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PICKLING OF FERROUS METALS

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This invention relates to the pickling of ferrous metals.

In the treating of iron, steel and other ferrous metals, it is accepted practice, in order to free the metal of scale, rust and other foreign substances that have formed on or become attached to the surface thereof, to immerse the metal in an auqeous pickling bath comprising dilute sulphuric acid or a dilute mixture of sulphuric and hydrochloric acids. Preferred procedure involves heating the pickling bath to temperatures of from 60 to 90° C. and subjecting the iron, steel or other ferrous metal to be pickled to the action of the pickling acid or acids for a period just long enough to produce a clean surface. Ordinarily, an inhibitor is employed to prevent unnecessary loss, by dissolution, of the metal being pickled; but even in cases in which an inhibitor is used, the acid or acids employed in the pickling bath eventually become contaminated to an extent such that they cannot satisfactorily be rejuvenated by the addition of fresh acid of higher concentration and must, therefore, be discarded.

Similar to a certain extent is the problem in the artificial silk and allied industries, in which viscose and analogous processes of manufacture require the employment of spin baths comprising aqueous solutions of a considerable degree of acidity. In these processes, an alkaline solution of a water-soluble cellulose compound is extruded into the solution comprising the spin bath, in which occurs precipitation, or regeneration, of the dissolved cellulose. The spin bath solution, usually made up in the first instance from sulphuric or other strong mineral acid, contains a high percentage of dissolved salts that experience has shown to be necessary to the practicable manufacture of artificial silk and allied substances. To a certain extent the solution so used becomes spent and is discarded for that reason; but more often the water introduced in and as a part of the extruded cellulose solution reduces the acidity of the spin bath solution by mere dilution to a degree such that, on rejuvenation by the addition of concentrated acid, a surplus of useable spin bath solution is created. To prevent the occurrence of this condition, it is customary to reject a substantial part of the spin bath solution without attempting to rejuvenate it.

Heretofore, in the pickling of ferrous metals on one hand and the manufacture of artificial silk and allied substances on the other, it has alike been virtually impossible, as a practical matter, to avoid wasting into sewers, lakes or running streams the materials so discarded. This has been due to a certain extent to competitive conditions within the respective industries, which have made it impracticable to dispose of these wastes by any but the simplest means, and in considerable measure to the fact that no way of utilizing any substantial part of these wastes has heretofore been known. In both instances, but particularly in the case of spin bath solution from the manufacture of artificial silk and allied substances, there has thus been involved the improvident economic loss necessarily entailed by the failure to use to the fullest possible extent the materials so wasted.

It is an object of the present invention to reduce the not inconsiderable economic loss entailed in this way. Another object of the invention is to provide a method of pickling ferrous metals giving rise in and as a part of the pickling operation to unusually bright, clean uniform surfaces free to a greater extent than otherwise would be the case of spots, stains, blisters and other blemishes. Still another object of the invention is to take advantage of properties inherent in spin bath solution that has been employed in the manufacture of artificial silk and allied substances to assist in reducing the amount of corrosion occurring during the pickling of ferrous metals. As a further object, the invention contemplates making possible the re-use in the pickling of ferrous metals of spent or reject spin bath solution, hereinafter for convenience generically referred to as waste acid or as waste sulphuric acid, that has been employed in the process of manufacture of artificial silk and allied substances. Other objects of the invention will in part be obvious and in part appear more fully as the description of the invention proceeds.

Difficulties in the way of the use in the pickling of ferrous metals of waste sulphuric acid that has been employed in the manufacture of silk and allied substances would appear offhand to lie in the fact that waste sulphuric acid, while devoid of or at least relatively low in hydrogen ion concentration, is nevertheless of such a degree of acidity, due to its high concentration of bi-

sulphate ions, that it readily attacks the metals of which drums and tank cars are ordinarily made. Sulphuric acid as originally purchased for use in the artificial silk and allied industries is shipped in highly concentrated form, in which condition it does not attack drum, tank car or other container metals to any great extent; so that the problem of corrosion in shipping is not encountered in connection with the purchase of sulphuric acid for use in the artificial silk and allied industries. Similarly, sulphuric acid purchased for employment in the pickling of ferrous metals is shipped in highly concentrated form and subsequently diluted to the required concentration; so that its shipment in drums, tank cars or other containers is entirely practicable. Thus the corrosive character of the sulphuric acid does not occasion trouble until such time as it has been prepared for use or is used in the manner mentioned. These important difficulties, as will be pointed out more fully hereinafter, are completely obviated in the present invention.

