252-149

CROSS REFERENCE

EXAMINER

165

Dec. 10, 1968 L. E. KOVALSKI 3,415,748

SULFURIC ACID PICKLING BATH

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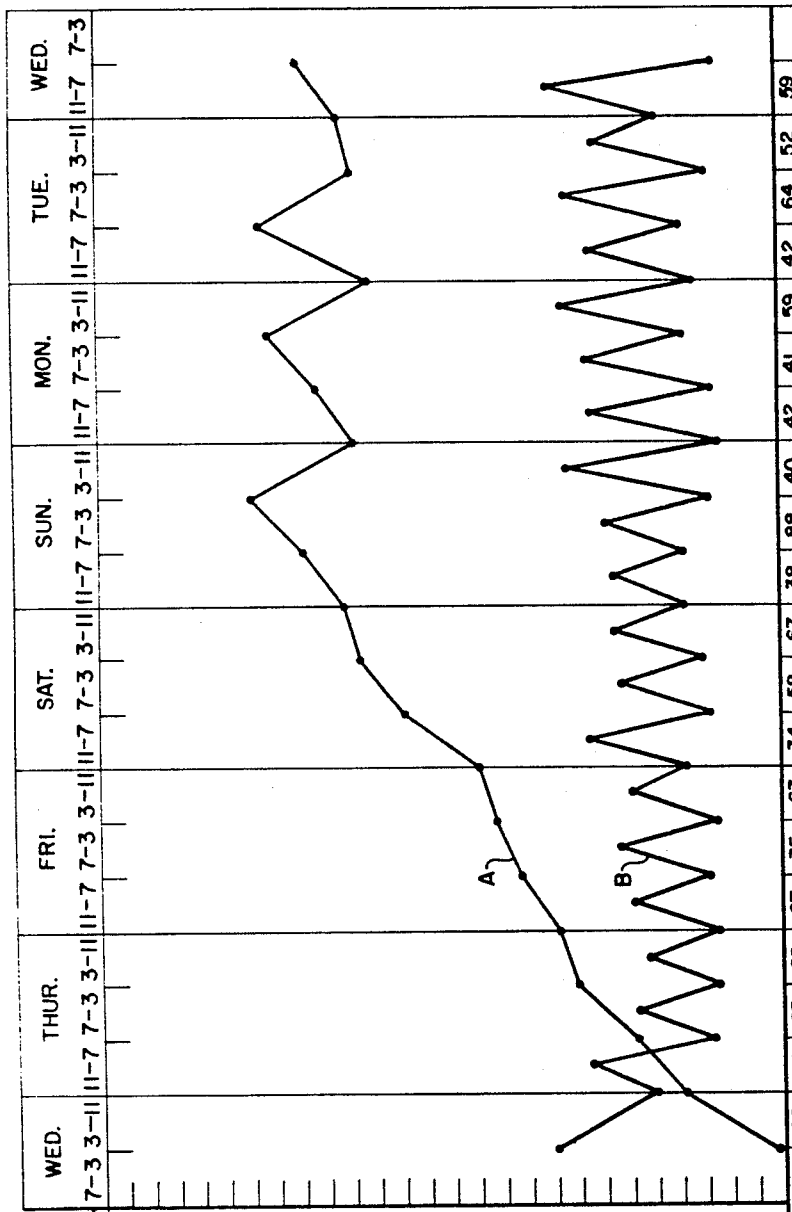

STEEL PICKLED (tons)	38	41	93	69	67	35	63	34	58	67	38	88	40	42	41	59	42	64	52	59										
STEEL-CUMULATIVE	38	79	172	241	308	343	406	440	498	565	603	691	731	773	814	873	915	979	1031	1090										
ACID ADDED (gal.)	250	100	125	125	150	175	150	150	150	175	150	150	175	150	150	175	175	150	150	125										
ACID-CUMULATIVE	250	350	475	600	750	925	1075	1225	1375	1550	1700	1850	2025	2175	2325	2500	2675	2825	2975	3100										
INHIBITOR ADDED (lb.)	20	5	10	5	5	10	5	5	5	5	5	5	5	5	5	5	5	5	5	5										
INHIBITOR-CUMULATIVE	20	25	35	40	45	55	60	65	70	75	80	85	90	95	100	105	110	115	120	125										
SURFACTANT ADDED (gal.)	5	3	2.5	2.5	2.5	3	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	3										
SURFACTANT-CUMULATIVE	5	8	10.5	13	15.5	18.5	21	23.5	26	28.5	31	33.5	36	38.5	41	43.5	46	48.5	51	54										
SOLUTION SIPHONED (gal.)					1217								1220			1220		850												
AVG. SP. GR. OF BATH	1.06	1.10	1.14	1.17	1.20	1.21	1.22	1.26	1.30	1.32	1.34	1.38	1.37	1.37	1.38	1.34	1.36	1.37	1.34	1.37										
ACID CONSUMPTION (lb/ton)	35	41	18	29	35	58	32	59	41	30	53	27	50	48	58	40	48	32	32	46										

