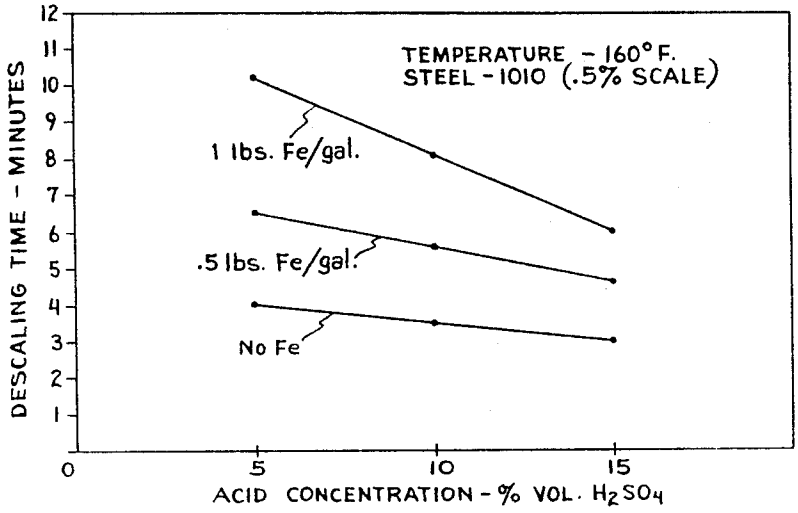
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July 27, 1971 J. C. PETERSON 3,595,799

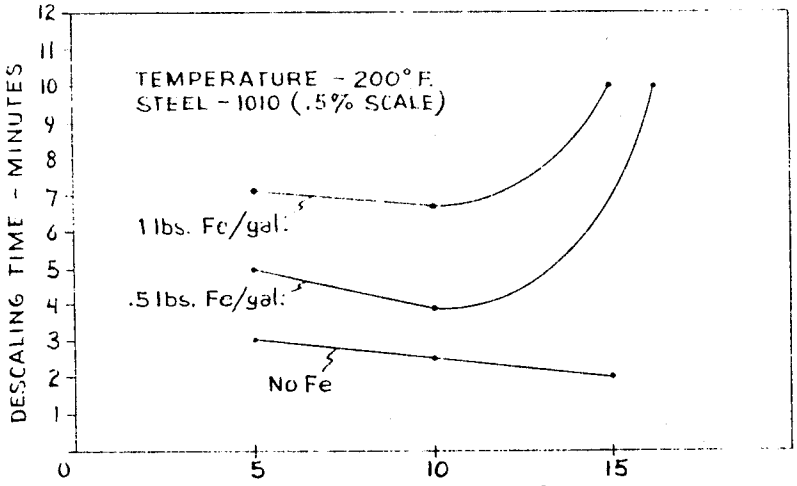
PICKLING ADDITIVE

Filed April 1, 1968 3 Sheets-Sheet 1



EFFECT OF IRON ON DESCALING RATE

Fig. 1.



EFFECT OF IRON ON DESCALING RATE

Fig. 2.

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PICKLING ADDITIVE

Filed April 1, 1968 3 Sheets-Sheet 2

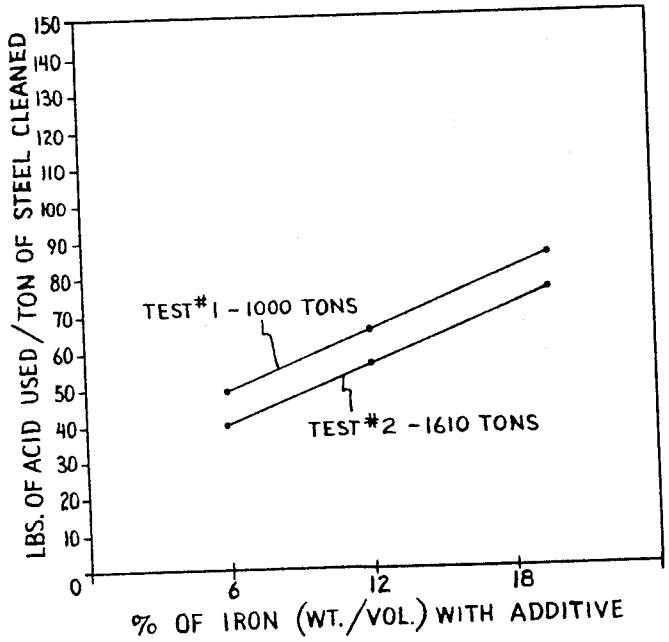


Fig. 3.

