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ACID CONCENTRATION IN PICKLING SYSTEM
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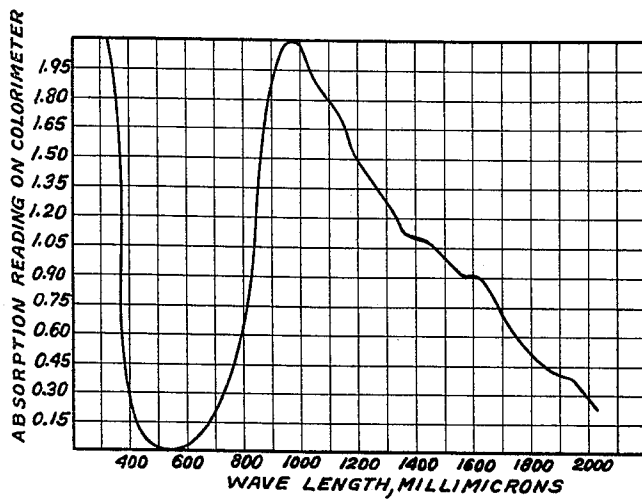
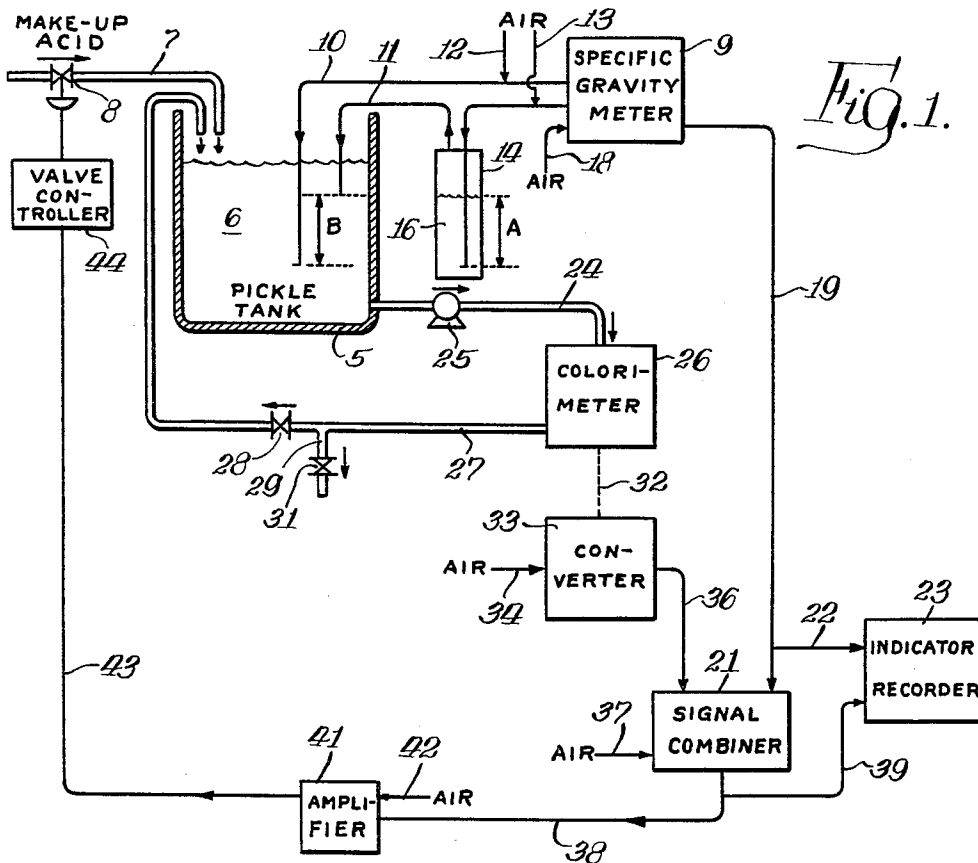


Fig. 2.

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1

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METHOD AND APPARATUS FOR AUTOMATIC CONTROL OF ACID CONCENTRATION IN PICKLING SYSTEM

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This invention relates to improvements in the pickling of iron or steel and more particularly to improvements in the control of acid concentration in a sulfuric acid pickling process.

