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TREATMENT OF FERROUS METAL SURFACES TO PREVENT CORROSION

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ABSTRACT OF THE DISCLOSURE

Ferrous metal is corrosion-proofed with a solution obtained by treating chromite ore or other oxide with gallic acid. Other chelating agents may replace the gallic acid. The solutions can also be used for the deposition of oxides on inexpensive mineral material to form attrition-resistant supported catalysts.

This invention relates to corrosion proofing and to the production of supported catalysts.

In accordance with one aspect of this invention I have found that ferrous metal may be made resistant to corrosion in the atmosphere and resistant to attack by aqueous dilute sulfuric acid (which is ordinarily quite corrosive to iron and steel) by treating the surface of the metal with a solution which can be obtained by a simple, economical method from readily available inexpensive impure ores.

One preferred solution for use in this invention is obtained by the treatment of inexpensive chromite (which is rich in chromium oxide) with aqueous gallic acid (a phenolic carboxylic acid). The gallic acid reacts with the ore to form a bluish solution which is, in the most preferred embodiment, then purified with an adsorbent material.

The treatment of the ferrous metal with the corrosion-proofing solution can be effected very simply and easily. Thus, contact between the metal surface and the solution, at room temperature, for a very short time (e.g., a few seconds), gives excellent results even though the treated surface (after the treating solution has been washed off with water) appears to the naked eye to be unchanged. The metal is preferably thoroughly cleaned before contacting it with the treating solution. One cleaning method involves treating the metal by the usual hot vapor-degreasing methods (e.g. with a chlorinated solvent) and then immersing it for several minutes in a cool aqueous solution containing about 2–3% ammonium carbonate and ½% sodium sulfate. However, many other methods for thoroughly cleaning the metal surface are common and will occur to those skilled in the art.

In making up the corrosion-proofing solution it is not necessary to employ concentrated gallic acid. Highly dilute gallic acid (e.g. having a concentration of 5 grams per liter) has been employed with excellent results.

I have also found that other heavy metal oxides can be used in place of the chromium oxide. Thus substitution of magnetite for the chromite ore has given outstanding corrosion resistance. Other suitable oxides for this purpose are hematite and copper oxide, molybdenite and cobaltite.

In a less preferred embodiment I have found that other chelating agents (including those which, like the gallic acid, have a carboxyl group) may be used in place of the gallic acid to impart corrosion resistance to the ferrous metal. Examples are succinic acid, succinamide, aspartic acid, salicylic acid, glycine, ethylene diamine, tetraacetic acid, malic acid and citric acid. While I do not wish to be bound by any theory, these results, taken with the results of analyses of the solutions formed by the use of gallic acid, lead me to believe that my treating solution

may contain dispersed chelated heavy metal which may be deposited, in very small amounts, onto the surface of the ferrous metal article during the corrosion-proofing treatment.

I believe that the treated metal surfaces may take on the chemical properties of the metal oxide from which the treating solution was made and react similarly.

An indicated above, the treated metal is resistant to dilute sulfuric acid. It is also resistant to other acids, such as hydrochloric.

Another aspect of this invention relates to the use of the solutions described above. Instead of applying them to ferrous metal for corrosion proofing purposes, one may apply them to various substrates to produce supported catalysts containing heavy metal oxides useful for catalyzing various chemical reactions. As the substrate, one may use inexpensive raw or partly processed minerals, including oxides and silicates. The treating solution in this case may be dilute or, when a heavier deposit of the metal oxide is desired, the solution may be more concentrated and viscous. The substrate, or support, need not be a mineral oxide, silicate or other compound; it may be, for example, ordinary steel wool. The oxide-coated substrate is attrition resistant. In a preferred treatment to produce a supported catalyst, the treating solution is one which has not been purified with an adsorbent material. Such solutions yield heavier deposits of the oxide on the support.

I have found that the waste rock obtained in the milling of chrysotile asbestos is extremely suitable as a substrate as it is not only resistant to attrition and to temperatures considerably above those usually used in catalysis but is also relatively porous. This material is basic and carries a positive electrical charge, and is receptive to electronegative materials. I have found also that chrysotile asbestos fiber may be similarly used as a substrate serving as a useful carrier of the oxide material. I may even employ as the substrate an ordinary granite or other rock, particularly if it is pretreated to increase its receptivity for the coating as by wetting it with an aqueous solution of gallic acid (e.g. by immersing it for a short time in a dilute solution, such as 5% solution at room temperature, and then drying, as by simple air drying).

