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AUTOMATIC pH CONTROL OF CHEMICAL TREATING BATHS

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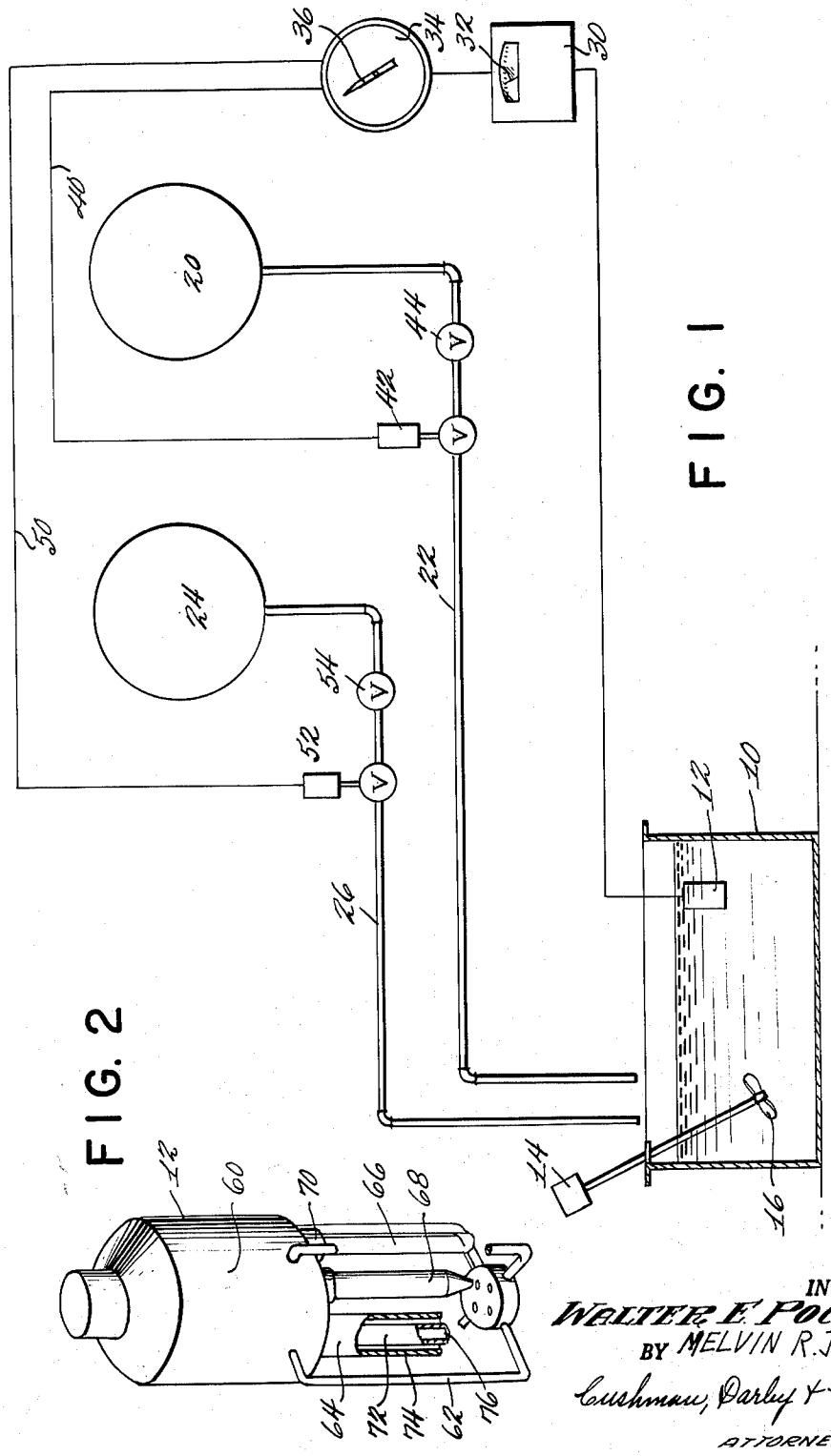


FIG. 1

FIG. 2

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AUTOMATIC pH CONTROL OF CHEMICAL TREATING BATHS

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This invention relates to the control of hydrogen ion concentration (pH) in chemical treating baths. More particularly, this invention relates to a method and apparatus for continuous and automatic control of pH in acidic chromate treating baths for deposition of corrosion resistant and paint-bonding coatings on metals.

