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PICKLING OF METAL

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This invention relates to the cleaning of metal surfaces by acid pickling, more particularly to pickling ferrous metals in dilute sulfuric acid solution.

It is among the objects of this invention to provide a method of pickling and an inhibitor therefor which afford efficient pickling and inhibiting, in the use of which satisfactorily uniform inhibiting action throughout the use of a given bath is attainable by periodic additions of inhibitor to the bath, in which uniformity of inhibiting action from bath to bath is readily obtainable. A particular object is to provide an inhibitor which avoids scum formation, is relatively cheap and is accurately reproducible, is efficient in inhibiting power, and which is not liable to be decomposed by the heat encountered through the methods commonly applied for heating pickling baths.

A further object is to provide a method of preparing an inhibitor embodying the features which characterize the foregoing object.

The present invention is predicated upon our discovery that its stated objects are attained by the use of an inhibitor comprising the sulfonation product of thiocarbanilide (diphenyl thiourea) ($[C_6H_5NH]_2CS$), and a cresol. Most advantageously the cresol is provided by using crude creosote which, as is well known, is composed largely of a mixture of cresols. There may also be used purified creosotes, such as the U. S. P. grade, but in general the best inhibiting effect is attained by using the crude creosote of commerce.

We have found that such a sulfonation product of thiocarbanilide and cresol provides an unusually efficient and desirable pickling inhibitor. For instance, very low concentrations of this inhibitor suffice to afford satisfactory inhibition, and the inhibitor appears to be comparatively stable to the various actions which ordinarily may, and in many instances do, cause deterioration of the inhibitors previously used. Likewise periodic additions of the inhibitor to the bath, as need be, provide a satisfactorily uniform pickling action throughout the life of the bath to which it is added, a feature not always attainable with other inhibitors. The inhibitor does not cause scum, and because it represents a material of rather definite character it is possible to attain uniformity of pickling action from bath to bath, the material being substantially reproducible to that end. Furthermore, the materials from which the inhibitor is made are relatively cheap, and this coupled with the ability to use extremely low concentrations of inhibitor affords low inhibiting cost per ton of steel pickled.

In the preferred practice of the invention the inhibitor comprises the product obtained by sulfonating 2 mols of cresol and 1 mol. of thiocarbanilide, as by exposing them to the action of sulfuric acid of appropriate strength, e. g., 60° to 66° Bé. Where creosote is used it can be assumed, for all practical purposes, to represent cresol in calculating the proportion to be used with reference to a given amount of thiocarbanilide.

The invention provides also a convenient method of preparing the inhibitor in an unusually effective and desirable form. This method comprises adding a portion of the cresol, or creosote, to an excess of concentrated sulfuric acid while controlling the reaction by the rate of cresol addition, stirring, and cooling of the reaction mixture. The thiocarbanilide is then added to the reaction mixture in the form of a paste made from the remainder of the cresol, the same precautions being observed to control the reaction. Usually about half of the cresol suffices to form the thiocarbanilide into a paste of suitable consistency, and ordinarily, therefore, about half of the cresol is first added to the acid as just described.

As a concrete example, from 8 to 10 gallons of crude creosote are added slowly and with constant stirring to 30 gallons of 66° Bé. sulfuric acid contained in a water-jacketed vessel. Sulfonation occurs rapidly with liberation of a considerable quantity of heat. The rate of addition of the creosote and the cooling of the reaction mixture are so controlled that the temperature of the mixture does not exceed about 100° F. If the temperature rises too high the reaction is accompanied by an evolution of sulfur dioxide in large quantities, which is undesirable. In a separate container about 53 pounds of thiocarbanilide are mixed with from 5 to 7 gallons of creosote to make a total of about 15 gallons of a thin paste which is capable of being handled as a liquid. When the sulfonation of the creosote appears to be complete, as indicated by a drop in temperature to, for example, 80° F. or lower, the paste is slowly added to the reaction mixture, again with constant stirring, and the rate of addition and cooling are controlled to hold the temperature at a point not exceeding about 100° F. When all of the paste has been added the preparation of the inhibitor is complete.

This provides the inhibitor in liquid form in which it can be handled readily and measured easily for proper dosing of the bath.

In the practice of the invention the inhibitor is added to a solution of a strong mineral acid of appropriate strength. Sulfuric acid is normally used for pickling ferrous metals. Low concentrations of the inhibitors suffice, and our work has shown that for pickling with an 8 per cent solution of sulfuric acid with temperatures up to 180° F. about 3 gallons of inhibitor, made as just described, per ton of 60° Bé. acid yields effective inhibition. Most suitably the inhibitor is added

to the concentrated acid prior to its dilution to form the pickle bath. The concentration just referred to is of general utility for pickling ferrous metal articles. If, however, the bath is to be used only for low carbon steel, lower concentrations of inhibitor than that just mentioned can be used successfully.

