

March 18, 1969

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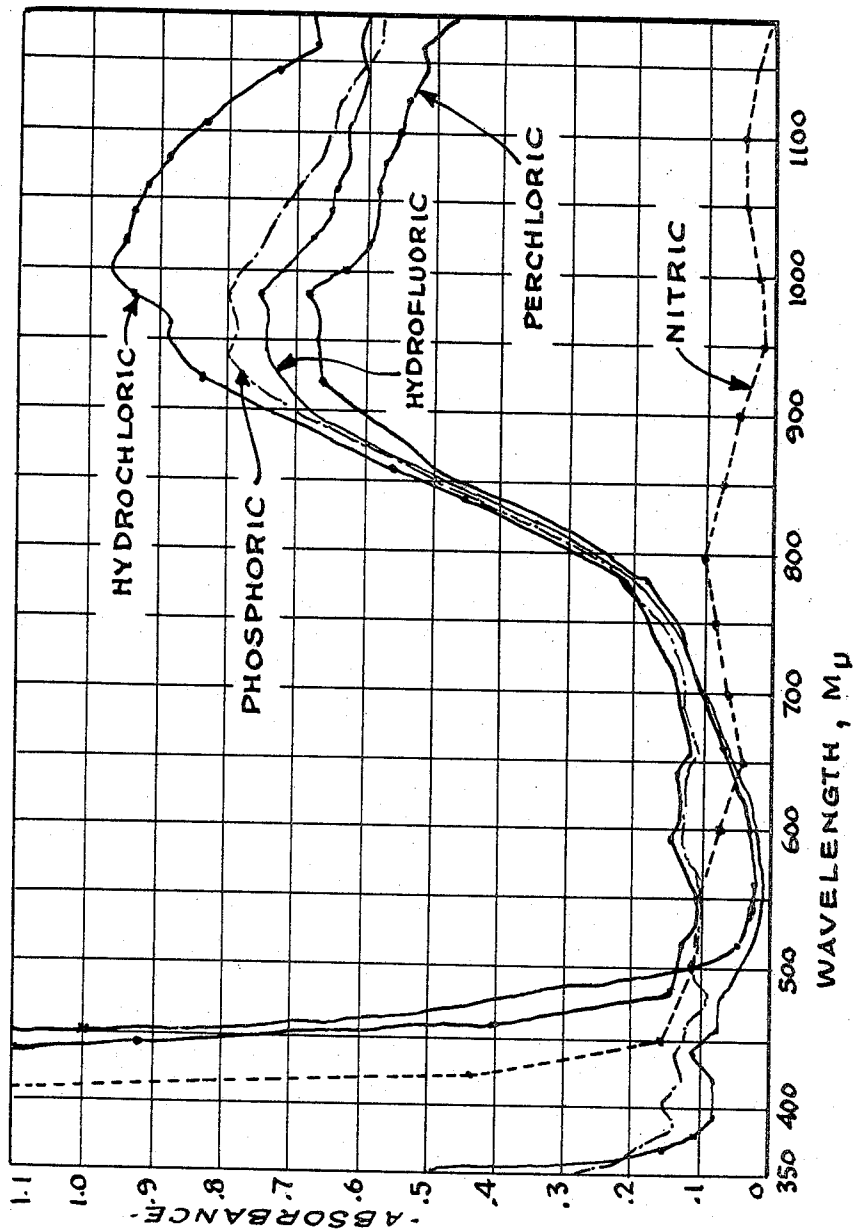
3,433,670

PICKLING BATH CONTROL APPARATUS AND METHOD

Filed Oct. 21, 1965

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Fig. 1
ABSORPTION SPECTRA OF FE ION IN HYDROCHLORIC,
PHOSPHORIC, HYDROFLUORIC, NITRIC, AND PERCHLORIC ACIDS.