Continuous pickling of iron or steel strip material involves passage of the iron or steel strip and an aqueous sulfuric acid pickle liquor through a series of pickling tanks or vessels. Although the movement of the strip may be concurrent with respect to the direction of acid flow, it is more usual to provide for countercurrent movement of the strip and pickle liquor through the series of tanks. In other words, the iron or steel strip enters the system at the tank containing the weakest acid which is removed and either discarded or regenerated, and the strip leaves the system from the tank containing the strongest acid and to which fresh or make-up acid is added as required to compensate for consumption of acid by conversion to ferrous sulfate. For example, the bath in the tank which the ferrous metal strip first enters may have a sulfuric acid concentration (volume percent basis) of from about 2% to about 10%, and the bath in the tank from which the strip emerges may have an acid concentration of from about 10% to about 25%, it being understood that there is a stepwise gradation of acid content in the intervening tanks.

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 sulfate content in each of the pickling tanks. Heretofore, this has been accomplished by routine chemical analysis of bath samples taken periodically from the tanks, and on the basis of such control analyses the operator of the line makes the necessary withdrawal of spent acid and addition of fresh or make-up acid. It has been recognized that such strictly manual control techniques are costly, time consuming, and inefficient. At best, the operator obtains only sporadic and belated information as to the actual chemical content of a given pickle tank. Moreover, the manual control scheme not only requires the continuous efforts of a number of workers but also results in substantially less than optimum utilization of acid. Accordingly, there is a definite need for a reliable automatic control system which is capable of providing continuous information regarding acid concentration and also automatically regulating the addition of fresh acid to maintain the acid concentration in the system within predetermined limits.

A primary object of the present invention is to provide a novel method of automatically controlling the acid concentration of a sulfuric acid pickling bath.

A related object of the invention is to provide novel apparatus for carrying out the aforementioned object.

A more specific object of the invention is to provide a novel automatic control scheme for measuring the acid concentration of a sulfuric acid pickle bath and for controlling the addition of fresh acid in accordance with such measurement.

Other objects and advantages of the invention will become evident from the subsequent detailed description taken in conjunction with the accompanying drawing wherein:

FIG. 1 is a schematic diagram illustrating one specific

2

embodiment of the control arrangement of the present invention; and

FIG. 2 is a chart showing a plot of certain photometric data pertinent to the invention.

Referring first to FIG. 1, the invention is illustrated in connection with a single pickle tank 5 containing an aqueous sulfuric acid bath 6 and having a conduit 7 with a flow control valve 8 for adding fresh acid. It will be understood that in an actual pickling system a plurality of such tanks may be employed and that fresh acid may be controllably added to more than one tank if desired. In FIG. 1 the various control instruments are illustrated in schematic or block form since they constitute well known mechanisms the details of which form no particular part of the present invention. The conduits or pipes for passage of fresh acid and pickle liquor are designated by double lines in FIG. 1 whereas single lines are employed to illustrate air tubes or pipes communicating with the various instruments.

The basic control principle of the invention involves the measurement of specific gravity of the sulfuric acid pickle liquor and the determination of the ferrous sulfate concentration of the liquor. Inasmuch as the specific gravity of the pickle liquor is an additive function of the acid concentration and the ferrous sulfate concentration, it is apparent that the acid concentration of the liquor is directly calculatable once the specific gravity and ferrous sulfate content are known. Thus, the elements of the control system of the invention include:

(1) Means for measuring specific gravity of the pickle liquor,

(2) Means for determining the ferrous sulfate concentration of the pickle liquor,

(3) Suitable means for totalizing or combining output signals from (1) and (2), and

(4) Flow control means in the make-up acid feed conduit which is responsive to the combined signal from (3) for regulating the introduction of fresh or make-up acid.

Although various instruments of well known types may be employed for specific gravity measurement, it is preferred to utilize a differential pressure type transmitter for purposes of the present invention. In a device of this type the pressure exerted by a column of reference liquid is balanced against the pressure of an equal head of the pickle liquor and the resultant differential pressure is transmitted to a receiver element such as a flexible diaphragm. One commercially available instrument of this type which is particularly suitable is the so-called "differential converter specific gravity transmitter" manufactured by Minneapolis-Honeywell Regulator Company. In this particular instrument the force of the measured differential pressure is opposed by air pressure acting on a pivoted beam. The air pressure which is developed to balance the differential pressure thereby becomes a measure of the differential pressure or specific gravity and transmits a suitable pneumatic signal.