A further difficulty might seem to reside in the fact that waste sulphuric acid that has been employed in the artificial silk and allied industries contains salts, such as sodium sulphate, sodium bisulphate, zinc sulphate, etc., as well as other chemical substances, that might be expected to interfere to a greater or less extent in pickling. It might be expected, for example, that a content of sodium sulphate approximating 20% might result in precipitation of dissolved salts in proportion as iron of the ferrous metal being pickled is attacked and dissolved. Likewise, waste sulphuric acid from the viscose process of manufacturing artificial silk and allied substances is known to contain colloidal sulphur and various identified and unidentified sulphur compounds the possible detrimental or non-detrimental effect of which upon the mechanics of the pickling process has been utterly unpredicatable. In addition, soluble cellulose compounds are also present, the effect of which might well be to interfere seriously with the pickling process. These anticipated difficulties do not, however, materialize in the practice of the present invention.

The surprising discovery has been made that waste acid from the artificial silk and allied industries contains one or more natural inhibitors the effect of which is to prevent undue attack upon ferrous metals. This is true both with respect to the iron and iron alloys of which drums, storage tanks, tank cars and other containers are ordinarily made and with respect to ferrous metals in the process of being pickled. In the case of the latter, it does not interfere with the removal of scale, rust and other foreign substances; in fact, the use of waste acid for this purpose has been found to impart to the ferrous metal being pickled a smoother, brighter and more desirable finish than is obtained by pickling in acids of the kinds ordinarily employed. Thus the invention involves, among other things, the twofold discovery that the presence therein of one or more natural inhibitors permits the shipment of waste sulphuric acid from the artificial silk and allied industries in drums, tank cars and other containers made of iron or iron alloys and its employment in the commercial pickling of ferrous metals without the expected attendant difficulties of precipitation of dissolved salts, interference with the pickling process, etc.

The presence of the natural inhibitor or inhibitors to which reference has been made has been established not only by laboratory experiments but by plant tests on a commercial scale.

In a first series of experiments, substantially identical flat, rust-free steel pieces measuring 4.25" x 1" were weighed and immersed in one case in 400 grams of waste sulphuric acid from the viscose process of artificial silk manufacture and in the other in 400 grams of 6% sulphuric acid comparable to that employed in the pickling of ferrous metals. So immersed, the pieces were allowed to stand at room temperatures ranging between 20 and 25° C. After 48 hours, it was found that the piece immersed in 6% sulphuric acid had suffered a loss of weight by corrosion of 9.807 grams; while that immersed in waste acid from the viscose process of artificial silk manufacture had suffered a loss of but 1.414 grams. These figures, while based on experiments conducted at temperatures considerably below the usual pickling temperatures, establish beyond doubt that waste sulphuric acid of the kind commonly used in the viscose process of artificial silk manufacture attacks ferrous metals very considerably less than does sulphuric acid of the kind normally employed in the pickling of ferrous metals. This is true notwithstanding the fact that waste sulphuric acid from the viscose process of artificial silk manufacture has an acidity of upwards of 8% as against an acidity of but 6% for ordinary pickling acid.