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SULFURIC ACID PICKLING BATH

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ABSTRACT OF THE DISCLOSURE

In a method of removing mill scale from steel articles, a steel article is immersed in an aqueous solution containing specific amounts of sulfuric acid, a thiourea and an alkali metal monohydric hydrocarbon secondary alcohol sulfate in which the alcohol radical has from 8 to 19 carbon atoms. The article is retained in the pickling solution until substantially all mill scale has been removed therefrom.

This invention relates to the pickling of ferrous metal surfaces, and more particularly to an improved composition for performing such pickling.

In the pickling of ferrous metals such as iron, carbon steel and alloy steel with an aqueous solution of a mineral acid, such as sulfuric acid, to remove mill scale from the surfaces of such metals, inhibitors are generally added to the pickling bath to decrease acid attack of the metal underlying the scale. Surface active agents, or surfactants, are also added in some instances to increase the efficiency of the pickling bath.

Generally, scaled iron or carbon steel surfaces can be pickled without any great difficulty by means of pickling compositions well known in the pickling art. The pickling of scaled alloy steel surfaces, however, presents additional problems due to the more complex system of anodic and cathodic areas present on the surface of these steels. The pickling problems are increased when a variety of alloys are pickled simultaneously in the same pickling bath.

It is a major object of this invention to provide a pickling composition for the rapid and efficient pickling of alloy steels.

Another object is to provide a bath which will operate efficiently with a high dissolved iron content.

The accompanying drawing is a graph illustrating the amount of ferrous iron (Fe^{++}) permissible in an operating bath of this invention.

I have found that by pickling alloy steels, as well as carbon steels, or mixtures of these steels, in a pickling bath of sulfuric acid, with a specific type of inhibitor and a specific type of surfactant, improved results are obtained in pickling rate, consumption of pickling acid, and surface quality of the pickled product, over the results obtained for similar steels pickled in baths of compositions heretofore known.

The invention comprises, briefly, pickling carbon and/or alloy steels in an aqueous pickling bath of sulfuric acid, thiourea or substituted thioureas, and a surfactant represented by an alkali metal alcohol sulfate derived from a secondary alcohol having from 8 to 19 carbon atoms.

Pickling of carbon steels and alloy steels, including those classed as stainless, tool and alloy constructional steels, in a bath composition of this invention, overcomes many of the problems encountered with known pickling

processes. Productivity, or pickling rate, is increased, even with heavily scaled alloy billets. Acid consumption is decreased, due to longer bath life realized by the fact that the bath functions efficiently even at low acid content. Sludging of the bath is restrained, and surface quality of the pickled steel is quite good. The bath has an unusually high tolerance for dissolved iron.

While the foregoing pickling benefits are obtained over the broad range of steels, they are evidenced particularly when treating alloy steels, including heterogenous mixtures of alloy steels, and steels of similar composition but different heat treatment. Furthermore, mixtures of mill scaled alloys can be pickled simultaneously or successively in the same bath without any significant loss of bath efficiency.

In addition, bath control is relatively simple, as the bath is operable at rather wide temperature and composition ranges.

The bath is particularly applicable to batch pickling of billets, bars, angles, flats or wire.

The composition of the bath of this invention may range as follows:

	Percent by weight
Sulfuric acid (100% H_2SO_4)	1–20
Inhibitor	0.01–0.1
Surfactant	0.03–0.2
Dissolved iron as Fe^{++}	0–15
Temperature	[1] 160–200

[1] Degrees Fahrenheit.

One mode of forming, operating and maintaining a bath according to this invention is given in the detailed example which follows.