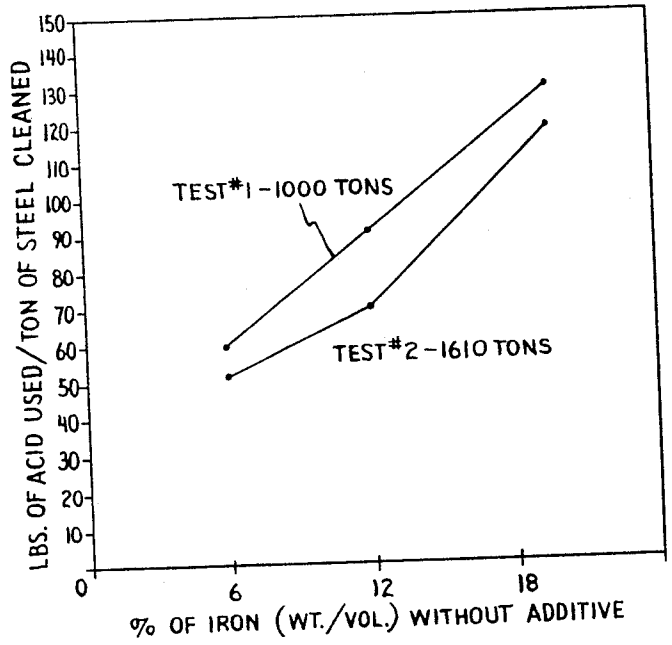


Fig. 4.

TEST CONDITIONS: 18% HCL (BY WT.)
TEMP. - 130° F
STEEL - LOW CARBON WIRE RODS

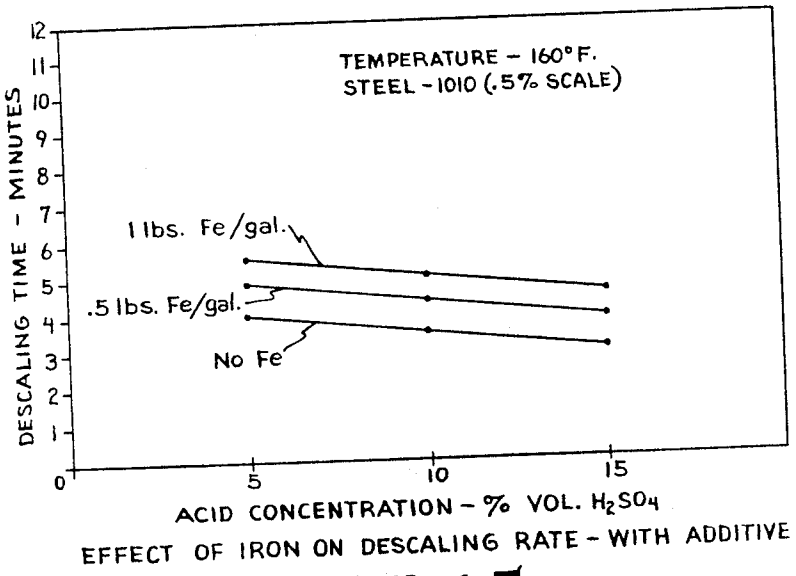
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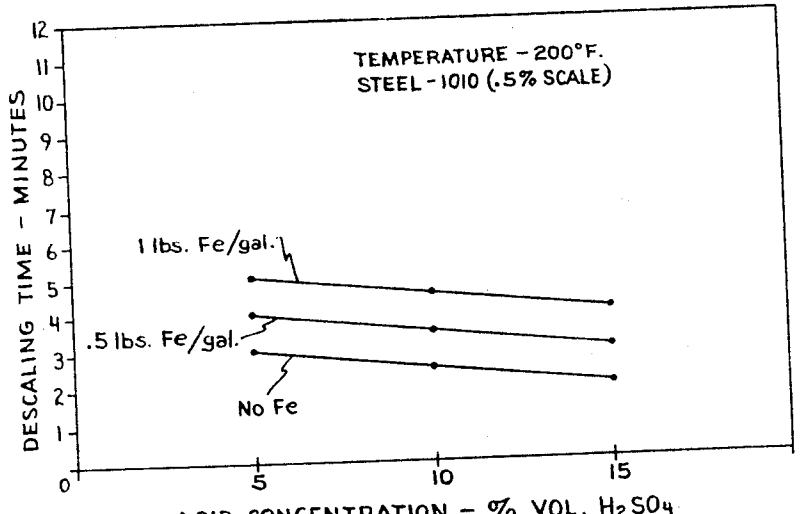
PICKLING ADDITIVE

Filed April 1, 1968 3 Sheets-Sheet 3



EFFECT OF IRON ON DESCALING RATE - WITH ADDITIVE

Fig. 5.



EFFECT OF IRON ON DESCALING RATE – WITH ADDITIVE

Fig. 6.

