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3,310,497 EMBRITTLEMENT-FREE PICKLING OF FERROUS METAL

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This application is a continuation-in-part of our copending application Ser. No. 235,853, filed Nov. 6, 1962, now abandoned.

The invention relates to limiting the hazards of hydrogen embrittlement and overpickling during removal of oxide scale from ferrous metal by acids.

Iron and steel products become coated with an oxide scale during their process of manufacture, the presence of which is objectionable in their further processing, as for example in coating the products or forming them by drawing in dies. A conventional method of scale removal involves contacting the material with an aqueous solution of an inorganic acid, typically sulfuric acid, usually by immersion in a bath thereof. Since the acids employed are capable of dissolving the base metal, a reaction which is more rapid than that of oxide dissolution, pitting of the metal results where acid attacks it through discontinuities in the oxide film. Also, after the oxide layer has been removed, continued contact of the metal with the acid results in undesirable dissolution of metal, a condition known os overpickling. Moreover, hydrogen produced in the metal dissolution reaction increases the likelihood of hydrogen embrittlement of the ferrous base, which latter condtion results from absorption of hydrogen by the base metal.

In order to alleviate the foregoing difficulties, it is common practice to add to the pickling solution an inhibitor for the metal dissolution reaction, thus permitting more selective action in effecting oxide removal and reducing hydrogen production.

It has been noted that the degree of prevention of hydrogen embrittlement during pickling, resulting with various inhibitors, is unpredictable, some inhibitors even increasing embrittlement.

The present invention concerns inhibited acid pickling solutions capable of controlling acid attack of the base metal, which solutions contain an inhibitor which is markedly effective as well in preventing hydrogen absorption, with its resulting embrittlement effect. These results are obtained by the addition to the pickling acid solutions of 2-butene-1,4-diol.

We have found that 2-butene-1,4-diol is effective when used in concentrations above about 15 grams per liter of a 2 N sulfuric-acid aqueous solution. In general, an approximate useful range is in the order of 1 to 50 grams of inhibitor, per gram equivalent weight of acid, while a range of 2.5 to 25 grams of inhibitor, per gram equivalent weight of acid, is preferred. While other ingredients may be present in the solutions, these should not be of such nature as to adversely affect the properties of the solutions for their intended purpose.

Table I is illustrative of test results obtained with the new pickling inhibitor. A commercially normalized and temper-rolled low-carbon sheet steel having the following composition was used: 0.022% C, 0.09% Mn, 0.009% P, 0.046% S, 0.006% Si, 0.01% Cu, 0.01% Ni, 0.01% Cr, 0.007% Al, the balance being essentially iron. The steel thickness was 0.035 inch and coupons of 2 by 3/8 inch were cut and vapor degreased with trichloroethylene before use. The specimens were pickled at 100° F. for various preselected times up to 24 hours by immersion in either uninhibited 2 N sulfuric-acid solutions or 2 N sulfuric-acid solutions containing various concentrations of

inhibitor. Specimens were weighed prior to pickling and after extraction of the hydrogen absorbed during pickling. The hydrogen concentration in pickled steel was determined by warm extraction at 160° C., according to the method described by R. M. Hudson, J. K. Magor, and G. L. Stragand (J. Amer. Ceram. Soc. 41, 23 (1958)).

TABLE I.—METAL DISSOLUTION AND HYDROGEN PICK-UP IN 2 NORMAL SULFURIC-ACID SOLUTION AT 100° F.

Inhibitor	Inhibitor Conc., g./l.	Weight Loss, mg./cm.²		Hydrogen Absorbed, cc./100 g.	
		4 hr.	24 hr.	4 hr.	24 hr.
None	0	21.1	130.2	8.3	19.1
2-butene-1,4-diol	15.9	0.8	2.6	2.1	2.9
Do	47.7	0.4	1.3	1.2	1.0
Do	79.6	0.2	1.3	0.7	1.0
Do	103.6	0.2	2.6	0.8	1.0
Do	141.2	0.6	11.7	1.0	13.8

It will be appreciated that the foregoing concentration ranges and specific examples are illustrative only, to permit ready practice of the invention, and that such variations in concentrations and combinations of ingredients as would occur to those familiar with the art to which this invention appertains are included herein and are within the scope of the following claims.

We claim:

1. A solution for embrittlement-free pickling of ferrous metal consisting essentially of an aqueous solution of sulfuric acid and 2-butene-1,4-diol, the concentration of said alcohol being sufficient to inhibit dissolution of the ferrous metal and to reduce hydrogen absorption therein.

2. A solution for embrittlement-free pickling of ferrous metal consisting essentially of an aqueous solution of sulfuric acid and 2-butene-1,4-diol, said alcohol being present in concentration range of about 2.5 to 25 grams per gram equivalent weight of said acid.

3. A process for embrittlement-free pickling of ferrous metal comprising immersing said metal in a pickling solution consisting essentially of an aqueous solution of sulfuric acid and 2-butene-1,4-diol, the concentration of said alcohol being sufficient to inhibit dissolution of the ferrous metal and to reduce hydrogen absorption therein.

4. A process for embrittlement-free pickling of ferrous metal comprising immersing said metal in a pickling solution consisting essentially of an aqueous solution of sulfuric acid and 2-butene-1,4-diol, said alcohol being present in concentration range of about 2.5 to 25 grams per gram equivalent weight of said acid.

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