The method and apparatus of this invention is applicable to acidic chromate treating baths in general for improving the corrosion resistance of metals. One particular application is found with treating baths wherein a source of the fluoride ion is a necessary constituent. Among the metals which may be so treated are aluminum and alloys thereof.

Various chemical processes are now available on the commercial market for the treatment of aluminum and aluminum alloys to provide a corrosion resistant and paint-bonding film. This type of process is described, for example in United States Patents 2,796,370, 2,796,-371 and other United States Patents.

Essentially, the treating baths are acidic solutions containing hexavalent chromium compounds together with fluorides or complex fluorides as "activator" compounds. The baths may also contain, as in the patents cited above, other activator compounds such as ferricyanides.

One of the limitations of all chromate conversion treatment processes and a constant problem in practical usage is the accurate control and replenishment of the treating bath, as it becomes depleted through usage, to maintain uniform performance in forming the desired film. It has been found that the concentration of hydrogen ion (measured as pH) is far more critical in its effect on bath performance than the concentration of any of the chemical substances present. Therefore, pH control is the major factor in controlling bath performance.

When the pH of acidic chromate treating baths is not adequately controlled, the properties of the resulting coatings are seriously affected. For example, a preferred chromate coating is usually in a color range from yellow to brown and exhibits corrosion resistance and paint-bonding characteristics. However, if pH of the bath is too high, the coating becomes thinner and lighter in color, thereby reducing the corrosion resistance and paint-bonding properties thereof. If the pH is too low, the coating becomes dark and thick and sometimes sloughs off or becomes powdery upon drying.

At present, pH control in chromate coating processes is substantially an entirely manual procedure. In a production operation, the pH of the bath increases of its own accord during use, as hydrogen ion is consumed from the bath as a result of the coating reaction and this consumed hydrogen ion must be replaced by the addition of a strong acid, such as nitric acid. Under present practice, the treating solution is checked periodically for pH by testing samples of the solution or by observing color or other properties of the coating. Thus, when the pH of the solution sample tests too high, or the resulting coating is too light or thin, acid is added manually until the condition is corrected. Ideally, the pH would not be expected to test too low during the course of normal operation. However, this may occur as the result of over addition, in which case a strong base, such as caustic soda, is added manually to adjust pH to the desired value.

Also, in certain instances it may be desired to either raise or lower the pH value at which the bath is being maintained as production requirements change, in which case the correct amounts of acid or base must be manually added. It is apparent that this method is both time consuming and lacks the accuracy of pH control and speed of pH correction which are necessary for uniform coating results.

Previous attempts to automatically control pH of chromate treating baths by presently available standard methods and equipment have been unsuccessful. In general, such attempts have been no better than, or even poorer than manual control; i.e., wide fluctuations in the bath still occur for the following reasons:

(1) Design of the sensing and control equipment does not take into account, on the one hand, the extremely critical nature of pH in the functioning of this type of bath and, on the other hand, in spite of this criticality, the relatively slow rate of change of pH as processing proceeds and the absolute necessity of adjusting the flow rate of the acid during the time it is being added to the bath to a very low value in conformity with the rate at which hydrogen ion is consumed from the bath and the acidity thereof is decreased.

(2) Glass electrodes conventionally used for sensing pH are attacked by the fluorides or complex fluorides oftentimes found in such baths, especially baths for the treatment of aluminum and alloys thereof.

(3) With the saturated potassium chloride electrolyte normally used in the reference electrode for pH measurement of aluminum treating baths there is a tendency for the pH reading to drift when fluorides or certain complex fluorides are present in the bath.