The preferred means of obtaining a differential pressure measurement in the pickle liquor bath involves the use of a pair of dip tubes immersed in the bath and terminating at different distances below the surface of the bath. Air under pressure is passed through the dip tubes at a low rate of flow sufficient to prevent the liquor from entering the dip tubes. The tubes are connected to the differential pressure measuring instrument, and any variation in the specific gravity of the pickle liquor is reflected by a change in differential pressure inasmuch as the depths of the respective tubes are constant. In order to increase the range of the instrument, it is desirable to interpose a reference liquid chamber in one of the dip tube lines, the height of the column of reference liquid being equal to the difference between the immersion depths of the two dip tubes in the pickle liquor bath.

Inasmuch as the difference between the immersion depths of the dip tubes is constant or fixed, it will be understood that any variation in the liquid level of the tank will not affect the differential pressure or specific gravity measurement.

In FIG. 1 the specific gravity measuring instrument is designated at 9, and a pair of dip tubes 10 and 11 extend into the pickle liquor bath 6 and terminate at different distances below the surface of the bath. Air under constant pressure is supplied through lines 12 and 13 to the dip tubes 10 and 11, respectively, and is bubbled into the bath 6 at a rate sufficient to purge the dip tubes and prevent entry of liquid, the back pressure from the dip tubes being transmitted to the instrument 9. As heretofore mentioned, in order to secure a range on the instrument chart or scale, a vessel 14 containing a reference liquid 16 is interposed in the dip tube 11 to provide a predetermined "suppression" of the pressure in the tube 11. The effective head of the reference liquid 16 (designated at A) is selected so as to be equal to the difference (designated at B) between the immersion depths of the dip tubes 10 and 11. Therefore, by selecting a reference liquid with a specific gravity equal to the lowest specific gravity value expected in the pickle liquor bath 6, a relatively wide range of specific gravity measurements is possible. Since the distance B is fixed, any variation in the level of the surface of the bath 6 will have an equal effect on both dip tubes 10 and 11 and the differential pressure measurement will remain unchanged. Consequently, any change in specific gravity of the pickle liquor 6 will be reflected in a change in differential pressure and a corresponding change in output signal will be transmitted by the instrument 9. Although any suitable type of output signal such as an electronic signal may be utilized, the invention as illustrated employs a pneumatic output signal. Thus, an air supply line 18 connects with the instrument 9 and the output pneumatic signal is transmitted through an air line 19 to a signal totalizing or combining device 21, hereinafter described. A branch line 22 communicates with a conventional indicating and recording device 23 for providing a permanent continuous record of the specific gravity of the pickle liquor.

In the determination of the ferrous sulfate concentration of the pickle liquor, it has been found that a photometric technique is particularly satisfactory. Referring to FIG. 2, a representative absorption spectrum of ferrous sulfate in aqueous sulfuric acid is shown which is applicable over a range of 0 to 100 grams of ferrous ion per liter. By passage of a beam of light of suitable wave length through a cell containing a pickle liquor sample, the intensity of the transmitted or unabsorbed light is a measure of the ferrous sulfate concentration of the sample. For the conditions shown in FIG. 2, it will be evident that the use of a filter transmitting light in the wave length region of from about 850 to about 1300 millimicrons, and particularly from about 940 to about 1000 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. is a typical device which may be used with good results in the control system of the present invention. As is well known in such devices, the sample liquid is passed through an absorption cell 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 sulfate concentration of the sample liquid.

Reverting to FIG. 1, it is desirable for best results that a continuous sample stream of pickle liquor be withdrawn from the bath 6 and passed through the absorption cell of the colorimeter. In accordance with well known