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United States Patent Office 3,595,799 Patented July 27, 1971

3,595,799

PICKLING ADDITIVE

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Filed Apr. 1, 1968, Ser. No. 717,667
Int. Cl. C11d 7/34; C23g 1/06
U.S. Cl. 252—137 2 Claims

ABSTRACT OF THE DISCLOSURE

A pickling additive composition comprising from 20–25% thiourea, 20–25% urea, 20–25% di-ammonium phosphate and 20–25% ethylenediaminetetracetic acid (EDTA), which, when added to an acid pickling bath, reduces acid consumption by at least 25%.

BACKGROUND OF THE INVENTION

This invention relates to an acid additive which extends the operating life of sulfuric and hydrochloric acid pickling solutions employed in the treatment of metals.

The treatment of metal surfaces with strong acids for the purpose of removing metal oxides and scale therefrom is generally referred to as "pickling." Pickling is one method of preparing a metal surface for processes such as electrodeposition, chemical coating, machining and like processes. In a typical pickling process, a metal object containing, for example, a high percentage of iron, is immersed in an aqueous acid bath, commonly referred to as the "pickling liquor."

The scale generally consists of outer layers of high oxygen content metal oxides such as Fe_2O_3 and Fe_3O_4, and an inner layer of a low oxygen content oxide such as FeO, and possibly intermediate layers consisting of mixed oxides. Generally speaking, scale with a high oxygen content is insoluble in sulfuric acid, while scale with a low oxygen content is more readily dissolved by sulfuric acid. The removal of scale depends upon the sulfuric acid penetrating the outer layer through cracks, dissolving some of the inner layer, and blowing off the outer layer by hydrogen evolution and by removal of its base.

Hydrochloric acid has been found to dissolve scale, regardless of its oxygen content, approximately ten times faster than sulfuric acid under the same conditions.

When steel is pickled in either sulfuric or hydrochloric acid, iron goes into solution as ferrous sulfate or ferrous chloride. In a sulfuric acid solution, an increase of the iron in solution tends to increase the descaling time necessary. This increase is particularly noticeable at higher iron concentrations when the operating temperature and acid concentrations are increased. The result is that it becomes almost impossible to remove scale in a reasonable time. See FIGS. 1 and 2. When my additive is used, acid consumption is greatly reduced as is time. See FIGS. 5 and 6.

The descaling ability of hydrochloric acid appears to be practically unaffected by the presence of ferrous chloride up to very high concentrations, but as the iron increases, the consumption rate of acid also increases. With the addition of my additive, acid consumption is reduced 25 to 30%. See FIGS. 3 and 4.

SUMMARY OF THE INVENTION

This invention relates to an additive which extends the operating life of sulfuric and hydrochloric acid pickling solutions employed in the treatament of metals. My novel pickling additive consists of 20–25 percent by weight of thiourea, 20–25 percent by weight of urea, 20–25 percent by weight of di-ammonium phosphate and 20–25 percent by weight of ethylenediaminetetracetic (hereinafter referred to as EDTA).

During the pickling process, the amount of available acid decreases and the amount of iron in solution increases. Inevitably as the acid strength declines and the iron content reaches 5–6 percent by weight in sulfuric acid baths pickling becomes impractical and the tub of spent acid normally has to be dumped. While sulfuric acid is relatively inexpensive, the amounts utilized yearly are substantial. Therefore, it is a primary objective of this invention to reduce the amount of acid consumed during the pickling process to extend the operative life of the pickling bath, and hence to reduce the cost of pickling steel.

When the additive composition of this invention is added to the sulfuric acid bath, normal pickling can be maintained even when the iron content reaches 12–14 percent by weight. Furthermore, the amount of acid consumed per ton of steel pickled is greatly reduced. The additive is normally added in the proportion of about two percent by weight based on the weight of raw acid.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The pickling additive of the present invention consists of 20–25 percent by weight of thiourea, 20–25 percent by weight of urea, 20–25 percent by weight of di-ammonium phosphate and 20–25 percent by weight of EDTA. When approximately 2 percent by weight of my additive based on the weight of the raw acid, is added to a sulfuric or hydrochloric acid pickling bath, the iron present in the sulfuric and/or hydrochloric acid baths is complexed, thereby thus allowing them to effectively remove "smut" and scale for much longer periods of time. The additive will complex iron up to 18 percent in hydrochloric acid baths. In experimental runs in actual steel mills, the life of the pickling baths have been increased from 100 to 200 percent and the acid consumption greatly reduced.