EXAMPLE 1

In the particular operation to be described, a mixture of alloy billets of varying size, ranging from 9 x 9 inches to 2.5 x 2.5 inches in cross-sectional area and having a length ranging between 10 and 36 feet, with the mixture having a total weight of between 15 and 20 tons, was pickled in a 6000 gallon capacity tank. To prepare the pickling bath, about 5000 gallons of industrial water were introduced into the tank, and 5 gallons of a 27% aqueous solution of the surfactant known as Tergitol Anionic 4 (sodium tetradecyl sulfate) were added to the water. A 27% aqueous solution represents 2.3 pounds of surfactant per gallon of solution. About 300 gallons of 56° Bé. sulfuric acid were then added to bring the acid concentration to approximately 5% by weight of 100% H_2SO_4. To the resultant mixture, 21 pounds of 1,3-dibutylthiourea were added. The dibutylthiourea, as well as the surfactant, was added in a manner such that the addition was distributed throughout the entire tank solution. The bath was brought to temperature (about 175° F.) by steam emitted from spargers located at each end of the tank. An air jet extending to the bottom of the tank was used to give adequate agitation. Air was emitted from the jet at the rate of 1–5 cu. ft. per min. The billets were immersed in the pickling bath for 2 hours, after which they were removed and rinsed.

The pickling treatment removed the heavy scale from the billets, the surfaces of which presented a clean bright appearance which could readily be inspected visually for surface defects.

A new bath, of the type just described, can be oper-

ated with successive charges of scaled billets for a period of about 8 hours without additions to the bath. The temperature should be maintained, preferably, between 175° and 185° F. For most efficient operation, the acid concentration should be above 3% by weight, although satisfactory operation is maintained with the acid as low as 1%.

If successive charges of billets each represent a weight approximately that of the example, the bath should be replenished at the end of about 8 hours. This can be done by adding 125–150 gallons of sulfuric acid (56° Bé.), about 5 pounds of 1,3-dibutylthiourea and between 2.5 and 3 gallons of the surfactant (27% aqueous solution). The amount of make-up acid and other make-up ingredients to be added, at the end of each 8 hour period, can be determined accurately by analyzing the bath for free sulfuric acid and adding ingredients sufficient to bring the bath up to its original strength. The amount of inhibitor and surfactant to be added, with addition of sulfuric acid, is as follows:

Inhibitor is added in the amount of 4–5.5 pounds for each 100 gallons of acid (100% H_2SO_4) added.

Surfactant is added in the amount of 2–3 gallons (27% by weight aqueous solution) for each 100 gallons of acid (100% H_2SO_4) added.

Such analysis and additions can of course be made at any time during bath operation if it is desired to replenish the bath more frequently than the 8-hour interval mentioned.

Normally, a bath of this invention may be operated for from 7 to 8 days, and for 3 full turns per day, before being dumped to permit cleaning of sludge from the pickling tank. However, the bath can be operated satisfactorily for longer periods if the dissolved iron does not appreciably exceed 15% by weight.

The types of alloy steels pickled in the above example included those designated as AISI 4027, 4118, 4620, 5130, 6150, 8740, 4320H, 5120H, 41L40, 43L70, 01, 06, A2 and W1.

No foam blanket was used on the bath, fumes being conducted away from the bath surface by overhead exhaust.

Bath components can be varied over a wide range, as previously noted. For Example 1, the preferred range of bath composition is as follows:

	Percent by weight
Sulfuric acid (100% H_2SO_4)	2–8
Inhibitor	0.01–0.05
Surfactant	0.05–0.12
Dissolved iron as Fe^{++}	0–15
Temperature	[1]175–185

[1] Degrees Fahrenheit.

The bath of Example 1 was run for seven consecutive days, during which time 930 tons of steel were pickled. Consumption of 56° Bé. sulfuric acid amounted to 3025 gallons, while 117 pounds of 1,3-dibutylthiourea and 53 gallons (27% aqueous solution) of sodium tetradecyl sulfate were consumed. Dissolved iron reached 150 grams per liter on the fifth day. This represented approximately 11% iron calculated as Fe^{++}.

EXAMPLE 2

In another pickling operation, this one utilizing a pickling tank of 4000 gallons capacity, where carbon steel bars, angles, flats, etc., as well as alloy billets are ordinarily pickled, about 1000 gallons of water were introduced into the tank, followed by addition of 15 pounds of 1,3-dibutylthiourea, uniformly distributed. After adding 150 gallons of 66° Bé. sulfuric acid, an additional 1000 gallons of water were added to bring the bath volume to 2150 gallons. At this point, 4 gallons (26% aqueous solution) of surfactant (sodium tetradecyl sulfate) were added with uniform distribution throughout the bath. During each addition, steam from spargers located in the tank walls was introduced into the bath to bring the bath up to temperature and to agitate the bath. To insure thorough distribution of bath components, water additions were made from a hose. When the bath temperature reached 160°–170° F., the volume was adjusted to 2500 gallons by adding more water. The pickling charge, in this case alloy steel billets, was introduced when the bath had acquired a temperature of about 160° F.

