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ACID PICKLING COMPOSITION WITH INHIBITOR

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The present invention relates broadly to the art of metal scale removal, and is more particularly concerned with the treatment of pickling solutions to enhance the scale removing properties thereof and to inhibit metal attack during immersion in the pickling solutions.

It is known that as a preparatory step to galvanizing iron and steel parts are immersed in a hydrochloric or sulfuric acid bath to remove scale formations thereon, after which the parts are rinsed, fluxed and zinc coated. It is further known that when iron salts and finely divided iron are carried by the metal surfaces from the pickling bath to the rinse tank and to the galvanizing kettle, dross is formed on the molten zinc and the effectiveness of the galvanized coating markedly reduced. Additionally, inhibitors have in the past been used with pickling solutions in an effort to reduce metal attack arising from prolonged immersion in the pickling solution. Insofar as applicant is aware, however, none of the currently used inhibitors have been completely effective in this regard, nor has there been provided a completely satisfactory method of cleaning the metal surfaces to assure the desired adhesion of the zinc coating to the iron or steel base which protects the base during the time interval between pickling and zinc immersion and prevents contamination of the galvanizing kettle by iron salts or finely divided iron remaining on the metal base.

It is accordingly a primary aim of the present invention to provide a composition for the treatment of pickling solutions which effectively prevents the transfer of finely divided iron and iron salts from the pickling to the galvanizing tank and which provides a protective film upon the metal surfaces to prevent oxidation thereof subsequent to pickling and prior to galvanizing.

Another object of this invention lies in the provision of an acid additive for pickling solutions of equal utility with both hydrochloric and sulfuric baths and which is productive of a relatively brighter, cleaner and more uniform galvanized coating upon the metal parts.

Still another object of the present invention is to provide a method of treating a pickling bath to obtain the noted advantages and which includes the step of adding to the pickling solution an aqueous mixture of a non-ionic surface active agent and a cationic surface active agent.

A further object of this invention lies in the provision of an acid additive for pickling solutions which comprises calculated amounts of a non-ionic surface active agent, a cationic surface active agent, and water.

Other objects and advantages of the invention will become more apparent as the description now proceeds.

In accordance with the principles of this invention, the advantages named and other improved results to be discussed herein are obtained by the addition to a hydrochloric or sulfuric acid pickling bath of a composition preferably comprising an ester-type non-ionic surface active agent, a quaternary ammonium salt, glucose and water in sufficient quantity to dissolve the named materials. While variations may of course be practiced in the formulation, one gallon or 3780 cc. of acid additive may be compounded by combining 330 cc. each of surfactant and quaternary ammonium salt, 20 cc. of glucose and 3100 cc. of water. If desired, an amount of glycerine equivalent to the volume of glucose may be added to this formulation to assure even more improved results in the pickling procedure.

As noted earlier, the acid additive of this invention is effective with pickling baths consisting either of hydrochloric or sulfuric acid solutions. While the concentration of acid additive in the pickling bath may be varied without substantial interference in the improved results obtained, a preferred range of additive is ½ to 2% additive by weight of sulfuric acid when the acid is in a concentration of from 5 to 15% acid by weight. On the other hand, when a hydrochloric acid pickling bath is used containing 20 to 50% by weight of acid, the desired range of additive is ½ to 3% based on weight of acid.

A second formulation which has similarly provided a superior zinc coating and the other improved results herein disclosed is compounded using 3.5 to 5.5 gallons each of ester-type non-ionic surface active agent and quaternary ammonium salt, and between ¾ and 4 gallons each of glucose and glycerine. The four compounds named are then mixed with the required volume of water to provide a formulation suitable for shipment in a 55 gallon drum or other desired container. A more specific formulation consists essentially of 4¾ gallons each of non-ionic surface active agent and quaternary ammonium salt, and 2 gallons each of glucose and glycerine, the four materials named providing 13 gallons of mixture which is then combined with 42 gallons of water to produce 55 gallons of additive. The additive is then combined with the hydrochloric or sulfuric acid solution in the concentration ranges noted in connection with the first formulation.

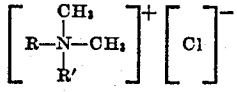
The ester-type nonionic surface active agent may be provided by various compounds, and the preferred class of compounds are ethylene oxide derivatives of fatty acids, fatty amines and fatty amides. A specific compound which has proven well in practice is identified by its manufacturer Armour & Company as Ethofat 242–25, the Ethofats generally being understood to be mono-fatty or rosin acid esters of polyoxyethylene glycols and to the following general formula:

$$RC(=O)O(CH_2CH_2O)_xH$$

The source of the alkyl radical in Ethofat 242–25 is understood to be 70% rosin fatty acids, and this compound has an average molecular weight of 974, and a specific gravity (25°/25° C.) of 1.081. Another etho-chemical which produces satisfactory results in the present invention is identified by Armour & Company as Ethofat 0/25, and the source of the alkyl radical in the compound is coco fatty acids. The average molecular weight of Ethofat 0/25 is understood to be 871, and the specific gravity thereof is approximately 1.059. Ethofat 0/25 has the type of linkage indicated above. While particularly good results have been obtained by use of the Ethofat compounds herein mentioned, it is to be appreciated that under particular conditions it may be found desirable to employ certain of the other Etho-chemicals. Such compounds which may be used in substitution for the Ethofats are surfactants identified by Armour & Company as Ethomeens and Ethomids. The Ethomeens are understood to be tertiary amines having one fatty alkyl group (derived from various fatty sources having from 12 to 18 carbon atoms) and two polyoxyethylene groups attached to the nitrogen, while the Ethomids are understood to be N,N-substituted fatty acid amides, the substituents being polyoxyethylene groups.