This invention is further illustrated by the following specific examples:

EXAMPLE I

Two hundred thirty tons of steel were pickled in a 4000 gallon tub which had previously been filled half-way with water. One hundred fifty pounds of my additive consisting of 25% by weight each of urea, thiourea, di-ammonium phosphate and EDTA, and five hundred gallons of sulfuric acid (approximately 12 percent by volume) were added to the water. Seven hundred pounds of rock salt was added to the pickling bath and the tub was heated to approximately 180° F. Titration showed 16 percent acid by weight. The 230 tons of steel was pickled in 57 hours. Prior to the use of my additive, the average time for pickling 230 tons of steel had been 70 hours. During the life of the pickling bath, 210 gallons of acid were added. The quality of the steel was greatly improved. The cost was reduced by over $1.00 a ton.

EXAMPLE II

Two pickling tubs were prepared according to the method of Example I using 400 gallons H_2SO_4 per tub (6,000 lbs.). The additive composition of Example I was added in an amount equal to about 2% by weight of the raw acid. Two hundred and fifty six tons of steel wire were cleaned in each tub. Utilizing my additive, about 47 lbs. of acid per ton of steel cleaned was utilized. Normal acid usage without my additive had been about 110 lbs. of acid per ton of steel.

EXAMPLE III

A raw stock pickle tub was selected for this test because of the possible adverse effects of the chemicals on phosphate coatings and cold draw. The additive composition was added in an amount equal to 2% by weight of the

weight of raw acid or 40 lbs. of the additive to 2000 lbs. of sulfuric acid. The tub was operated by making several additions of sulfuric acid during the run so that the acid strength was maintained between 6 and 9%. The material pickled in the tub was smut free and cleaner than normal. This cleaner pickling was obvious and continued throughout the life of the tub. The results of this run were compared with previous tubs run without the additive with the following results:

	Tub with additive	Tub without additive
Total acid used, gal.	1,373	425
Concentration at make up, percent H_2SO_4	11.6	9.6
Concentration at dump, percent H_2SO_4	[1] 2.8	[1] 2.8
Life working days	25	9
Sq. footage pickled	386, 248	119, 257

[1] Plus 7.8% Fe.

EXAMPLE IV

High carbon rods (1,272 tons) were pickled in a pickling bath containing 10.8 percent sulfuric acid to which had been added 2 percent by weight of my pickling composition. The bath was maintained at a temperature of 140° F. The tub solution lasted 10 days. The normal tub life without the additive had been 5 days. Waste treatment costs were reduced by 50 percent.

EXAMPLE V

A pickling tub was prepared containing 8% sulfuric acid. The tub was maintained at about 180° F. The additive of this invention was added in an amount equivalent to 2% by weight of the raw acid. Two hundred and sixty-four tons of wire rods were pickled in the tub. 44 lbs. of acid was used per ton of steel cleaned. The tub lasted 42 hours. Tub life prior to the use of the additive had been 24 hours. Costs were reduced by 16¢ per ton of steel cleaned. Based on an average of 20,000 tons of steel cleaned per month, the use of the additive will result in a savings of $40,000 per year.

EXAMPLE VI

Steel rods were cleaned in 3 tubs, one tub containing a conventional sulfuric acid pickling bath and the other two tubs having the additive added thereto. The results were as follows:

	Tub 1 (without the additive)	Tub 2, with additive	Tub 3, with additive
Tub life, hours	13¾	43	50
Tons pickled, tons	75	219.6	229.5
Cost per ton, cents	73	54	54.8

Tub No. 1 was dumped twice and a total of three tubs used in contrast to one tub runs for tubs No. 2 and 3. On the basis of 30,000 tons per month of steel pickled, savings would be $68,000 per year using the additive.

While the invention has been disclosed and described in some detail in the foregoing description, the descriptions are to be considered as illustrative and not restrictive in character, as other modifications may readily suggest themselves to persons skilled in this art and within the broad scope of the invention, reference being had to the appended claims.

What is claimed is:

1. A pickling additive formulation consisting of the following ingredients:
   (a) from 20 to 25% by weight thiourea,
   (b) from 20 to 25% by weight of urea,
   (c) from 20 to 25% by weight di-ammonium phosphate, and
   (d) from 20 to 25% by weight EDTA.

2. In a process for pickling steel using hydrochloric acid, sulfuric acid, or a mixture of the two acids in a pickling bath, the improvement consisting of the step of adding about 2% by weight of the weight of the acid component of a formulation in accord with claim 1.

References Cited

UNITED STATES PATENTS

1,736,118	11/1929	Gravell	252—149
2,485,529	10/1949	Cardwell et al.	252—149
3,077,381	2/1963	Bergsteinsson et al.	252—148X
3,223,649	12/1965	Langguth	252—146X
3,492,238	1/1970	Wohlberg	252—148X

OTHER REFERENCES

Putilova, Balezin, and Barannik, Metallic Corrosion Inhibitors, Pergamon Press, New York, 1960, p. 89.

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U.S. Cl. X.R.

134—3; 252—137, 148, 149, 152