In this operation, a foam blanket was used as there was no exhaust hood over the pickling tank. In order further to control fuming, the bath temperature was maintained at between 160° and 170° F. To maintain a desirable pickling rate, at the lower temperature, the acid concentration of the starting bath was higher than that of Example 1.

The pickling time for each charge of between 12–15 tons of steel was about 1.5 hours. It was necessary to add 1 gallon of surfactant and 5 pounds of 1,3-dibutylthiourea after each 8 hour pickling period. Sufficient acid was supplied to maintain the concentration at 7.9% by weight.

With a bath of the type used in Example 2, where it is desired to control fuming, the acid content, as noted above, should be somewhat higher than the preferred operating range for the bath of Example 1. Bath components for Example 2 may preferably range as follows:

	Percent by weight
Sulfuric acid (100% H_2SO_4)	3–15
Inhibitor	0.03–0.08
Surfactant	0.08–0.15
Dissolved iron (Fe^{++})	0–15

With the higher acid content of this bath, the operating bath temperature should range between 160°–170° F.

Alloy billets of the type described in Example 1 were pickled in the bath of Example 2 when the fresh bath was first used. Later, a mixture of alloy and carbon steel billets were pickled simultaneously. All articles pickled displayed a clean surface after 1.5 hours. It is necessary, in the case of billets, to remove the scale sufficiently completely to reveal any surface defects, so that any defects present can be removed by scarfing, etc. Improperly pickled billets often retain sufficient tenacious scale in localized parts to completely obscure the underlying surface defects.

While the baths of Examples 1 and 2 were each run for a one-week period before dumping, baths of the same composition described in each of the examples have been in use for a period of at least three months at the same installations, wherein the baths were renewed at the end of each weekly period. The advantages of the baths heretofore mentioned were realized throughout the entire three month period.

In order to illustrate the advantages which can be expected from a pickling operation with a bath of this invention, a laboratory test run was made on alloy steel specimens. Weighed specimens of alloy steel billets with mill scale, measuring 4 by 4 by 4 inches were suspended in approximately 3.2 gallons of an aqueous solution containing 5.0–5.8% by weight of sulfuric acid, 0.05% by weight of 1,3-dibutylthiourea and 0.10% by weight of 27% aqueous solution of sodium tetradecyl sulfate at 185°–195° F. The solution, contained in a 5½ gallon glass cylinder, was preheated by ceramic immersion heaters and agitated with a stirring motor. The billet specimens were at room temperature when introduced into the bath, and were allowed to remain in the bath until completely descaled. When descaled, the specimens were rinsed with cold water, blown dry with air, and reweighed. The bath was analyzed to determine acid consumption, ferrous iron increase, and volume loss.

A similar test was conducted in an aqueous bath containing uninhibited sulfuric acid in an amount of approximately 5.5% by weight, as a control.

Results of the tests are given in the following table:

Test Billet Grade	Initial Weight of Billet (lbs.)	Descaling Time (min.)	Loss of Weight of Billet (lb.)	Sulfuric Acid (100%) in Bath Initial (lb.)	Sulfuric Acid (100%) Consumed (lb.)	Increase of Iron (Fe^{++}) in Bath (lb.)	Volume Loss of Bath (gal.)	Reduction in Descaling Time (percent)
Pickling Solution—Bath of Invention Series I:								
1. AISI 4619	18.6	30	0.024	1.566	0.042	0.015	0.13	45.4
2. AISI 51B60H	13.6	10	0.022	1.588	0.046	0.013	0.13	33.3
3. AISI 4620	22.4	30	0.033	1.618	0.079	0.024	0.26	50.0
4. AISI 4620	20.4	35	0.044	1.435	0.062	0.035	0.13	(1)
Total	75.0	----------	0.123	----------	0.229	0.087	0.65	----------
Uninhibited Sulfuric Acid Baths Series II:								
1. AISI 4619	20.3	55	0.271	1.466	0.611	0.205	0.26	----------
2. AISI 51B60H	14.3	15	0.044	1.433	0.099	0.037	0.26	----------
3. AISI 4620	20.5	60	0.426	1.444	0.668	0.388	0.40	----------
4. AISI 4620	18.2	35	0.293	1.438	0.569	0.212	0.40	(1)
Total	73.3	----------	1.034	----------	1.947	0.842	1.32	----------

[1] Each pickled for same length of time; about 80% of scale removed in uninhibited sulfuric acid. Each of the other specimens were pickled to substantially complete scale removal.