As noted above, presently available equipment does not offer criticality of pH control essential for effective use with chromate treating baths. For example, when treating most metals control is necessary to ± 0.2 pH units and when treating aluminum or alloys thereof control is necessary to ± 0.1 pH units. Similarly, the equipment is not adapted to make additions for correction of pH of a bath slowly enough to prevent "overshooting" and consequent lack of uniformity in coatings deposited therefrom.

It is therefore an object of this invention to provide a method and apparatus for accurate control and replenishment of chemical treating baths.

It is another object of this invention to provide such a method and apparatus for chromate treating baths by which uniformity of coating characteristics may be obtained.

It is still another object of this invention to provide such a method and apparatus by which pH of a chemical treating bath may be accurately and automatically controlled.

It is a further object of this invention to provide such a method for the treatment of aluminum wherein glass electrodes customarily utilized for pH measurement are not attacked by ingredients of the treating bath.

It is a still further object of this invention to provide such a method which obviates drift of pH readings.

It is still another object of this invention to provide such a method and apparatus by which the criticality in control of pH, necessary in chromate treating baths, may be achieved.

Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description, while indicating preferred embodiments of the invention, is given by way of illustration only, since various changes and modifications within the spirit and scope of the inven-

tion will become apparent to those skilled in the art from this detailed description.

It has now been found that the above objects may be attained by use of our chemical processing and pH control system, the essential features of which are as follows:

(1) The recording and controlling portions of the system have a total range of 3 pH units, i.e., ±1.5 units from the average operating pH of a particular bath, thus allowing for increased graduation between unit designations.

(2) A unique system and arrangement of solenoid and needle valves is provided in the apparatus of this invention to allow closely controlled and accurate addition of an acid or base to quickly and automatically adjust for variations in pH of the treating bath.

(3) Critical location of the component parts of the apparatus and the advantages flowing from use of agitation in the bath are recognized.

(4) In the particular instance of a treating bath for aluminum the complex fluoride used is a silicofluoride (fluosilicate) and a proper electrolyte is used in the reference electrode, preferably one other than saturated potassium chloride.

The present system answers a crying need for uniformity in chromate conversion processes and is particularly adaptable to high volume production, e.g., in aluminum strip lines wherein lack of satisfactory pH control has an adverse effect on economy.

The aforementioned and other objects of this invention and the essential features thereof will be fully understood from the following detailed description of a preferred form and application of the invention, throughout which description reference is made to the accompanying drawing in which:

FIGURE 1 is a schematic illustration of an apparatus for carrying out the automatic pH control of a chemical treating bath in accordance with the process of our invention; and

FIGURE 2 is a perspective view with parts broken away of an electrode assembly which may be used in the apparatus of FIGURE 1.

Reference is made now to the drawing, and specifically to FIGURE 1 wherein treating tank **10** has submerged therein an electrode assembly **12**. The treating tank **10** is shown in cross-section for convenience, while the rest of the figure is shown schematically. A previously prepared solution is maintained in tank **10**. Motor **14** drives agitator **16** which is positioned in tank **10** and spaced a substantial distance away from electrode assembly **12**. Alkali from feed tank **20** is delivered to tank **10** through gravity feed line **22**. Similarly, acid from feed tank **24** is delivered to tank **10** through gravity feed line **26**. The outlet ends of lines **22** and **26** are also spaced a substantial distance away from electrode assembly **12** and in close proximity to agitator **16**. Electrode assembly **12** measures continuously the pH value of the solution in tank **10** and is operated in conjunction with panel-mounted indicator **30**, which indicates the measured value of pH by the position of needle **32**. Indicator **30** is in turn operated in conjunction with recorder-controller **34** which contains pointer **36** and switches not shown. The first of said switches is arranged in an electrical circuit **40** which includes an appropriate power source, not shown, and solenoid valve **42** situated in feed line **22**. A needle valve **44** is also interposed in line **22** between feed tank **20** and solenoid valve **42**. Similarly, a second switch is arranged in electrical circuit **50**, including the power source and solenoid valve **52** situated in feed line **26**. Interposed in line **26** between feed tank **24** and solenoid valve **52** is needle valve **54**.