A second series of experiments, conducted with the aid of a synthetic artificial silk spin bath solution not actually used in the precipitation of cellulose and waste sulphuric acid from the viscose process of artificial silk manufacture, revealed a similar striking difference. The waste sulphuric acid from the viscose process of artificial silk manufacture had a specific gravity of 1.26, an acidity of 9.01%, a sodium sulphate content of approximately 20%, and a zinc content of 0.37%. The synthetic artificial silk spin bath solution, made up from 1123 grams of water, 554 grams of sodium bisulphate ($NaHSO_4.2H_2O$), 400 grams of anhydrous sodium sulphate, and 23 grams of zinc sulphate ($ZnSO_4.2H_2O$), was found to have a specific gravity of 1.39, an acidity of 8.11%, a sodium sulphate content roughly 10% higher than that of the waste acid, and a zinc content of 0.37%. Weighed pieces of steel measuring, as before, 4.25" x 1" were immersed in 400 grams of the respective solutions and weighed after 15 hours' and again after 42 hours' immersion. The loss of weight after 15 hours in the synthetic artificial silk spin solution acid was 3.106 grams, while that after 15 hours in the waste sulphuric acid was .310 grams. After 42 hours, the loss of weight of the piece immersed in the synthetic artificial silk spin bath solution was 6.185 grams; that in the case of the piece immersed in waste sulphuric acid, .856 grams. It may be inferred from these data that waste sulphuric acid from the viscose process of artificial silk manufacture contains one or more natural inhibitors.

Similar results were obtained in a third series of experiments carried out at somewhat higher temperatures with the aid of a synthetic artificial silk spin bath solution prepared from 695 grams of water, 11 grams of zinc sulphate ($ZnSO_4.2H_2O$), 200 grams of anhydrous sodium sulphate, and 94 grams of 96% sulphuric acid. The synthetic artificial silk spin bath solution so made up had a specific gravity of 1.255, an acidity of 9.08%, a zinc content of 0.41% and a sodium sulphate content of 19.95%, as against corresponding val-

ues for waste sulphuric acid employed in the same series of experiments of 1.261, 9.05%, 0.37% and 20.22%, respectively. The following tabulations show the results obtained in the tests, the data given in Table A being those obtained with pieces of tank steel measuring 4.25" x 1" and those in Table B with pieces of sheet steel measuring 3.25" x 2.5".

Table A

	Original weight in grams	Weight in grams after 10 minutes at 80-82° C.	Loss in weight in grams	Loss in weight in mg./sq. in.
Synthetic artificial silk spin bath solution	34.080	33.985	.095	11
Waste sulphuric acid	34.040	33.982	.058	6.8

Table B

	Original weight in grams	Weight in grams after 10 minutes at 80-82° C.	Loss in weight in grams	Loss in weight in mg./sq. in.
Synthetic artificial silk spin bath solution	44.354	44.205	.149	9.1
Waste sulphuric acid	45.125	45.096	.029	1.8

These tests definitely establish that the waste sulphuric acid contains a natural inhibitor or inhibitors not found in synthetic artificial silk spin bath solution not actually used in the spinning of artificial silk. In these tests, as in the others described herein, unusually bright, uniform surfaces were obtained on pickling with waste sulphuric acid, the finish being much better than that obtained with the synthetic artificial silk spin bath solution.

The nature of the inhibitor or inhibitors producing this wholly unexpected action is not known; but, whatever their nature, it is clear from the third series of experiments described above that the inhibitor or inhibitors that are present are not volatile at pickling temperatures. It can be shown, further, that the inhibitor or inhibitors are not removed by filtration. It might be supposed at first blush that gamma cellulose would have inhibiting properties; but this is disproved by the fact that, in still other experiments, steel pieces immersed respectively in synthetic artificial silk spin bath solution and similar solution containing additionally a small quantity of gamma cellulose showed a slightly greater loss in weight in the case of the latter than in the case of the former. Glucose possesses inhibiting properties, but the waste sulphuric acid employed in the first, second and third series of experiments was definitely known to contain no glucose whatsoever from any source. It would appear to follow that the inhibiting action characterizing waste acid is to be credited not to a cellulose derivative, but rather to colloidal sulphur, to the possible presence of dixanthogen, or to the action of some unidentified organic sulphur compound. It is, however, not impossible that cellobiose or some derivative thereof may be responsible.