As illustrative of the benefits to be derived from the invention, reference may be made to tests which show the efficacy of the inhibitor of this invention. The pickle bath was a 7.6 per cent solution of sulfuric acid held at a temperature of 150° F. Cold-rolled strip 0.005 inch thick of low carbon steel containing about 0.1 per cent of carbon was cut into rectangles 3 inches by 1.5 inch. High carbon steel containing about 0.7 per cent of carbon, about 1 per cent of chromium, and about 0.2 per cent of molybdenum, likewise in the form of 0.005 inch cold-rolled strip, was cut into rectangles 2.75 by 1.5 inches. The samples were immersed in 230 cc of the acid pickle to which there was added 0.1 cc of an inhibitor prepared as described above. The samples were preliminarily cleaned, dried and weighed. After 30 minutes immersion in the pickling bath they were again cleaned and dried, and the weight loss was determined. For comparison identical tests were made using an identical pickling bath without inhibitor, and one containing the same amount of a well-known commercially used inhibitor. The tests showed the following results.

Inhibitor	Low carbon	High carbon
	Average weight loss—gm.	
None	0.0873	0.1693
Commercial inhibitor	0.0073	0.1039
Inhibitor *—crude creosote	0.0017	0.0592
Inhibitor *—U. S. P. creosote	0.0018	0.0605

* Made as described hereinabove.

From the foregoing tests it appears clearly that the inhibitor provided by the invention very substantially reduces the action of the pickle solution on the metal, affording commercially desirable inhibition as appears from the fact that the inhibitor is much more effective than one of the better inhibitors commercially available at the time of this invention.

The use of higher concentrations of our inhibitor, for instance, in amounts of 1 cc. per 230 cc. of pickling acid solution, did not materially improve the inhibiting action, showing that very small amounts indeed suffice. Also, inhibiting action of about the same order of magnitude as in the various tests just reported was obtained with operation of the bath at 180° F.

Without restricting ourselves to this theory, we now believe that the thiocarbanilide is broken down by the sulfuric acid to aniline and phenyl mustard oil, and that it is the phenyl mustard oil with the cresol which forms the inhibitor under the action of the sulfuric acid. Regardless of whether this theory is correct, the product is a better inhibitor than thiocarbanilide or creosote used alone. The use of thiocarbanilide is desirable also because the product is free from the obnoxious odor of phenyl mustard oil and the difficulties which attend its handling.

According to the provisions of the patent statutes, we have explained the principle of our invention and have described what we now consider to represent its best embodiment. However, we desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

We claim:

1. That method of pickling metal in a strong mineral acid bath comprising subjecting said metal to a bath of said acid containing a small amount of a product obtained by sulfonating a mixture of creosote and thiocarbanilide.

2. That method of pickling ferrous metal in a dilute sulfuric acid bath, comprising subjecting said metal to said bath containing a small amount of a product obtained by sulfonating a mixture of creosote and thiocarbanilide.

3. That method of pickling ferrous metal in a bath of dilute sulfuric acid, comprising adding to said bath a small amount of a product obtained by sulfonating a mixture of creosote and thiocarbanilide, heating the bath to about 150 to 180° F., and immersing the metal in said bath.

4. That method of pickling ferrous metal in a bath containing about 5 to 8 per cent of sulfuric acid, comprising subjecting said metal to said bath containing a small amount of a product obtained by sulfonating a mixture of creosote and thiocarbanilide.

5. That method of pickling metal in a strong mineral acid bath, comprising subjecting said metal to a bath of said acid containing a small amount of a product obtained by sulfonating a mixture of about 2 mols of creosote and 1 mol. of thiocarbanilide.

6. That method of pickling ferrous metal in a bath containing about 5 to 8 per cent of sulfuric acid which comprises subjecting said metal to a bath of said acid containing an inhibitor made by sulfonating a mixture of 2 mols of creosote and 1 mol. of thiocarbanilide.

7. That method of pickling metal in a strong mineral acid comprising subjecting said metal to a bath of said acid containing a small amount of an inhibitor prepared by sulfonating creosote in the proportion of about 8 to 10 gallons of creosote and 30 gallons of 66° Bé. sulfuric acid and then adding thereto a mixture of about 5 to 7 gallons of creosote and 53 pounds of thiocarbanilide, and during the entire sulfonation maintaining the temperature not in excess of about 100° F.

8. A pickling inhibitor comprising sulfonation product of a mixture of creosote and thiocarbanilide.

9. A pickling inhibitor comprising sulfonation product of a mixture of 2 mols. of creosote and 1 mol. of thiocarbanilide.

10. A pickling inhibitor comprising sulfonation product of creosote and thiocarbanilide made by adding crude creosote in the proportion of about 8 to 10 gallons to 30 gallons of 66° Bé. sulfuric acid, and then adding thereto a mixture of about 5 to 7 gallons of creosote and 53 pounds of thiocarbanilide, and during the entire sulfonation maintaining the temperature not in excess of about 100° F.

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