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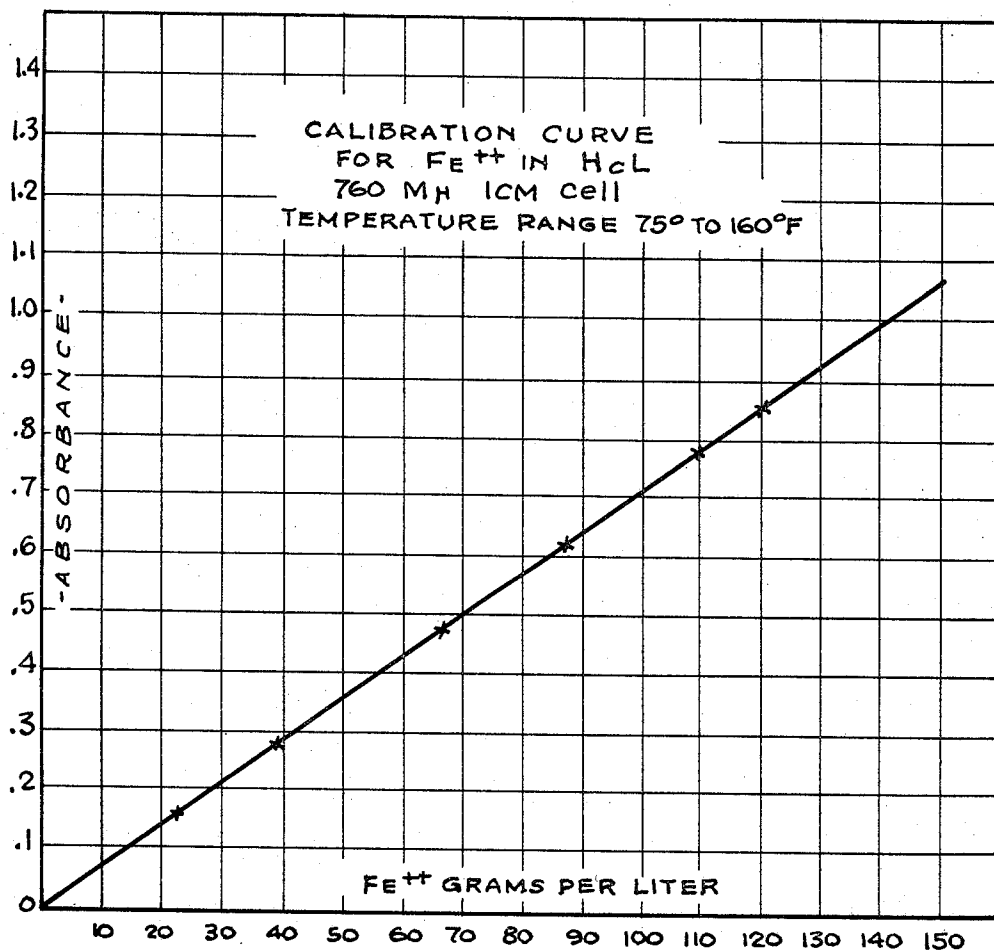
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Sheet 2 of 4