Experimentally obtained data further establish that it is practicable to fortify waste acid from the manufacture of artificial silk and allied substances with an extraneous inhibitor in order to obtain an even greater inhibiting effect. It is possible to introduce, for example, the mixed di-acetone amine and tri-acetone diamine inhibitor capable of being prepared from acetone and ammonium acetate: such an inhibitor, introduced into waste sulphuric acid of the kind employed in the first series of experiments described above and present in an amount comprising 0.12%, prevented the occurrence of a loss greater than 0.463 grams. Similarly, in an experiment paralleling the second series of experiments described above, 5 grams of thiocarbanilide were dissolved in 30 grams of 96% sulphuric acid, 3 grams of the resulting solution being added to 400 grams of the waste sulphuric acid employed. The extraneously inhibited waste sulphuric acid so made up gave a loss of .061 grams of iron after 15 hours' immersion and after 42 hours' immersion of .856 grams of iron, as against 3.106 and 6.185 grams, respectively, in the case of the uninhibited synthetic artificial silk spin bath acid. In still other tests, waste sulphuric acid containing an extraneous inhibitor prepared from formaldehyde and the reaction product of acetone and ammonium phenyl dithiocarbamate was tested against synthetic artificial silk spin bath acid of the kind heretofore described. Waste sulphuric acid containing .5% of the inhibitor so made up gave rise to a loss in weight at the end of 24 hours at room temperatures of 0.003 grams, whereas the synthetic artificial silk spin bath acid described above was responsible for a loss of weight under similar conditions of 1.55 grams. Other extraneous inhibitors that may be employed are, for example, glucose, the quinolines, morpholines, mercapto thiazoles, mercapto aryl thiazoles, the aldehyde-amine condensation products, and the aldehyde-ammonia condensation products. The extraneous inhibitor is preferably dispersed in 96% sulphuric acid and the resulting solution introduced into the waste acid.

In all of these experiments, the various samples of steel tested in waste acid were found at the conclusion of the respective experiments to be uniformly bright and clear; to be, in fact, wholly free from spots, strains and blisters. There was no indication that the dissolved salts contained in the waste acid had precipitated out. Similar experiments on a commercial scale revealed no incrustations on the pickling tanks at the end of the experiments, indicating that dissolution of iron does not throw out sodium sulphate, sodium bisulphate, or other dissolved contents of waste sulphuric acid. In any event, it would be necessary after pickling merely to flush the pickling tanks and/or the pickled ferrous metal with water with a view to dissolving any dissolved salts that might have crystallized in solid form. So far as known, the use in the manner described of waste acid from the manufacture of artificial silk and allied substances is without inherent disadvantages.

It is not necessary that only waste sulphuric acid from the viscose process of artificial silk manufacture be employed pursuant to the practice of the invention: it is equally practicable to employ waste sulphuric acid in which viscose has been coagulated in the form of regenerated cellulose paper. The use in pickling of hydrochloric and like strong mineral acids other than sulphuric acid that have been used in the precipitation from viscose of cellulose, either in the form of artificial silk or in the form of regenerated cellulose paper, is also feasible, such acid being capable of employment in pickling either as such or in conjunction with sulphuric acid. Waste acid

from the cuprammonium process of manufacture of artificial silk and other articles of regenerated cellulose, whether sulphuric, hydrochloric or other strong mineral acid, may be similarly employed. The advantages of the invention are, however, realized to the fullest extent in the use of waste sulphuric acid from the viscose process of manufacturing artificial silk and allied substances, constituting the preferred embodiment of the invention.

Thus the invention makes possible the re-employment, with consequent material economic gain, of industrial wastes from the artificial silk and allied industries. Inasmuch as the invention has established, among other things, that waste acid from the manufacture of artificial silk and allied substances may, in spite of its corrosive character, be held in drums, storage tanks, tank cars and other containers made of ferrous metals, it is obviously possible to ship such acid to steel mills, where, as shown above, it can be employed to good advantage in the pickling of iron, steel and other ferrous metals. The presence of the natural inhibitor or inhibitors referred to makes unnecessary the employment of commercial inhibitors in pickling, although, as pointed out above, enhanced results may be obtained by the fortification of the waste acid by a commercial inhibitor. Thus the invention not only makes possible an inexpensive source of material for use in the pickling of ferrous metals, but also provides an important industrial outlet for waste acid from the process of manufacturing artificial silk and allied substances.

