal to or greater than about 260° C. The liquid carbonyl is vaporized so as to liberate atomic iron in contact with the corroded layer. In one suitable method of doing this, a heated container containing the liquid iron carbonyl is placed in the article to be protected, consisting for example of a steel conduit, the iron carbonyl is vaporized and the vapour comes into contact with the surfaces to be protected liberating iron in the atomic state. It will be understood that instead of operating at atmospheric pressure, the process may be carried out under superatmospheric pressure at the corresponding vaporization temperature of the iron carbonyl.

Equally, according to a variant of this procedure, vaporization can be carried out under vacuum; for example the article to be protected is maintained under reduced pressure, for example under a pressure of 10^{-2} to 10^{-3}, and liquid iron carbonyl is injected at a temperature equal to or near room temperature, which is substantially greater than the boiling temperature of iron carbonyl at the pressures mentioned.

The quantity of liquid employed is such as to obtain a small deposit of free iron in excess on the surface to be protected.

For these procedures iron carbonyl alone (i.e., pure) or in solution with an additive such as for example acetone, ethyl acetate or carbon tetrachloride, can be employed.

According to a second specific method of carrying out the above process, the corroded layer consisting essentially of kansite is converted into pyrrhotine by heating the corroded layer to a temperature higher than 130° C., preferably equal to or greater than about 220° C., in an inert atmosphere; advantageously a temperature of 250° C. is maintained for from 15 to 30 minutes.

According to a third specific method of carrying out the above process, the corroded layer consisting essentially of kansite is converted into pyrrhotine or pyrite with vaporized sulphur; the treatment is preferably carried out in an inert atmosphere at a temperature higher than 150 °C., advantageously equal to or greater than 320° C. in the presence of a deficiency of sulphur, or equal to or greater than 200° C. in the presence of an excess of sulphur.

According to a fourth specific method of carrying out the above process, the corroded layer consisting essentially of kansite is converted into pyrite with sulphur formed in situ in the vapour state; for this purpose a vaporized catalyst which favours the formation of sulphur from the hydrogen sulphide contained in the corrosive medium is projected on the level of the corroded layer. An example of such a catalyst is nickel carbonyl.

In order to protect new materials, a corrosion layer consisting essentially of kansite is first formed on said materials, for example by contacting said materials with hydrogen sulphide or with a corrosive medium containing it, and the corrosion layer is then converted into pyrrhotine or pyrite by one of the above-described procedures.

The conversion of kansite into pyrite or into pyrrhotine is profound, stable and irreversible so that the protection obtained is practically permanent.

In order that the invention may be more fully understood, the following examples are given by way of illustration only:

Example 1

In a first series of experiments, the action of iron and of sulphur in the atomic state on kansite was studied, in the absence of air and at temperatures of from 20° to 340° C.

For this purpose, samples of pure kansite were placed in tubes of Lindermann glass together with iron pentacarbonyl or sulphur, the tubes were sealed at both ends and heated in a furnace. For each temperature studied, the samples were allowed to remain in the furnace for at least 24 hours. They were then cooled and submitted to X-ray examination by the Debye-Scherrer powder diffraction diagram method in order to follow the conversions of the kansite.

In a first experiment in which kansite was treated with vaporized iron carbonyl in the absence of air, the following results were observed:

Kansite existed up to a temperature of 260° C. Its conversion into an intermediate sulphide took place in the range 30 to 200° C. and the formation of pyrrhotine commenced above 130° C. Above 260° C., all the kansite was converted into pyrrhotine. This experiment shows that there is conversion of kansite into pyrrhotine

in an inert medium in the presence of atomic iron above 130° C. and that this conversion is complete above 260° C.

In a second experiment in which kansite was treated with a small quantity of vaporized sulphur in the absence of air, the following results were observed.

Kansite existed up to 160° C. The formation of an intermediate sulphide took place in the range 20° to 320° C. The formation of pyrrhotine commenced above 190° C. Above 320° C. all the kansite was converted into pyrrhotine.

In a third experiment in which kansite was treated with an excess of vaporized sulphur in the absence of air, the following results were obtained:

Kansite existed up to 140° C. The formation of an intermediate sulphide took place in the range 20° to 200° C. Formation of pyrite commenced above 150° C. Above 200° C. all the kansite was converted into pyrite. These two latter experiments show that there is conversion of the kansite, on the one hand, into pyrrhotine in an inert medium and in the presence of a deficiency of atomic sulphur at temperatures above 190° C. and that this conversion is complete at 320° C. and, on the other hand, into pyrite in an inert medium and in the presence of an excess of atomic sulphur at temperatures above 150° C. and that this conversion is complete at 200° C.

In a second series of experiments, the action of iron or of sulphur in the atomic state in the presence of dry air and at temperatures from 20° C. to 340° C., was studied in the same way as previously.

Study of the powder diffraction diagrams of the samples enables the conversions of the kansite to be followed.

In a fourth experiment in which kansite was treated with vaporized iron carbonyl in the presence of dry air, the following results were observed:

Kansite existed up to 240° C.; the formation of an intermediate sulphide took place between 30° and 270° C.; the formation of pyrrhotine commenced above 130° C. and of pyrite above 230° C.; the formation of iron oxides Fe_3O_4 and Fe_2O_3 was observed above 190° C. This experiment shows that there is conversion of kansite into pyrrohotine in the presence of atomic iron and dry air above 120° C., and into a mixture of pyrrhotine and pyrite above 230° C., but oxides of iron are also formed.

In a fifth experiment in which kansite was treated with an excess of vaporized sulphur in the presence of dry air, the following results were observed:

Kansite exists up to 160° C.; the formation of an intermediate sulphide took place between 20° and 270° C.; the formation of pyrite commenced above 170° C. Above 270° C. all the kansite was converted into pyrite.