Fig. 2



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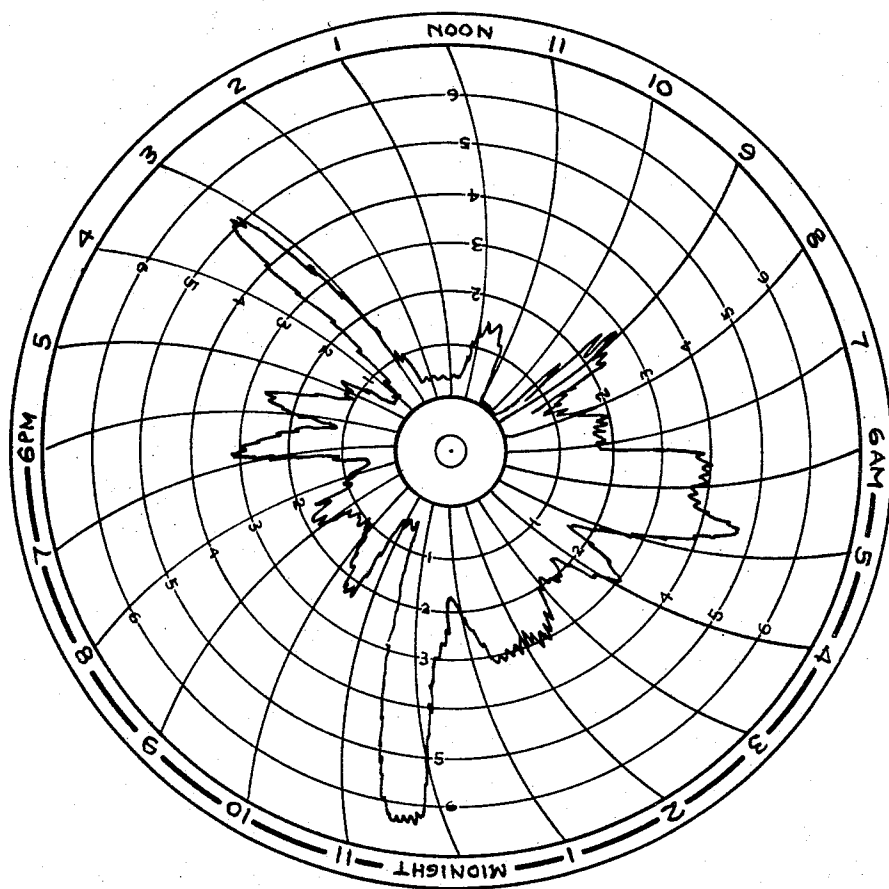
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Fig. 5



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PICKLING BATH CONTROL APPARATUS AND METHOD

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Chicago, Ill., a corporation of Delaware
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The portion of the term of the patent subsequent
to Jan. 22, 1980, has been disclaimed

U.S. Cl. 134-10

Int. Cl. B08b 3/10

7 Claims

This invention relates generally to improvements in the process and apparatus for cleaning and pickling metals, and more particularly for improvements in cleaning and pickling iron and steel by means of continuous coil pickling.

Mill scale and other contaminants are generally removed from a hot rolled steel strip prior to cold rolling or other operations by means of mineral acids, such as sulfuric and hydrochloric acid, while stainless steel can be pickled in hydrofluoric and/or nitric acids. The operation is usually carried out continuously by passing the steel strip at relatively high speeds through a series of tanks containing an aqueous solution of a pickling acid. Although the movement of the strip can be concurrent with respect to the direction of flow of the pickling solution, it is conventional to employ countercurrent movement of the steel strip and acid pickle liquor through a series of tanks so that the strip first enters the tank containing the weakest acid and leaves the tank containing the strongest acid. Fresh acid is added to the tank from which the strip finally leaves the pickling solution as required to compensate for the acid consumed by chemically reacting with the ferrous metal surface of the strip. The pickle bath in the tank which the ferrous metal strip first enters may have an acid concentration from about 2% to 10% on a volume percentage basis, and the acid concentration in the bath of the tank from which the strip emerges can have an acid concentration from about 10% to about 25% with a stepwise gradation of acid concentrations in the intermediate tanks. The maximum allowable ferrous ion concentration in the tanks is about 10% on a weight basis.

In order to obtain effective operation of the pickling line and to avoid undue waste of acid, it is necessary to keep a continuous check on the acid concentration and the ferrous ion content in the pickling tanks. Heretofore a system has been devised for continuously measuring and controlling the concentration of sulfuric acid and ferrous sulfate salt in a pickling bath, as in the Hill Patent No. 3,074,277. There is, however, increasing use of acids other than sulfuric for pickling ferrous metals. For example, hydrochloric acid permits an increased rate of scale removal and has recently been used in increasing amounts for pickling iron and steel strips to remove mill scale.

In pickling iron and steel products it is also important to maintain a proper concentration of pickling inhibitor in the acid pickling bath in addition to controlling the acid and ferrous ion concentrations. Heretofore the inhibitor has been added intermittently throughout the pickling process, and there has not been an optimum amount of inhibitor present in the bath. As a result, excess ferrous metal is solubilized after the mill scale has been completely removed.