One use for the supported catalysts of this invention is as a replacement for the large quantities of "iron sponge" used in the removal of sulfides of coke oven gas; the "iron sponge" is, as is generally known, heavy and relatively costly. By my method all that is required is to treat the chrysotile waste rock in the treating solution made from an iron oxide, as described herein, air-dry the treated rock and subject it to a stream of carbon monoxide at a temperature suitable for the purpose of reducing the deposited iron oxide to the metalic state. While catalytic iron sponge is usually produced only in relatively small particles, by my method any size is attainable.

Another use for my supported catalysts is in the desulfurization of oil where large quantities of cupric oxide are now used. In this case one can employ chrysotile rock, or other substrate, which has been treated with the solution made from copper oxide.

Still another use for my low cost supported catalysts is in the treatment and control of air pollution. Here one can employ a supported catalyst comprising one or more of the oxides on attrition resistant substrates of light weight, such as asbestos rock, asbestos fiber and even steel wool or other steel fiber such as woven fibers.

I have found, too, that frequently it is desirable to have the catalytic material in spherical or other special configuration of various or varying sizes. This may be readily obtained by substituting for the sized chrysotile rock unsifted crrysotile fiber which contains also ground rock. By using a relatively concentrated treating solution (and

omitting the previously mentioned treatment of the solution with charcoal or other adsorbent material), the adhesive properties of gallic acid solution are thus brought into play; and when the treating solution is mixed with the short-fiber chrysotile a putty-like substance is formed, which may be shaped into spheres by methods known to those skilled in the art. When these spheres are formed the oxide material of the treating solution appears to become concentrated at their surfaces, yielding an oxide-coated sphere.

Any of the heavy metal oxides commonly used as catalysts may be treated with gallic acid and form the base materials. It is possible to mix the solutions to obtain a variety of desired results. One may start with a crude ore containing the oxide and remove impurities such as silicates, sulfates, etc. so as to form a relatively pure oxide, then treat the oxide with the gallic acid to form the solution to be applied to the substrate. Should the treated substrates require heat activation, they can, because of their resistance to heat, be so treated. The treating solution may be applied to the substrate very simply, as by immersing the substrate in the solution, which may be at room temperature, for a short time, e.g. 10–20 minutes. If desired the substrate may be vacuum-treated, to remove air from its pores, before applying the solution, according to well known techniques.

In the following examples, all temperatures are room temperatures and all pressures are atmospheric unless otherwise indicated.

EXAMPLE 1

In this example, there is used a powdered chromite ore, of a fineness to pass a 325 mesh screen (U.S. Standard), having the following analysis:

	Percent
Cr_2O_3	44.04
MgO	9.74
FeO	25.10
$Al_2O_3 \pm TiO_2$	14.91
SiO_2	4.03

5 grams of gallic acid (technical grade) is added to 1 liter of water which is brought to a boil to substantially complete the dissolution of the gallic acid, and then filtered to remove insoluble impurities.

50 grams of the powdered chromite ore is mixed with a small quantity of the dilute gallic acid solution, sufficient to thoroughly wet the particles, to form a syrupy mixture at room temperature. A color change (like marbleizing) is observed in portions of the syrup. The syrup is then blended with the balance of the dilute gallic acid solution and agitated. The mixture is allowed to stand for a day or more. A brownish powder settled gradually and agglomerates to a hard, rock-like substance. A black, slimy gel-like substance floats to the top and is removed. The remaining liquor, which is bluish black, is then decanted and the mixture is then filtered through bone charcoal, and is separated completely from the charcoal.

The resulting bluish black solution is employed for the corrosion-proofing of SAE 10—10 carbon steel. The surface of the steel is first thoroughly cleaned and is then dipped in the charcoal-treated gallic acid solution; it need remain in the solution for a very short time (e.g. 5 seconds). The treated steel is then washed thoroughly with hot water.

After this treatment with the gallic acid solution, the steel retains its bright clean steel color with no evidence of a surface deposit. No evolution of gas during the treatment is observed, unless the metal surface has not been thoroughly cleaned (e.g. unless the metal carries certain organic contaminants).