This experiment shows that kansite is converted into pyrite in the presence of an excess of atomic sulphur, in dry air, above 170° C. and that the conversation is complete at 270° C.

The results of these two series of experiments show that iron or sulphur in the atomic state effectively bring about the conversion of kansite into pyrrhotine or into pyrite.

Example 2

In this example, the conversions of kansite under the action of heating in the absence of air and in the presence of dry air respectively were studied.

In a first experiment, kansite was heated in a sealed tube in the manner described in Example 1, but in the absence of iron and of sulphur. The following results were observed by the powder method:

Kansite existed up to 210° C.; an intermediate sulphide was formed between 30 and 190° C.; pyrrhotine was formed above 130° C. Above 210° C., all the kansite was converted into pyrrhotine.

In a second experiment, the preceding experiment was repeated but heating was carried out in the presence of dry air. The following results were observed:

Kansite existed up to 140° C.; an intermediate sulphide

was formed between 30 and 210° C.; pyrrhotine was formed between 130 and 190° C. and pyrite above 160° C. Iron oxide Fe_2O_3 was also formed above 190° C.

These experiments show that in the absence of air, kansite is converted into pyrrhotine above 130° C. and that this conversion is complete above 210° C. In the presence of air, kansite is completely converted into pyrite at 210° C. but the pyrite is mixed with iron oxide Fe_2O_3.

Example 3

Two series of steel test pieces were immersed in a corrosive medium consisting of the acidic natural gas of Lacq. Examination of the X-ray diffraction spectra of the corrosion products formed on these test pieces showed the presence of very badly crystallized kansite which was permeable to the corrosive medium.

The first series of test pieces was then subjected to a treatment, according to the process of the invention, in which the corroded layer was saturated with iron or sulphur in the atomic state. For this purpose, a first group of test pieces of this series were exposed to the action of vaporized iron carbonyl, a second group of test pieces to the action of vaporized sulphur, and a third group of test pieces to the action of vaporized nickel carbonyl in the presence of hydrogen sulphide.

Examination of the X-ray diffraction spectra of the corrosion products on the test pieces thus treated showed the presence of the characteristic spectrum lines of pyrrhotine for the first group of test pieces, and the presence of the characteristic spectrum lines of pyrite for the second and third groups of test pieces; the characteristic spectrum lines of kansite were of very low optical density or invisible.

By way of comparison, the second series of test pieces were treated by immersion for 15 minutes in a solution of colloidal sulphur inhibitor.

Examination of the X-ray diffraction spectra of the treated test pieces showed the presence of very badly crystallized kansite and of sulphur. No conversion of the corrosion layer was observed after the treatment.

This example shows that the saturation or supersaturation of the crystal lattice of kansite in order to convert the latter into pyrite or into pyrrhotine can only be effected by means of elements in the state of free atoms, preferably provided by the vapour of products which contain them, and that kansite cannot be converted in pyrite by means of colloidal sulphur in the form of a solution.

What we claim is:

1. A process for the protection of steels and other ferrous metals which are exposed to the action of a hydrogen sulphide-containing corrosive medium so as to form a layer permeable to said medium consisting essentially of crystalline kansite thereon by converting the permeable kansite corrosion layer into a crystalline impermeable protective layer consisting essentially of at least one member selected from the group consisting of pyrrhotine and pyrite which comprises the step of heating said layer of kansite to a temperature above 130° C. in an an hydrous atmosphere so as to form said impermeable layer.

2. A process according to claim 1, in which heating is effected to a temperature of at least 220° C.

3. A process according to claim 1, in which heating is effected at 250° C. for from 15 to 30 minutes.

4. A process according to claim 1, in which the conversion of the permeable corrosion layer into an impermeable protective layer is effected by saturation of the crystal lattice of the corrosion layer with iron in the atomic state by heating said kansite layer at said temperature and simultaneously supplying thereto vaporized iron.

5. A process according to claim 4, in which iron in the atomic state is provided by vaporization of iron carbonyl.

6. A process according to claim 5, in which the conversion is carried out at a temperature of at least 260° C.

7. A process according to claim 5, in which the conversion is carried out at less than atmospheric pressure and at room temperature.

8. A process according to claim 1, in which the conversion of the permeable corrosion layer into an impermeable protective layer is effected by saturation of the crystal lattice of the corrosion layer with sulphur in the atomic state by heating said kansite layer at said temperature and simultaneously supplying thereto vaporized sulphur.

9. A process according to claim 8, in which sulphur in the atomic state is provided by vaporization of sulphur.

10. A process according to claim 8, in which the conversion is carried out in an anhydrous atmosphere using an amount of sulphur insufficient to convert said kansite layer into pyrite and at a temperature greater than 150° C.

11. A process according to claim 10, in which the conversion is carried out at a temperature of at least 320° C.

12. A process according to claim 8, in which the conversion is carried out in an anhydrous atmosphere using an amount of sulphur at least sufficient to convert said kansite layer into pyrite and at a temperature greater than 150° C.

13. A process according to claim 12, in which the conversion is carried out at a temperature of at least 200° C.

14. A process according to claim 1 wherein said atmosphere is selected from the group consisting of vaporized sulphur, vaporized iron, dry air, and mixtures thereof.

15. The process according to claim 14 wherein the vaporized sulphur is produced from an atmosphere of vaporized hydrogen sulphide in the presence of a vaporized catalyst which will liberate sulphur from said hydrogen sulphide gas.

16. A process according to claim 15, in which the catalyst is nickel carbonyl.

17. An article of a ferrous alloy having a corrosion protecting, crystalline and impermeable layer of pyrrhotine provided thereon.

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