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ACID PICKLING OF METALS AND COMPOSITIONS THEREFOR

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This invention relates to the acid pickling of metals, more particularly to the acid pickling of ferrous metals such as steel, and to new and useful compositions suitable for this purpose.

One of the objects of the invention is to provide a new and improved acid pickling bath in which ferrous metals can be cleaned to produce a product of enhanced whiteness.

Another object of the invention is to provide new and improved acid pickling baths in which the rate of pickling ferrous metals is greatly accelerated.

A further object of the invention is to provide a new and improved method of pickling ferrous metals by a process in which there is a substantial saving of acid.

Another object of the invention is to provide new and improved pickling baths for the acid pickling of ferrous metals which function to prevent the oxidation of aqueous solutions of iron salts remaining on the surface of ferrous metals which have been immersed in such baths. Other objects will appear hereinafter.

In accordance with the invention these objects are accomplished by providing an acid pickling bath containing a compound capable of liberating colloidal sulfur, preferably sodium thiosulfate, and a water soluble ionizable ferrocyanide, preferably sodium ferrocyanide.

The employment of a substance such as sodium thiosulfate which liberates colloidal sulfur in the pickling solution is not claimed herein per se but is the subject of another application of one of the joint inventors, United States application Serial No. 694,424, filed August 31, 1946, now matured into U. S. Patent 2,636,009. It will be understood that other substances capable of liberating colloidal sulfur as, for example, sodium polysulfide may be employed in the practice of the invention.

The sodium ferrocyanide makes it possible to obtain a whiter pickled product. It will be understood that other water soluble ferrocyanides such as, for example, potassium and ammonium ferrocyanides may be employed to replace a part or all of the sodium ferrocyanide.

In the practice of the invention improved results are obtained by incorporating the ferrocyanide into an acid pickling bath which also contains a compound capable of liberating colloidal sulfur, but a further improvement in the results can be obtained by adding to the same bath containing the colloidal sulfur and ferrocyanide a cationic acid stable wetting agent preferably an aldonic acid salt of an oxyalkylated fatty amine. The cationic wetting agent provides a more uniform metal surface in conjunction with cathodic depolarization. It also provides a foam head and makes it possible to operate the acid pickling bath with higher concentrations of ferrous iron. The operation of the bath can be continued for a longer period of time than would otherwise be possible. As a result the effective usefulness of the acid pickling solution is prolonged and a greater quantity of ferrous metal can be processed in the same body of solution.

The invention will be illustrated but is not limited by

the following examples in which the quantities are stated in parts by weight unless otherwise indicated.

Example I

A solid composition suitable for use as an addition agent to an acid pickling bath was prepared by mixing together the following ingredients.

25 parts sodium thiosulfate
25 parts dextrose
50 parts sodium ferrocyanide

This composition was added to a sulfuric acid pickling bath containing 6% to 20% sulfuric acid in proportions of approximately ¼ pound of said composition per hundred pounds of H_2SO_4. Cold rolled carbon steel sheets were pickled in this bath with excellent results.

Example II

The pickling procedure was the same as that described in Example I except that there was added to the acid pickling bath ½ to 1 part of an addition agent per thousand gallons of acid pickling solution, said addition agent being prepared by reacting 13.5 parts of 50% gluconic acid with 86.5 parts of a soybean amine oxyalkylated with approximately 10 moles of ethylene oxide and containing approximately 20 carbon atoms in its alkyl chain (e. g., Ethomeen S–20 having an average molecular weight of 714 made by Armour & Company). The results obtained in the employment of the bath described in this example were substantially better than those obtained with the bath described in Example I, particularly with respect to surface conditioning of the metal and the retention of a foam head during the acid pickling operation.

In the foregoing examples the dextrose is an optional ingredient which is added as a reducing agent. The time required for the pickling procedure will vary depending upon a number of factors, for example whether a continuous or batch type pickling operation is used. However, by employing the addition agents of the present invention the time period can be reduced and at the same time a substantial savings in the pickling acid can be effected.

The addition agents provided in accordance with the invention can be employed in any acid pickling bath or solution but are primarily useful in sulfuric acid pickling solutions having a concentration of 6% to 20% by weight H_2SO_4 and in hydrochloric acid pickling solutions having a concentration of 10% to 15% by weight HCl.

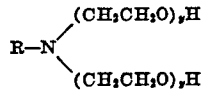
The pickling temperatures are preferably within the range of 120° F. to 200° F. in sulfuric acid solutions and within the range of 60° F. to 120° F. in hydrochloric acid solutions.

The thiosulfate or other colloidal sulfur liberating compound tends to prevent the formation of alpha and gamma iron oxide and the sulfur which is liberated to some extent also acts as a depolarizing agent. The quantity of sodium thiosulfate or chemically equivalent amount of a sulfur liberating compound is subject to variation but is preferably within the range of 1 to 8 parts of sodium thiosulfate per 700 parts of 7% sulfuric acid or about 1 to 8 parts colloidal reactive sulfur in 5000 parts of sulfuric acid or in the equivalent amount of another acid.