The corrosion resistance of the treated steel is tested by immersing it in aqueous sulfuric acid of various concentrations (in the range of 10 to 40%) immersing it in aqueous in 20% HCl, and subjecting it to A.S.T.M. salt spray tests (e.g. at 95° for 10 days). No corrosion is observed.

On continued immersion in dilute sulfuric acid, the surface of the treated metal darkens, eventually becoming almost black. After removal from the dilute sulfuric acid, the metal may be allowed to dry, without rinsing, without evidence of corrosion even on long standing.

The analysis of the chromite ore given above was furnished by the supplier, Foote Mineral Company.

When the steel is kept in the gallic acid for an hour instead of a few seconds, corrosion-resistance is also obtained.

The decanted (untreated) solution used in this example was analyzed in the following manner: (a) by spectrographic analysis it was found to contain iron and chromium; (b) it showed a Tyndall effect indicating the presence of colloidally dispersed particle; (c) on warming with an activated charcoal (bone charcoal) and filtering, a blue-violet solution was obtained; when the charcoal residue of this treatment was heated with HCl and then tested for iron with potassium thiocyanate, a negative test was obtained although the test method is sensitive to concentrations of 10^{-7} M of iron. Portions of said decanted solution were then made distinctly basic with NaOH and NH_4OH, forming a yellow solution (indicative of the presence, in this yellow basic solution, of CrO_4^{-2} ions); (II) made distinctly acidic with HCl, forming an orange solution (indicative of the presence, in this orange acidic solution, of $Cr_2O_7^{-2}$ ions); the orange solution was tested for the presence of iron with dipyridyl and with orthophenanthroline, which, in both cases, gave negative tests although these test methods are sensitive to concentrations of 10^{-6}–10^{-7} M of iron.

EXAMPLE 2

Example 1 is repeated except that no carbon treatment is used, the solution being simply allowed to stand for a week. A black slimy gel-like substance floats to the top; most of this is skimmed off and the solution is then filtered.

Cleaned steel is dipped for a few seconds in the above filtered solution and rinsed with cold water. It is found to be resistant to dilute sulfuric acid.

EXAMPLE 3

Example 1 is repeated except that the mixture of charcoal and gallic acid solution is heated to about 150° F. for about 15 minutes. The steel is allowed to weather in the atmosphere; after such weathering its surface has a green color (probably due to formation of chromic oxide).

EXAMPLE 4

Example 1 is repeated using finely powdered magnetite in place of the chromite. Similar or improved corrosion resistance is obtained.

The magnetite, of technical grade (supplied by Foote Mineral Co.), has the following analysis, according to the supplier.

	Percent
Fe	67.40
SiO_2	4.77
P	0.019
S	Trace

EXAMPLE 5

Example 1 is repeated, except that the charcoal-treated gallic acid solution is diluted with four times its volume of New York City tap water (containing fluoride and chlorine). The diluted solution is highly effective for the corrosion preventive treatment.

EXAMPLE 6

Example 1 is repeated using SAE 10–20 carbon steel in place of the 10—10 steel. Excellent corrosion resistance is obtained.

EXAMPLE 7

The charcoal-treated gallic acid solution of Example 1 is applied to the surface of a piece of commercial chromium treated steel (carrying a thin chromium layer about 2½ mils thick) which is ordinarily not resistant to mineral acids. The product is found to be unaffected by immersion in dilute sulfuric acid.

EXAMPLE 8

A bluish black solution is made as in Example 1, but without the charcoal treatment, and is applied to a chrome-plated plumbing fixture carrying a very thin layer of the chromium plating, which had not been cleaned to remove all grease. The treated surface has a bluish-brown cast which cannot be removed by hard rubbing with scouring powder (containing a chlorine bleach) and steel wool.

EXAMPLE 9

The charcoal-treated solution of Example 1 is allowed to stand for months in a container open to the atmosphere. During the period, it loses about ½ its volume, by evaporation. Water is added to bring the solution to its original volume. The solution is found to retain its properties of imparting corrosion resistance.

EXAMPLE 10

A mass of industrial steel wool carrying the usual cutting oil is treated, by simple immersion therein, with the charcoal-treated solution of Example 1 for about 7–8 minutes. During the first few minutes of the latter treatment the steel retains its original bright color; it then gradually turns dark and by the end of the treatment period is substantially ebony-colored. After the steel is rinsed in water to remove adhering liquid, it retains its black color. In contrast to untreated steel wool, the steel wool does not disintegrate when it is exposed to the weather (including rain) for a week; on such exposure, it turns brown (possibly due to the presence of residues derived from the oil on the original steel wool), but on shaking the mass of steel wool there is no indication of the formation of loose particles.