Referring now to FIGURE 2, electrode assembly **12** comprises housing **60** and guard frame **62** depending therefrom. There are three threaded holes (not shown) in the bottom of housing **60** which receive reference electrode **64**, temperature compensator **66** and glass electrode **68**. Leak-proof compression fittings **70** hold these components in place. Reference electrode **64** comprises a salt bridge tube **72** having therein a suitable electrolyte. Salt bridge tube **72** is fitted within a sleeve-type compression fitting **74** which provides pressure equalization at liquid junction **76**. The particular electrode assembly **12** which is illustrated in FIGURE 2 is provided by the Leeds & Northrup Company of Philadelphia 44, Pennsylvania, and includes Immersion Unit #7782 having received therein Reference Electrode #117105 and Glass Electrode Std. 1199–49, 50 or 51 depending on the temperature range of the bath.

In operation, the apparatus shown in the drawing provides continuous and accurate control of pH in the chemical treating bath maintained in tank **10** in the following manner:

The solution in tank **10** is moderately but continuously agitated by agitator **16** and pH of the solution is continuously measured by electrode assembly **12** and indicated by indicator **30**. Pointer **36**, as it reaches a point corresponding to a predetermined minimum pH value, trips the first of the switches in recorder-controller **34**, thereby closing circuit **40** and energizing solenoid valve **42** to the open position, permitting alkali to pass through line **22** and into tank **10**. This state of operation continues until the pH value, measured by electrode assembly **12**, is changed to the desired optimum value at which point the switch is tripped to the open position by pointer **36** thus de-energizing solenoid valve **42** which closes and thus stops introduction of alkali to the treating solution.

When pointer **36** reaches a predetermined maximum value, the second of said switches is tripped to the closed position, thereby closing circuit **50** and energizing solenoid valve **52** to the open position permitting acid to pass through feed line **26** and into tank **10**. This operation also continues until the desired optimum value, intermediate said minimum and maximum values, is reached and indicated by indicator **30** at which point the second switch is tripped to the open position by pointer **36** thus de-energizing solenoid valve **52** which closes and thus stops introduction of acid into the treating solution in tank **10**. Recorder-controller **34**, preferably has a total range of 3 pH units, i.e., ±1.5 from the optimum operating pH of the baths making for maximum accuracy in the electrical control system.

The use of needle valves **44** and **54** on alkali feed line **22** and acid feed line **26**, respectively, permits the flow rate therethrough to be adjusted to a desired low level, thus preventing "overshooting" when solenoid valves **42** or **52**, situated between needle valves **44** and **54** and the outlet ends of lines **22** and **26** respectively, open to allow alkali or acid to flow from the feed tanks. Needle valves **44** and **54** are initially manually adjusted to set a desired opening depending upon the characteristics of a particular operation, such as size of treating tank **10**, amount of treating solution, amount and characteristics of the material to be treated, etc. The needle valves preferably adjust the flow so that it is necessary for either of solenoid valves **42** or **52** to be open only a portion of the total treating time. For effective operation, a flow rate of as little as 0.1 gallon per hour may be required in some cases.

In the course of actual usage when operating the apparatus of this invention in connection with an acidic aqueous chromate treating bath, acid only is normally added since the pH of the bath tends to rise. In other words, the acidity of the bath continuously decreases as the coating operation proceeds. In this instance, needle valve **44** on alkali feed line **22** is kept closed. The previously prepared solution in tank **10** contains hexavalent chromium compounds and activators, including sulfides, chlorides, etc., and in the treatment of aluminum, simple or complex fluorides. Since the acidity decreases as the operation proceeds, only a replenishing acid is normally added to the bath. The introduction of acid commences

immediately when the measured pH attains a predetermined maximum optimum value not substantially greater than a predetermined optimum operating value for the bath. The addition of acid thereafter proceeds at a rate of flow slow enough to assure an abrupt termination of the feed when the measured pH is reduced to a predetermined minimum lower value not substantially less than the aforementioned optimum value.