It is therefore an object of the present invention to provide an improved and more economical pickling process for the cleaning and removal of mill scale and other objectionable material from metal surfaces.

It is a further object of the present invention to provide an improved process for the continuous coil pickling of iron and steel.

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It is still a further object of the present invention to provide a continuous process for controlling the acid inhibitor concentration in an acid pickling bath.

Still another object of the present invention is to provide an improved process for controlling the acid concentration and the ferrous ion concentration of a ferrous metal pickling bath containing an acid which forms a substantially colorless ferrous metal salt in aqueous solution.

Other objects of the invention will be apparent from the detailed description and claims to follow when read in conjunction with the accompanying drawings wherein:

FIG. 1 is a graph showing the absorption of ferrous ion in various ferrous metal acid pickling solutions over the indicated range of light wave lengths;

FIG. 2 is a graph showing the calibration curve for ferrous ion in a hydrochloric acid pickling solution;

FIG. 3 is a schematic diagram of a continuous coil pickling line;

FIG. 4 is a schematic diagram of one control arrangement of the present invention; and

FIG. 5 is a reproduction of a chart showing a recording of the additions of hydrochloric acid to a pickling solution over a 24-hour period by a control arrangement of the present invention.

It has been found that in a ferrous metal pickling bath the concentration of a certain mineral acid, particularly hydrochloric, hydrofluoric and phosphoric acids, which produce substantially colorless ferrous iron salts in an aqueous acid solution, can be accurately determined by measuring with colorimetric means the absorption of the substantially colorless acid pickling solution. Thus, by passing continuously a stream of the pickling bath through an optical flow cell and exposing the cell to light having a wave length, preferably in the infra-red region and particularly between about 750 and about 1100 millimicrons, while simultaneously determining the specific gravity of the acid pickling solution, and combining the signals obtained in the foregoing measurements to correct the specific gravity reading by subtracting therefrom the contribution to the specific gravity made by the ferrous salt in the pickling solution, a resultant corrected signal is obtained which corresponds to the concentration of only the acid in the pickling solution. And, by feeding the corrected signal corresponding to the acid concentration to suitable acid control means, it is possible to continuously and accurately control the concentration of the said acid in the pickling bath.

The foregoing system of measurement and control of the acids which form substantially colorless ferrous salts in aqueous solution is based on the unexpected finding that the ferrous ion in the said acids in an aqueous acid pickling solution exhibits a definite and characteristic absorption spectrum when exposed to light, preferably having a wave length in the infra-red region of between about 750 and 1150 millimicrons. The ferrous ion in an aqueous solution of acids, such as hydrochloric, hydrofluoric, phosphoric and perchloric acids or a combination of these acids, exhibits substantially the same absorption spectra as does the ferrous ion in an aqueous solution. It is thus possible to obtain accurate photometric reading corresponding to the concentration of a ferrous ion in the aqueous acid pickling solution, even in the absence of a markedly colored ferrous salt of the acid being formed in the pickling bath. It has been found that uniform results are obtained for all concentrations of ferrous iron and acid so that the Beer-Lambert law applies up to the boiling point of the pickling solution (see FIG. 2).

It will be evident from FIG. 1 that the absorption spectrums of ferric ion in an aqueous solution of nitric acid, is somewhat different from the spectrum of the other acids

used for pickling iron and low carbon steel. And while the infra-red colorimetric absorption technique used for the latter acids can be used, it is less suited for use on nitric acid pickling solutions for ferrous metals and ferrous metal alloys where high sensitivity is required. If desired, however, other wave lengths in the usable spectrum can be used. For example, in nitric acid pickling solutions, the iron is oxidized to the ferric ion and ferric nitrate containing solutions have a visible yellow color. The use of infra-red light rays, however, is preferred wherever possible because the absorption thereof is largely independent of temperature and errors introduced by variations in temperature are avoided.