EXAMPLE 11

Example 1 is repeated except that in place of the chromite there is used.

(a) molybdenite
(b) commercial cupric oxide

In each case, the treated steel is resistant to attack by dilute sulfuric acid.

EXAMPLE 12

Example 10 is repeated except that in place of the chromite ore there is used:

(a) magnetite (as in Example 4) or
(b) commercial cupric oxide

In each case, the treated steel wool substantially retains its black color after the one week exposure to the weather.

EXAMPLE 13

Example 1 is repeated except that in place of the gallic acid there is employed:

(a) succinic acid or
(b) succinamide, or
(c) aspartic acid, or
(d) salicylic acid, or
(e) glycine, or
(f) EDTA (ethylene diamine tetraacetic acid), or
(g) malic acid, or
(h) citric acid

The resulting solutions have a light green cast, and the gel-like substance that forms, and is removed, was much less colored than the black gel described in Example 1. In each case, corrosion resistance is imparted to the metal by treatment with the solution.

The following examples illustrate the production of supported oxide catalysts. The treated steel wool of Examples 10 and 12 may also be used as a catalyst.

EXAMPLE 14

The bluish-black solution made as Example 1, but without charcoal treatment, is concentrated, by evaporation at room temperature, to one-half its former volume, and cleaned chrysotile fibers are then tumbled in a container with this solution. The fibers gradually turn black; after washing and drying the black fibers are found to have increased markedly in weight.

Similar results are obtained when the solution is made in the same way except that in place of the chromite ore there is used a commercial grade of

(b) magnetite (as in Example 5)
(c) cupric oxide (as in Example 12)
(d) cuprous oxide,
(e) molybdenite,
(f) hematite,
(g) cobaltite

EXAMPLE 15

In this example each of various solutions used in Example 14 is employed for the treatment of chrysotile rock. The sample of chrysotile rock used here is grayish Vermont chrysotile rock, a basic crude asbestos material. In each case, particles (e.g. about 1/16–1/14 inch in diameter) of the rock are immersed in the treating solution and eventually turn black, retaining their black color on washing.

EXAMPLE 16

In this example there are used solutions made as in Example 1, from aqueous gallic acid and a metal oxide, but without treating the liquor with charcoal. The oxide used is, in one case, magnetite (as in Example 5) and in another case, commercial cupric oxide. Each solution is concentrated by evaporation of water therefrom at room temperature, to one-fourth its original volume. Uncleaned chrysotile asbestos fibers of short fiber length (e.g. 1/16 inch or shorter) containing non-fibrous particles are mixed with the solution. In each case the solution and the uncleaned fibers are blended in proportion to form a putty-like mixture which is cut up into small pieces and rolled to produce bead-like spheroids about 1/8 to 1/10 inch in diameter and then dried; these harden on standing in air.

Although the present invention has been described with reference to particular embodiments and examples, it will be apparent to those skilled in the art that variations and modifications can be substituted therefor without departing from the principles and true spirit of the invention. The "Absract" given above is for the convenience of technical searchers and is not to be used for interpreting the scope of the invention or claims.

I claim:

1. Process which comprises applying to a ferrous metal surface, to increase the corrosion resistance of said surface, an aqueous liquid, which aqueous liquid is prepared by reacting a heavy metal oxide with aqueous acid to produce, on standing, a liquid phase, a solid residue and a gel-like material that floats on said liquid phase and separating said residue and gel-like material from said liquid phase, said oxide being chromite, magnetite, hematite, copper oxide, molybdenite or cobaltite, and said acid being gallic acid, succinic acid, aspartic acid, salicylic acid, glycine, maleic acid, citric acid or ethylenediamine tetraacetic acid.

2. Corrosion-resistant product of the process of claim 1.

3. Process as in claim 1 in which said oxide is magnetite.

4. Process as in claim 1 in which said acid is gallic acid.

5. Process as in claim 4 in which said oxide is chromite.

6. Process as in claim 5 in which the concentration of

gallic acid in said aqueous gallic acid is 5 grams per liter and said liquid is bluish black, the ferrous metal is carbon steel and the resulting treated steel surface appears to the naked eye to be unchanged.

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