practice, a suitable filter or baffling arrangement should be employed to insure the withdrawal of a sample stream which is free of suspended particles. Thus, a sample stream is withdrawn from the tank 5 through a line 24 and is circulated by means of a pump 25 through a colorimeter 26 and may thence be returned to the tank 5 by a line 27 having a valve 28. In some instances the effluent sample stream from the colorimeter 26 may be discarded, as through a branch line 29 having a valve 31, rather than being recirculated to the pickle tank 5. The electrical output signal from the photoelectric circuit of the colorimeter 26 is transmitted, as indicated by the dotted line 32, to a potentiometric device 33 or the like capable of converting the electrical signal to an equivalent pneumatic signal. The electrical output signal of the colorimeter 26 is non-linear and varies in a substantially logarithmic manner with changes in ferrous sulfate content, but the output signal from the specific gravity meter 9 is linear. Consequently, before the two signals can be combined or totalized, it is necessary that the signal from the colorimeter 26 be linearized. This is readily accomplished in a well known manner by means of a suitable cam in the potentiometric device 33 which is preferably a null balance potentiometer. Supply air is directed to the instrument 33 through a line 34 and the resultant linearized pneumatic signal is transmitted through a line 36 to the signal combiner or totalizer 21 heretofore mentioned. For maximum convenience, the potentiometric instrument 33 may also comprise an indicator or indicator-recorder capable of making a permanent record of the ferrous sulfate concentration of the pickle liquor.

The linear pneumatic signals transmitted by the lines 19 and 36 and representing the specific gravity and ferrous sulfate content, respectively, of the liquor are suitably combined by the signal combining or totalizing mechanism 21 which may be of any well known convenient type. In this instance, the function of the instrument 21 is essentially a computing function wherein the output signal pressure of the line 36 is subtracted from the output signal pressure in line 19. Air is supplied to the instrument 21 through a line 37 and a net output pneumatic signal or differential is transmitted through a line 38. The signal transmitted by the line 38 represents, in effect, the specific gravity signal from the instrument 9 corrected by the ferrous sulfate concentration signal of the instrument 26 so as to provide a net signal which is a measure of the sulfuric acid concentration of the pickle liquor. A branch line 39 transmits this corrected signal to the indicator-recorder 23 to provide a continuous record of acid concentration. For the instrument 21, the so-called "ratio totalizer" manufactured by Hagan Corporation is particularly convenient. This device operates on a force balance principle wherein input signal pressures act on a pivoted beam and the beam movement is transmitted to a pilot valve which meters a separate air supply and provides a single output pneumatic signal.

For flow control purposes, it will usually be necessary to amplify the pneumatic output signal of the line 38 as shown diagrammatically at 41. Supply air to the amplifier 41 is provided through a line 42 and the final pneumatic signal, which may be, for example, twice the pressure of the input signal of the line 38, is transmitted through a line 43 to a valve positioner or control device 44 which is connected to the diaphragm of the control valve 8 disposed in the make-up acid conduit 7. By suitable setting of the control instrument 44, it will be understood that the addition of fresh or make-up acid is regulated in response to the combined or corrected output signal of the control apparatus whereby the acid content of the liquor in the tank 5 may be maintained within predetermined limits.

The above-described combination of instrumentation for measurement of specific gravity with optical or photometric means for determining ferrous sulfate concentration provides a highly convenient and effective means for

automatic control of acid concentration in a pickling system of the character described. Use of this control system eliminates the tedious analytical procedures previously required and provides accurate and timely information so that optimum acid utilization is realized with minimum waste.

Although the invention has been described with reference to a particular specific 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 the pickling of iron or steel by contact with an aqueous sulfuric acid bath wherein acid is consumed by conversion to ferrous sulfate and wherein make-up acid is added to the bath to maintain the acid concentration of the bath within predetermined limits, the improvement which comprises measuring the specific gravity of the bath and obtaining a first pneumatic signal which is a measure of the specific gravity of the bath, photometrically measuring the ferrous sulfate content of the bath and obtaining an electrical signal which is a measure of the ferrous sulfate content of the bath, converting said electrical signal to a second pneumatic signal, and combining said first and second pneumatic signals to obtain a corrected pneumatic signal which is a measure of the acid concentration of the bath and is adapted to be used to regulate the addition of make-up acid to the bath for maintaining the acid concentration of the bath within predetermined limits.

2. The method of claim 1 further characterized in that said electrical signal is converted from a non-linear electrical signal to a substantially linear pneumatic signal.

3. In the pickling of iron or steel by contact with an aqueous sulfuric acid bath wherein acid is consumed by conversion to ferrous sulfate and wherein make-up acid is added to the bath to maintain the acid concentration of the bath within predetermined limits, the improvement which comprises measuring the difference in hydrostatic pressure at selected distances below the surface of the bath and obtaining a pneumatic output signal which varies substantially linearly with the specific gravity of the bath, withdrawing from the bath a sample stream, exposing said stream to a beam of light of predetermined wave length in a colorimeter and obtaining an electrical signal which varies non-linearly with the ferrous sulfate content of the stream, converting said electrical signal to a substantially linear pneumatic output signal, and combining said pneumatic output signals to obtain a corrected linear pneumatic signal which is a measure of the acid concentration of the bath and is adapted to be used to regulate the addition of make-up acid to the bath for maintaining the acid concentration of the bath within predetermined limits.