In the determination of the ferrous chloride concentration of a hydrochloric acid pickle liquor, for example, it has been found that a photometric technique is particularly satisfactory. By passage of a beam of light of suitable wave length as indicated herein through a cell containing the ferrous metal pickle liquor sample, the intensity of the transmitted or unabsorbed light is a measure of the ferrous ion concentration which can be readily converted to give a direct indication of the concentration of the ferrous salt in the pickling solution. It will be evident from FIG. 1 that the use of a filter transmitting light in the wave length region of from about 750 to about 1100 millimicrons, will give maximum sensitivity for the instrument. Various colorimetric or spectrophotometric devices are well known for use with a continuous stream of liquid. The industrial flow colorimeter manufactured by Beckman Instruments, Inc., for example, is a typical device which may be used with good results in the control system of the present invention. The sample liquid is passed through an absorption cell of glass, plastic, or the like having transparent walls and arranged to provide a light path of predetermined length. A constant voltage light source is employed with a suitable filter to obtain a beam of light of the desired wave length which is passed through the sample liquid in the absorption cell. The unabsorbed or transmitted light is received by a photoelectric cell, and a suitable electrical output signal is transmitted which is a measure of the ferrous ion concentration of the sample liquid.

One application of the present invention to controlling the acid concentration of a ferrous metal pickling bath in a continuous coil pickling line is shown schematically in FIG. 3 of the drawing, wherein a series of four tanks, 10, 10a, 10b and 10c, are connected in continuous flow arrangement with the water inlet 11, acid inlet 12, and an acid inhibitor inlet 13 feeding water, acid and acid inhibitor, respectively, into tank 10c, and with tank 10 having a pickle bath overflow to waste. An endless strip of ferrous metal 15, such as black plate, enters tank 10 from a continuous coil 16 and passes countercurrently through the pickling bath in each of the tanks, leaves the pickling bath from tank 10c and is wound onto a coil.

In FIG. 4 of the drawing is shown schematically a preferred control system embodying the present invention having in combination the principal components comprising a photometric means 20 for measuring the concentration of the ferrous metal ion in the pickling fluid sample withdrawn continuously from tank 10c, water valve flow and controller means 25, specific gravity determining means, such as a density flow-through transmitter 30 for determining the specific gravity of the pickling solution, compensator means 40 for combining the measured values for the ferrous ion concentration and the specific gravity of the pickling solution to give a resultant value corresponding to the concentration of the acid in the pickling solution, recorder means 45 for indicating the specific gravity and concentration of the pickling solution, and acid flow control means 50 for indicating and controlling the flow of acid to the pickling tank in order to maintain a predetermined concentration of acid in the pickling solution.

In photometrically determining the ferrous ion concentration of a ferrous metal pickling solution comprising an acid, a sample of pickling solution is withdrawn from tank 10c by sample withdrawal line 17 and is conveyed to a control apparatus designated 18. A small aliquot of the pickle solution is continuously passed through the photometric cell (not shown) of a colorimeter 20 having a beam of light of suitable wave length which passes through the sample of pickle solution in the cell. In the system presently used wherein a maximum concentration of metal of about 110 grams per liter is encountered, a wave length of 760 millimicrons provides the required sensitivity with the standard instrumentation commercially available. In other applications, however, another wave length in the infra-red region can be used. The colorimeter 20 measures the ferrous metal ion concentration in the pickling solution by photoelectric comparison of light transmission. The colorimeter 20 can be either a single beam or a split beam colorimeter.

The electrical output signal from the colorimeter 20 passes through an amplifier means 22 and preferably actuates a chart recorder-controller means 25 which preferably makes a continuous recording of the concentration of ferrous ion in the pickling solution. The recorder-controller means 25 delivers a signal to an automatic flow control valve 26 in the water feed line 12 leading to the tank 10c for introduction of an amount of water required to keep the ferrous metal ion concentration below a predetermined maximum permissible level. If desired, a water flow meter and an integrating recorder can be used to give a continuous measurement and record of water flow to the pickling tank 10c.