The quantity of the sodium ferrocyanide or chemically equivalent amount of another water soluble ionizable ferrocyanide is subject to variation, being preferably one and a half to ten times the amount of the sodium thiosulfate or other sulfur liberating compound on a chemical equivalent basis. Where a cationic wetting agent is employed as illustrated in Example II it is preferable to use a tertiary amine which is derived by oxyalkylating a fatty amine with an alkylene oxide, for example ethyl-

ene oxide or mixtures of ethylene oxide and 1,2-propylene oxide.

The fatty amines are amines derived from fatty acids and normally contain 8 to 36 carbon atoms. They differ in the number of carbon atoms in their alkyl groups, in the degree of saturation of the alkyl groups, and in the number of alkyl groups attached to the amino nitrogen. Examples of fatty amines are those derived from soya beans, those derived from coconut oil and those derived from tallow. A general chemical formula for a preferred type of oxyalkylated fatty amine may be written



where R represents the aliphatic chain of the fatty amine and y represents the number of oxyalkylene groups attached to the nitrogen atom of the fatty amine. The number of carbon atoms in the alkyl groups may be as high as 60, but especially good results have been obtained where the number of carbon atoms in the alkyl groups has been within the range of 15 to 30. The number of moles of the alkylene oxide should be at least 4 moles per mole of primary fatty amine and is preferably around 10 to 20 moles per mole of primary fatty amine. The fatty amines per se are water insoluble but oxyalkylation results in the addition of ether and hydroxy solubilizing groups to the molecule increasing the degree of water solubility and decreasing the cationic strength of the resultant material.

The oxyalkylation fatty amines form salts with the mineral acids used in acid pickling. Hence, an oxyalkylated fatty amine salt is formed in situ in the acid bath when the oxyalkylated fatty amine per se is added thereto. However, it is preferable to add the oxyalkylated fatty amine as a substantially neutral aldonic acid salt. For the purpose of the present invention the oxyalkylation is preferably oxyethylation or a mixed oxyethylation and oxypropylation because it is desired that the products have some solubility in aqueous acid solutions and also retain some cationic activity.

The quantity of the cationic oxyalkylated fatty amine employed for the purpose of the invention is subject to variation but generally satisfactory results can be obtained by using a relatively small amount as illustrated in Example II.

The aldonic acid when reacted with the oxyalkylated fatty amine produces a salt which is acid stable and more soluble than the oxyalkylated amine itself. Although it is preferable to employ gluconic acid in the preparation of this salt, it will be understood that other aldonic acids can be employed, e. g., mannonic, galactonic and arabonic, as well as the lactones of these acids.

The addition agents employed in the practice of the invention act to unify the electrostatic charge over ferrous metal surfaces and remove hydrogen polarization films from cathodic areas. They also serve to prevent the oxidation of aqueous solutions of iron salts remaining on the surfaces of metals which have been immersed in sulfuric or hydrochloric acid pickling solutions. The result is a uniform micro-etch without excessive acid attack on anodic areas or crystal boundaries and with substantially no burning or discoloration.

The excellent results obtained in the use of the acid pickling baths of the present invention can be attributed to the combined action of the addition agents rather than to any individual characteristic of a specific additive. One of the combined effects obtained is the reduced retention of iron salts and oxides in the pores of the pickled object. As a result the rusting tendency of the object during its transfer from the acid pickling bath to a rinsing bath is materially reduced. The acid pickling solutions herein provided are also very effective in penetrating the pores and cavities of the object and in removing carbonaceous smudges.

The oxyalkylated fatty amines, for instance as employed in Example II, are very effective in maintaining a foam head up to the point of saturation of ferrous sulfate in the acid pickling bath. Thus, by employing such oxyalkylated compounds the foam head may be maintained in the acid pickling bath to a concentration of 14–16% Fe, whereas anionic wetting agents, such as sodium isopropyl naphthalene sulfonate, are satisfactory in maintaining a foam head only until the iron concentration reaches about 10–11% Fe at which point they will no longer provide an effective foam head. It is believed that in some manner the cationic wetting agents employed in the practice of the present invention prevent the salting out of iron salts. In any event the presence of the oxyalkylated aliphatic amine salts in the bath makes it possible to operate the bath with a satisfactory foam head and a higher iron concentration over a longer period of time than in ordinary practice.

The invention is hereby claimed as follows:

1. A sulfuric acid pickling bath containing 6% to 20% sulfuric acid, sodium ferrocyanide and sodium thiosulfate, the quantity of sodium thiosulfate being sufficient to liberate about 1 to 8 parts colloidal reactive sulfur per 5000 parts of H_2SO_4 and the quantity of sodium ferrocyanide being approximately 1.5 to 10 times the quantity of sodium thiosulfate.