In Series I, Tests 1–4 were made in the same bath, starting with 3.17 gallons of pickling solution in Test 1. In Tests 1–3, no addition was made to the original bath volume of 3.17 gallons, while in Test 4, the bath was brought back initially to the original volume of 3.17 gallons.

In Series II, Tests 1 and 2 were made in one bath, while Tests 3 and 4 were made in a second bath. In each test in Series II, the bath was brought initially to the same volume (3.17 gal.) and acid content.

As will be seen from the table, the bath of this invention effects a rapid descaling of alloys, with a low acid consumption and a low weight loss of the pickled product.

One of the outstanding features of this bath is its high ferrous iron tolerance. Referring to the drawing, curve A represents the ferrous iron (Fe^{++}) content in grams per liter of one pickling tank for a production run of one week. Curve B represents the acid content range in grams per liter.

Starting with a clean tank on the first operating turn of the first day of the run, with a pickling bath of 4000 gallons of water, 250 gallons of sulfuric acid (56° Bé.), 20 pounds of 1,3-dibutylthiourea and 5 gallons of 27% aqueous solution of sodium tetradecyl sulfate, the acid was maintained at between 1% and 6% by weight (as 100% H_2SO_4). Some siphoning of pickling solution was necessary at intervals to maintain a proper volume of solution in the tank, but ferrous iron was permitted to build up steadily. After four full days of operation, the iron level had reached 200 grams per liter, at which point 691 tons of steel had been pickled. The bath was run for approximately three more days with the ferrous iron content above 150 g./l., during which time 394 additional tons of steel were pickled. As will be observed from the specific gravity values shown in conjunction with the graph, the gravity of the bath ranged between 1.32 and 1.38 when the iron was maintained at 150 g./l. or above, and at 200 g./l. iron, for example, the iron content of the bath was approximately 14.5%, or approximately 39.5% $FeSO_4$. All specific gravities were determined at room temperature.

The run was discontinued at the end of a week to permit cleaning. Steels pickled included those designated as AISI 4037, 4145, 4340, E52100, 8640, 4815H, 4150H, 8620H, 01, A4, W2, 55, L6 and P6, all of which presented clean surfaces when removed from the pickling operation.

Thiourea, or any of the substituted thioureas, may be used in the bath, although the symmetrical thioureas of the group including, for example, diethyl-, diisopropyl-, dibutyl- and ditolylthiourea are preferred for the pickling of alloy steels, with 1,3-dibutylthiourea producing the best results.

The surfactant may be any available alkali metal secondary alcohol sulfate in which the alcohol radical has from 8 to 19 carbon atoms. Examples of compounds within this group are 2-ethyl hexyl sulfate, sodium hexadecyl sulfate, sodium tetradecyl sulfate, sodium heptadecyl sulfate and sodium undecyl sulfate. Other surfactants of this group are disclosed in U.S. Patent No. 2,088,020 to Wickert. It is preferable, when using compounds of between 12 and 19 carbon atoms, to have the sulfate radical attached to a carbon atom near the center of the alkyl chain. Compounds in the lower range of carbons, i.e. those from 8 to 11 carbons, have some tendency to foam.

While the mechanism by which this pickling bath operates is not fully understood, it is recognized that the effect of ferrous iron in the bath is suppressed. There is little foaming, especially when surfactants in the higher carbon ranges of the group disclosed are used. The bath pickles a variety of alloy and carbon steels rapidly and cleanly, with no special control problems.

I claim:

1. A pickling method for removing heavy mill scale from an alloy steel article having a coating of mill scale which comprises immersing said article in an aqueous solution in which the active pickling solute consists essentially of sulfuric acid, calculated as 100% H_2SO_4, in an amount of from 1% to 20% by weight, a thiourea in an amount of from 0.01% to 0.1% by weight, and an alkali metal monohydric hydrocarbon secondary alcohol sulfate in which the alcohol radical has from 8 to 19 carbon atoms in an amount of from 0.03% to 0.2% by weight for a time sufficient to remove substantially all of the scale from said article, said solution containing from zero up to 150 grams/liter dissolved iron during pickling.

2. The method according to claim 1 in which sulfuric acid is present in an amount of from 2% to 8%, the thiourea is present in an amount of from 0.01% to 0.05%, and the alkali metal alcohol sulfate is present in an amount of from 0.05% to 0.12%.

3. The method according to claim 1 in which the thiourea is 1,3-dibutylthiourea.

4. The method according to claim 1 in which the sulfate is sodium tetradecyl sulfate.

5. The method according to claim 3 in which the sulfate is sodium tetradecyl sulfate.

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U.S. Cl. X.R.

252—149, 152; 134—3, 41; 156—18; 148—6.24; 117—49