While the specific gravity of the pickling solution can be determined by any of the well known types employed for determining the specific gravity of liquids, it is preferred to pass the pickle solution sample from the colorimetric flow cell to a specific gravity flow-through transmitter 30, such as manufactured by the Minneapolis-Honeywell Regulator Company of Philadelphia, Pa. The density transmitter 30 gives one signal which preferably goes directly to one pen 43 of a two-pen recorder means 45 for continuously indicating the specific gravity of the pickling solution. Another line from the transmitter 30 also sends a signal to the compensator means 40 to which the signal from the colorimeter 20 is simultaneously fed. The output from the compensator 40 is the impulse from the density transmitter 20 minus the signal from the colorimeter 20 corresponding to the ferrous metal ion concentration and the corrected output signal represents the percentage concentration of the acid in the pickling solution, in accordance with the known relationships between the specific gravity and concentration. The resultant or corrected output signal preferably goes to the second pen 44 of the two-pen recorder 45 for continuous recording of the acid concentration by percent acid. The corrected output signal goes to the acid flow controller means 50. The acid flow is measured by a magnetic meter 52 which sends impulse back to the acid flow controller means 50. The acid flow controller of the controller means 50 regulates the acid flow valve 55 interposed between the pickle acid tank 56 and the tank 10c, and as required to maintain the desired acid concentration in the pickle solution. FIG. 5 of the drawing is a reproduction of an actual graph recording the additions of hydrochloric acid to a continuous pickling bath for black plate over a 24-hour period.

In order to further improve the efficiency of the pickling operation, automatic means coordinated with the acid flow control means 50 are provided for controlling the addition of acid inhibitor to the acid pickling bath. It is important to have sufficient inhibitor in the pickling solution to prevent excess removal or solubilizing of the ferrous metal by the pickling acid after the mill scale has been removed. Thus, by providing means for adding inhibitor in a fixed proportion to the amount of pickling acid added

to the pickling tank, it is possible to maintain at all times the optimum amount of acid inhibitor in the pickling bath. A particularly effective means for adding the required amount of inhibitor is shown in FIG. 4 of the drawing, wherein the output signal from the acid flow controller means 50 is fed to a ratio relay 60 which has associated therewith a ratio set device 62 which limits the output of the ratio relay to a fixed or set proportion of the acid flow control output. The proportioned signal from the inhibitor ratio relay 60 goes to an inhibitor flow control valve 65 which allows inhibitor to be added to the pickling tank through the acid inhibitor inlet 13 in a direct and constant ratio to the volume of acid added to the pickling tank through acid flow valve 55, and provides continuous and automatic means for adding said inhibitor in view of proportion to the widely varying amounts of acid added to the pickle bath.

The improved efficiency of the pickling process employing the improved automatic control system of the present invention, as compared with the conventional manual control system, is evidenced by the following table:

TABLE OF COMPARISON OF MANUAL AND AUTOMATIC CONTROL OF STEEL PICKLING

Run	Manual Control		Run	Automatic Control		Steel processed as percent of manual control rate
	H ₂ SO ₄	Fe		H ₂ SO ₄	Fe	
A1-----	9.6	30.0	G1-----	12.5	29.0	109.0
A2-----	11.3	16.6	G2-----	12.5	29.0	
A3-----	7.4	26.0	G3-----	12.5	30.0	
A4-----	10.5	15.0	G4-----	12.5	30.0	
A5-----	12.5	33.0	G5-----	12.5	30.0	
B1-----	9.7	26.0	H1-----	12.0	33.0	127.8
B2-----	10.0	18.0	H2-----	12.5	31.0	
B3-----	12.4	12.0	H3-----	12.5	30.0	
B4-----	11.7	23.0	H4-----	15.0	30.0	
B5-----	8.5	24.4	H5-----	15.0	30.0	
C1-----	9.4	17.0	I1-----	16.0	31.0	110.9
C2-----	9.0	17.5	I2-----	15.5	30.0	
C3-----	10.3	20.0	I3-----	15.0	30.0	
C4-----	9.5	22.0	I4-----	15.0	30.0	
C5-----	10.5	22.0	I5-----	15.0	30.0	
D1-----	10.0	30.0	J1-----	15.0	30.0	109.5
D2-----	8.7	12.5	J2-----	15.5	30.0	
D3-----	9.3	25.0	J3-----	16.0	30.0	
D4-----	8.9	8.0	J4-----	15.5	30.0	
D5-----	7.8	25.0	J5-----	15.5	30.0	
E1-----	10.6	16.0	K1-----	15.5	30.0	120.5
E2-----	11.0	34.0	K2-----	16.0	31.0	
E3-----	15.0	37.0	K3-----	16.5	27.5	
E4-----	10.6	20.0	K4-----	17.0	33.0	
E5-----	9.6	19.0	K5-----	17.0	30.0	
F1-----	9.0	18.0	L1-----	16.5	30.0	111.6
F2-----	8.1	11.8	L2-----	16.0	30.0	
F3-----	8.5	13.8	L3-----	15.5	30.0	
F4-----	10.5	21.5	L4-----	16.0	30.0	
F5-----	12.9	14.0	L5-----	16.5	30.0	

Acid used: Manual 100%; automatic 96.8%.

It will be understood that, if desired, the herein disclosed system for automatically controlling the addition of inhibitor to a metal pickling bath can be used with any control system which provides a signal, whether mechanical, electrical or pneumatic, corresponding to the concentration of the acid in the pickling solution at any given time, such as with the system disclosed in my U.S. patent No. 3,074,277 and in my copending application Ser. No. 218,786, filed Aug. 22, 1962, now abandoned.

While sulfuric acid and hydrochloric acid are most commonly used for pickling low carbon steel strips, such as black plate, it should be understood that in pickling other metals, such as stainless steel or other alloy steels or high carbon steels, it is generally advisable to use other acids or combination of acids. The process of the present invention can also be used for controlling the acid and metal concentrations in the latter pickling baths.

Although the invention has been described with reference to a particular embodiment thereof, it is to be understood that various modifications and alternatives may be resorted to without departing from the scope of the invention as defined in the appended claims.

I claim:

1. In a ferrous metal treating process using a pickling solution containing an acid selected from the group consisting of hydrochloric, hydrofluoric, nitric, phosphoric, and perchloric acids and wherein the said acid is consumed by reaction with the metal in aqueous solution, and wherein makeup pickling acid is added to said solution during the pickling process, an improved method of controlling the addition of pickling acid to said pickling solution which comprises; photometrically measuring the concentration of the ferrous ion concentration in said pickling solution containing said pickling acid to obtain a first signal which is a measure of the concentration of said ferrous ion of said pickling solution, measuring the specific gravity of said pickling solution to obtain a second signal, combining the said first and second signals to obtain a corrected signal which is a measure of only the acid concentration of the said solution, and feeding said corrected signal to an acid valve flow control means which effects addition of acid to said solution when the acid concentration drops to a predetermined value.

2. In a ferrous metal acid pickling process using a pickling solution containing an acid selected from the class consisting of hydrochloric, hydrofluoric, phosphoric, and perchloric acids and wherein the said acid is consumed by reaction with the ferrous metal to form a substantially colorless ferrous metal salt in aqueous acid solution, and wherein makeup pickling acid is added to said pickling solution during the pickling process, an improved method of controlling the addition of pickling acid to said pickling solution which comprises; photometrically measuring the ferrous ion concentration of said pickling solution containing a said pickling acid by passing a beam of light having a wave length in the infra-red spectrum through a portion of said pickling solution and obtaining a first signal which is a measure of the ferrous salt concentration of said solution, measuring the specific gravity of said solution to obtain a second signal, combining the said first and second signals to obtain a corrected signal which is a measure of the acid concentration of the said solution, and feeding said corrected signal to an acid valve flow control means which effects addition of acid to said solution when the acid concentration drops to a predetermined value.