The quaternary ammonium salt used in the formulations set forth above may similarly be provided by various compounds known to the trade, and in investigations conducted to date a material identified by Armour & Company as Arquad 2C–50 has proven quite satisfactory.

The Arquad compounds are broadly dialkyl quaternary ammonium chlorides, and more specifically dialkyl dimethyl ammonium chlorides. The general formula of these compounds is as follows:



In the formula above, each R and R' represents a long hydrocarbon chain derived from a fatty acid. Arquad 2C–50 is a semi-liquid at room temperature and is essentially insoluble in water. It does, however, form a stable dispersion in water in the concentrations herein employed, and is of course compatible with the ester-type non-ionic surface active agent disclosed.

The acid additive or inhibitor formulations noted above may be observed to contain equal quantities of ester-type non-ionic surface active agent and quaternary ammonium salt, as well as equal volumes of glucose and glycerine. It is of course to be appreciated that equal parts of these materials are not at all times required, and that the ratio of non-ionic surfactant to quaternary ammonium salt may be either 3 to 2 or 2 to 3, and that the ratios of glucose to glycerine may be 5 to 1 or 1 to 5. However, in most applications, the best results are obtained by essentially equal volumes of the two surface active agents and equal volumes of glucose and glycerine. Further, while the glucose may be provided by various commercially available materials, in actual practice of the invention good results have been obtained by use of Argo corn syrup.

Each of the acid additive formulations herein disclosed are essentially true solutions as compounds, showing a water clarity with no suspensoids therein, either immediately after mixture or after standing for periods of the order of two weeks. The action of the present acid additive when used in either hydrochloric or sulfuric acid pickling solutions is to draw down or precipitate the iron salts in the form of either chlorides or sulfates and sulfites. The iron salts formed on the iron or steel surfaces by action of the acid are accordingly maintained in the pickling tank at the bottom thereof, and are not carried by the workpiece during transfer to the rinse tank or the galvanizing kettle. Dross formation in the galvanizing pot from iron salts or finely divided iron left on the metal surfaces is thus essentially entirely eliminated, and in work performed to date it has been noted that the dross is reduced approximately 16% by reason of the more effective cleaning provided by the present invention. In addition, actual practice of the invention has shown that the instant inhibitor provides a protective film on the metal surfaces which resists acid attack or burning of threaded portions of workpieces required to be immersed in the pickling solution for prolonged periods. As for example, a 20% sulfuric acid pickling solution which had been treated with 2% additive by weight of acid produced no burning on machine cut threads of pipe nipples which had been soaked overnight for approximately 18 hours. Experience has shown that the threads on such parts would be essentially completely eaten away in less than three hours of immersion in the same concentration of sulfuric acid to which known inhibitors had been added.

The film forming properties of the additive of this invention are also of proven value in preventing oxidation of the metal surfaces during transfer of the workpiece from the pickling tank to the water rinse bath, and from said bath to the fluxing tank and from said tank to the kettle of molten zinc. It has been found that the surfaces remain essentially rust-free and sealed for a period at least as great as three hours against the influence of

fumes in the pickling and galvanizing rooms. At the same time, however, the film is readily removed when the workpiece is immersed in the molten zinc, and by reason of the effectiveness of the additive in providing metal surfaces essentially free of dissolved iron, sludge, iron salts and the like, there is obtained a marked improvement in the uniformity of all of the various zinc-iron alloy layers and the pure zinc layer in the structure of the galvanized coating. Further, dry zinc ashes and zinc oxide on the surface of the galvanizing kettle are reduced due to the cleaner pickling procedures, and on all types of steel as exemplified by hot rolled, cold rolled or cast parts, a smoother, cleaner, brighter and more uniform galvanized coating is obtained. Further, in connection with the stated advantage of inducing deposit of iron salts in the pickling tank, it is frequently not necessary to combine the washing or rinsing step with scrubbing, as has been the practice in the past in order to remove iron salts and finely divided iron carried by the workpiece from the pickling tank.

While specific surface active agents have been set forth herein by way of example, and illustrative formulations provided, it will of course be appreciated that various changes and modifications may be made therein without departing from the novel concepts of the present invention. Specifically, in certain applications the glycerine may be eliminated, although in work conducted to date it has been noted that a slight weight loss increase occurs when glycerine is not present in the formulation. Further, while the additive of this invention is of particular utility in connection with pickling procedures preceding zinc coating, the additive as compounded in accordance with the second formulation may be combined in the amount of about 4 gallons of additive with 220 lbs. of zinc chloride crystals and 50 lbs. of sal-ammoniac crystals and water sufficient to make 55 gallons, one part of this mixture being diluted with about 8 parts of water to produce a predip flux effective in the suppression of fuming from the galvanizing bath and metal spatter during introduction of the workpiece into the molten zinc.

I claim as my invention:

An acid pickling bath comprising an aqueous solution of an acid selected from the group consisting of sulfuric and hydrochloric acids, and an inhibitor therefor comprising a combination of (1) a cationic surface active agent consisting of a tetra-aliphatic ammonium chloride containing at least one long chain hydrocarbon group (2) a non-ionic surface active agent consisting of a polyoxyethylene derivative of a compound selected from the group consisting of long chain aliphatic acids, amines, and amides, (3) glucose and (4) glycerine, the ratio of (2) to (1) being from 3:2 to 2:3, and the ratio of glucose to glycerine being from 5:1 to 1:5.

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