4. Apparatus for use in automatically controlling the addition of make-up acid to a sulfuric acid pickling bath comprising the combination of means for measuring the specific gravity of the bath and transmitting a first output signal, means for measuring the ferrous sulfate content of the bath and transmitting a second output signal, and means cooperable with both of said aforementioned means for receiving and combining said first and second output signals and transmitting a corrected output signal which is a measure of the acid concentration of the bath and is adapted to be used to regulate the addition of make-up acid to the bath whereby to maintain the acid concentration of the bath within predetermined limits.

5. The apparatus of claim 4 further characterized in that said means for measuring ferrous sulfate content comprises photometric means.

6. Apparatus for use in automatically controlling the addition of make-up acid to a sulfuric acid pickling bath comprising the combination of means for measuring the specific gravity of the bath and transmitting a first pneumatic signal which is a measure of the specific gravity of

the bath, photometric means for measuring the ferrous sulphate content of the bath and transmitting an electrical signal which is a measure of the ferrous sulfate content of the bath, potentiometric means cooperable with said photometric means for converting said electrical signal to a second pneumatic signal, and signal combining means cooperable with said specific gravity measuring means and with said potentiometric means for receiving and combining said first and second pneumatic signals and transmitting a corrected pneumatic signal which is a measure of the acid concentration of the bath and is adapted to be used to regulate the addition of make-up acid to the bath whereby to maintain the acid concentration of the bath within predetermined limits.

7. The apparatus of claim 6 further characterized in that said potentiometric means includes means for linearizing the electrical signal so as to obtain a substantially linear second pneumatic signal.

8. Apparatus for use in automatically controlling the addition of make-up acid to a sulfuric acid pickling bath comprising the combination of means for measuring the specific gravity of the bath and transmitting an output signal which is a measure of the specific gravity of the bath, a colorimeter, conduit means for withdrawing a sample stream from the bath and flowing the stream through said colorimeter for exposure therein to light and transmission therefrom of an electrical signal which is a measure of the ferrous sulfate content of the bath, and means cooperable with said specific gravity measuring means and with said colorimeter for receiving and combining said output signal and said electrical signal and for transmitting a corrected output signal which is a measure of the acid concentration of the bath and is adapted to be used to regulate the addition of make-up acid to the bath whereby to maintain the acid concentration of the bath within predetermined limits.

9. The apparatus of claim 8 further characterized in that said means for measuring specific gravity comprises a differential pressure measuring device.

10. Apparatus for use in automatically controlling the addition of make-up acid to a sulfuric acid pickling bath comprising the combination of a differential pressure measuring device adapted to measure the difference in hydrostatic pressure at selected distances below the surface of the bath and to transmit a pneumatic output signal which varies substantially linearly with the specific gravity of the bath, a colorimeter, conduit means for withdrawing a sample stream from the bath and flowing the stream through said colorimeter for exposure therein to a beam of light of predetermined wave length, said colorimeter being adapted to transmit an electrical signal which varies non-linearly with the ferrous sulfate content of the stream, potentiometric means cooperable with said colorimeter for converting the non-linear electrical signal to a substantially linear pneumatic output signal, and signal combining means cooperable with said differential pressure measuring device and with said potentiometric means for receiving and combining said pneumatic output signals and transmitting a corrected linear pneumatic signal which is a measure of the acid concentration of the bath and is adapted to be used to regulate the addition of make-up acid to the bath whereby to maintain the acid concentration of the bath within predetermined limits.

11. Apparatus for determining the acid concentration of an aqueous liquor containing sulfuric acid and ferrous sulfate, which comprises, in combination, means for determining the specific gravity of the liquor, independent means for determining the ferrous sulfate content of the liquor, and means cooperable with both of said aforementioned means for correcting the specific gravity determination by the ferrous sulfate determination whereby to obtain a net measurement corresponding to the acid concentration of the liquor.

12. The apparatus of claim 11 further characterized in

that said means for determining ferrous sulfate content
comprises photometric means.

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