It will be understood that as used in the accompanying claims the terms "spin bath solution" and "waste spin bath solution" have reference to and include both spent and reject spin bath solutions from the above mentioned processes of manufacturing artificial silk; also, that these terms are intended to include similar solutions employed in the manufacture of regenerated cellulose paper and other substances. It will likewise be understood that the type of corrosion to which reference is made herein is corrosion by chemical dissolution of metal in consequence of the action thereon of one or more acidic substances, not corrosion by simple oxidation. It is intended that the patent shall cover, by suitable expression in the appended claims, whatever features of patentable novelty reside in the invention.

I claim:

1. In the pickling of ferrous metals, the method of inhibiting corrosion of the metal being pickled comprising pickling in the presence of spin bath solution that has been employed in the viscose process of manufacturing artificial silk.

2. In the pickling of ferrous metals, the method of inhibiting corrosion comprising pickling in the presence of an acid spin bath solution in which artificial silk has been precipitated.

3. In the pickling of ferrous metals, the method of inhibiting corrosion comprising pickling in the presence of spin bath solution that has been used in the regeneration of cellulose from viscose.

4. In the pickling of ferrous metals, the method of inhibiting corrosion comprising pickling in the presence of an acid spin bath solution that has been used in the regeneration of cellulose.

5. In the pickling of ferrous metals, the method of inhibiting corrosion comprising pickling in the presence of spin bath solution that has been employed in the ciscose process of manufacturing regenerated cellulose paper.

6. In the pickling of ferrous metals, the method of inhibiting corrosion comprising pickling in the presence of waste acid in which artificial silk has been precipitated.

7. In the pickling of ferrous metals, the method of inhibiting corrosion comprising pickling in the presence of waste acid in which cellulose has been regenerated.

8. In the pickling of ferrous metals, the method of inhibiting corrosion comprising pickling in the presence of waste acid in which viscose has been coagulated.

9. In the pickling of ferrous metals, the method of inhibiting corrosion comprising pickling in the presence of waste acid in which has been precipitated artificial silk prepared by the viscose process.

10. A ferrous metal pickling bath in which corrosion is inhibited comprising waste acid in which has been precipitated artificial silk prepared by the viscose process.

11. A ferrous metal pickling bath in which corrosion is inhibited comprising waste acid in which viscose has been coagulated.

12. A ferrous metal pickling bath in which corrosion is inhibited comprising waste acid in which cellulose has been regenerated.

13. A ferrous metal pickling bath in which corrosion is inhibited comprising an acid spin bath solution in which artificial silk has been precipitated.

14. A ferrous metal pickling bath in which corrosion is inhibited comprising spin bath solution that has been employed in the viscose process of manufacturing artificial silk.

15. A ferrous metal pickling bath in which corrosion is inhibited comprising spin bath solution that has been employed in the viscose process of manufacturing regenerated cellulose paper.

16. A ferrous metal pickling bath in which corrosion is inhibited comprising waste acid in which artificial silk has been precipitated.

17. A ferrous metal pickling bath in which corrosion is inhibited comprising spin bath solution that has been used in the regeneration of cellulose from viscose.

18. A ferrous metal pickling bath in which corrosion is inhibited comprising an acid spin bath solution that has been used in the regeneration of cellulose.

19. In the pickling of ferrous metals, the method of inhibiting corrosion of the metal being pickled comprising pickling in the presence of artificial silk spin bath solution containing a high concentration of soluble sulphuric acid salts.

20. In the pickling of ferrous metals, the method of inhibiting corrosion of the metal being pickled comprising pickling in the presence of a viscose process spin bath solution containing a high concentration of soluble sulphuric acid salts.

21. In the pickling of ferrous metals, the method of inhibiting corrosion of the metal being pickled comprising pickling in the presence of a viscose process spin bath solution containing a high concentration of soluble sulphuric acid salts, said spin bath solution being one in which artificial silk has been precipitated.

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