3. In the pickling of a ferrous metal by contact with an aqueous acid pickling solution containing an acid selected from the group consisting of hydrochloric, hydrofluoric, phosphoric and perchloric acids wherein said acid is consumed by conversion to ferrous acid salt and wherein makeup acid is added to said solution, the improved method of controlling a ferrous acid salt content and the concentration of said acid pickling solution which comprises; withdrawing a sample stream of said pickling solution, passing said stream through a colorimeter and photometrically determining by means of a colorimeter the ferrous metal ion content of said stream of said pickling solution and obtaining a first signal which is a measure of the ferrous metal salt concentration of said pickling solution, measuring the specific gravity of said pickling solution to obtain a second signal which is a measure of the specific gravity of said pickling solution, combining said first and second signals and obtaining a corrected signal which is a measure of the acid concentration of said pickling solution, feeding said corrected signal to an acid flow valve means and regulating the addition of makeup acid to said solution in response to said corrected signal.

4. In the pickling of a ferrous metal by contact with an aqueous hydrochloric acid pickling solution wherein hydrochloric acid is consumed by conversion to ferrous chloride and wherein makeup hydrochloric acid is added to said solution during the pickling process, the improved method of controlling the hydrochloric acid concentration which comprises; removing a sample portion of said

pickling solution and photometrically measuring the ferrous ion content thereof and obtaining a first signal which is a measure of the ferrous chloride concentration of said solution, measuring the specific gravity of at least a portion of said solution and obtaining a second signal which is a measure of the specific gravity of said solution, combining said first and second signals and obtaining a corrected signal which is a measure of the hydrochloric acid concentration of said solution, regulating the addition of makeup hydrochloric acid to said solution by means of said corrected signal.

5. In an acid pickling process for a metal wherein acid is consumed by conversion to a metal salt and wherein makeup pickling acid and a pickling acid inhibitor are added to the pickling solution during the pickling process, the improved method of controlling the addition of inhibitor to said metal pickling solution in a constant proportion to makeup acid added to said pickling solution, which comprises; obtaining a signal which is a measure of the pickling acid concentration of said solution, feeding said signal simultaneously to a pickling acid valve flow control means which controls the flow of makeup acid to said solution and to a device which converts said signal to a predetermined proportion of the original value thereof to provide an output signal, and feeding said output signal from said device to an inhibitor flow valve control means which controls the flow of inhibitor into said pickling solution; whereby inhibitor is added to said pickling solution in a predetermined proportion to the concentration of pickling acid in said pickling solution.

6. In an acid pickling process for a ferrous metal wherein acid is consumed by conversion to ferrous acid salt and wherein makeup pickling acid and pickling acid inhibitor are added to said solution during the pickling process, the improved method of controlling the addition of a pickling acid inhibitor to said ferrous metal pickling solution as a constant proportion of makeup acid added to said pickling solution which comprises; obtaining a signal which is a measure of the pickling acid concentration of said solution, feeding said signal simultaneously to a pickling acid valve flow control means which con-

trols the flow makeup acid to said solution and to a ratio relay device which converts the signal from said acid flow control means to a predetermined constant proportion thereof, and feeding the output signal from said ratio relay device to an inhibitor flow valve control means; whereby said inhibitor is added to said pickling solution in a predetermined proportion of the addition of said makeup acid.

7. Apparatus for automatically controlling the addition of inhibitor to an acid pickling solution in a predetermined proportion to the amount of pickling acid added which comprises means for measuring the concentration of pickling acid in said pickling solution to provide a first signal which is proportional to said pickling acid concentration, means responsive to said first signal for regulating the addition of makeup acid to said pickling solution, means for simultaneously conveying said first signal to an inhibitor flow valve control means, said inhibitor flow valve control means having associated therewith a ratio relay means for converting said first signal to a predetermined proportion of said first signal and giving a corrected signal, and said inhibitor flow valve means being responsive to said corrected signal and adding inhibitor to said pickling solution in proportion to the amount of pickling acid added thereto.

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U.S. Cl. X.R.

23—230, 253; 73—439; 134—15, 18, 41, 57