2. A process of conditioning metal surfaces which comprises immersing the metal surface to be conditioned in an aqueous acid pickling bath containing 6% to 20% sulfuric acid, sodium ferrocyanide and sodium thiosulfate, the quantity of sodium thiosulfate being sufficient to liberate about 1 to 8 parts colloidal reactive sulfur per 5000 parts of H_2SO_4 and the quantity of sodium ferrocyanide being approximately 1.5 to 10 times the quantity of sodium thiosulfate.

3. A sulfuric acid pickling bath consisting essentially of an aqueous solution of sulfuric acid, elemental colloidal sulfur liberated in situ in said bath and a water soluble ionizable ferrocyanide, the quantity of elemental colloidal sulfur being within the range of about 1 to 8 parts per 5000 parts by weight of H_2SO_4, and the quantity of water soluble ionizable ferrocyanide being about 1.5 to 10 times the quantity of sulfur, calculated as sodium thiosulfate.

4. An acid pickling bath consisting essentially of an aqueous solution of an acid from the group consisting of sulfuric acid and hydrochloric acid, sodium ferrocyanide and sodium thiosulfate, the quantity of sodium thiosulfate being sufficient to liberate about 1 to 8 parts colloidal reactive sulfur per 5000 parts by weight of said acid, and the quantity of sodium ferrocyanide being approximately 1.5 to 10 times the quantity of sodium thiosulfate.

5. An addition agent for acid pickling baths consisting essentially of a water soluble ionizable ferrocyanide and a compound capable of liberating elemental colloidal sulfur when dissolved in an aqueous solution of an acid from the group consisting of sulfuric acid and hydrochloric acid, the quantity of said sulfur liberating compound corresponding to 1 to 8 parts by weight, calculated as sodium thiosulfate, per 700 parts of said acid solution, calculated as 7% H_2SO_4, and the quantity of said water soluble ionizable ferrocyanide being approximately 1.5 to 10 times the quantity of said sulfur liberating compound, calculated as sodium thiosulfate.

6. An addition agent for acid pickling baths consisting essentially of sodium ferrocyanide and sodium thiosulfate in a weight ratio of sodium ferrocyanide to sodium thiosulfate within the range of 1.5:1 to 10:1.

7. An aqueous acid pickling bath containing a mineral pickling acid from the group consisting of sulfuric acid and hydrochloric acid, a quantity of elemental colloidal sulfur liberated in situ in said bath, a quantity of a water soluble ionizable ferrocyanide, and an oxyalkylated fatty amine salt which is soluble in said bath, the oxyalkyl groups in said fatty amine salt being from the group consisting of oxyethylene and both oxyethylene and oxy-

propylene, the quantity of said elemental colloidal sulfur liberated in said bath being within the range of about 1 to 8 parts by weight of colloidal reactive sulfur per 5000 parts by weight of said mineral acid, calculated as H_2SO_4, the quantity of said water soluble ionizable ferrocyanide, calculated as sodium ferrocyanide, being approximately 1.5 to 10 times the quantity of sulfur, calculated as sodium thiosulfate, and the quantity of said oxyalkylated fatty amine salt being sufficient to form a foam head on said bath.

8. An acid pickling bath as claimed in claim 7 in which said oxyalkylated fatty amine salt is an oxyethylated fatty amine salt containing 10 to 20 mols of ethylene oxide per mol of fatty amine.

9. A process of conditioning ferrous metal surfaces which comprises immersing the metal surface to be conditioned in an aqueous acid pickling bath containing a mineral pickling acid from the group consisting of sulfuric acid and hydrochloric acid, elemental colloidal sulfur liberated in situ in said bath, and a water soluble ionizable ferrocyanide, the quantity of said elemental colloidal sulfur being within the range of about 1 to 8 parts by weight of elemental colloidal sulfur per 5000 parts by weight of said mineral acid, calculated as H_2SO_4,

and the quantity of said water soluble ionizable ferrocyanide being approximately 1.5 to 10 times the quantity of said elemental colloidal sulfur, calculated as sodium thiosulfate.

10. A process as claimed in claim 9 in which said acid pickling bath also contains an oxyalkylated fatty amine salt which is soluble in said bath, the oxyalkyl groups in said amine salt being from the group consisting of oxyethylene and both oxyethylene and oxypropylene, and the quantity of said salt being sufficient to form a foam head on said bath.

11. A process as claimed in claim 10 in which said oxyalkylated fatty amine salt is an oxyalkylated fatty amine salt of an aldonic acid containing 10 to 20 mols of ethylene oxide per mol of fatty amine.

References Cited in the file of this patent

UNITED STATES PATENTS

1,061,089	Levy	May 6, 1913
2,249,383	Hilty	July 15, 1941
2,453,429	Gorman	Nov. 30, 1944
2,516,685	Douty et al.	July 25, 1950
2,636,009	Irwin	Apr. 21, 1953