It has been found that when this flow rate is adjusted by means of the needle valve to a value approximately 1.5 to 5 times the required overall rate of acid addition, such that acid is being added to the bath during the corresponding 20 to 67% of the actual operating time, the pH can be effectively controlled automatically. This needle valve adjustment is readily determined, and based on the known rate of production in any particular case. In other words, the amount of hydrogen ion which will be consumed in a particular treating period may be closely approximated and therefore the rate of acid addition to compensate for the consumed hydrogen ion is also readily determined. By adjusting the needle valve such that the flow of acid is at a value, as indicated above, from 1.5 to 5 times the required rate, the solenoid valve will be actuated to the open position only during 20 to 67% of the operating time. We have found that this is important in preventing overshooting the optimum addition of acid.

If it is desired to raise the operating pH of the bath as referred to hereinbefore, alkali feed is cut into the system by opening the needle valve by an amount depending upon the speed at which it is desired to raise the pH to its new value, then gradually closing it down as the pH approaches the desired value and finally closing it altogether when this value has been reached. Similarly, if it is desired to lower the pH rapidly to a new operating level, needle valve **54** in acid feed line **26** is likewise opened wider then closed as the desired value is approached.

When the chromate baths are used for the treatment of aluminum and the presence of the fluoride ion is indicated, the preferred compounds for providing the same include fluosilicic acid and salts thereof and particularly the alkali metal and alkaline earth metal salts thereof. These complex fluorides are of limited solubility, thereby providing a simple means for carefully controlling fluoride ion concentration of the coating bath. Furthermore, these complex fluorides have been found not to attack siliceous materials such as glass, earthenware, etc. This is attributed to the fact that in the fluosilicate ion, the fluoride ion is already in equilibrium with silica, a constituent of siliceous materials normally attacked by fluorides. Therefore, the versatile, accurate and economical glass electrode may be used for measurement of pH in these baths. The coating operation may also be performed in earthenware or glass-lined containers. Another factor indicating the preference of the fluosilicates is that they are a by-product of the phosphate industry and are therefore more economical and more easily available than other compounds yielding the fluoride ion in solution. Among the types of formulations which can be used with the present system are acidic solutions containing hexavalent chromium compounds and fluosilicic acid or salts thereof, with or without ferricyanic acid or salts thereof. Substances in addition to those above mentioned, with the exception of fluorides or complex fluorides which might attack siliceous materials, are not objectionable.

It has also been found that satisfactory functioning of the pH sensing and control system in a treating bath including the fluoride ion requires a proper choice of electrolyte in reference electrode **64**. With the saturated potassium chloride electrolyte normally used in pH measurement devices, there is a tendency of the pH reading to drift. This is overcome by replacing the saturated potassium chloride, preferably with saturated ammonium chloride. Experience and general principles also demonstrate that ammonium chloride solutions at less than saturation concentrations, potassium chloride at 1 normal or lower concentrations; and sodium chloride at saturation or less than saturation concentrations, are all effective.

The explanation for the above is believed to be that the pH drift encountered when potassium chloride is used is due to a localized precipitation of potassium fluosilicate, K_2SiF_6, a salt of low solubility, at the capillary liquid junction **76** between electrode **64** and the chromate treating solution in tank **10**. An essential feature, then, of this embodiment of the invention is use in reference electrode **64** of an electrolyte which will not react with constituents such as fluosilicates in the bath to form compounds of low solubility.

The use of moderate agitation and the relative location of electrode assembly **12**, agitator **16** and the feed-in ends of lines **22** and **26**, shown in FIGURE 1 and described hereinbefore, permit optimum response of the control system, i.e., recorder-controller **34** and valves **42** and **52**, to the sensing system, i.e., electrode assembly **12** and indicator **30**.

As the alkali used in the present invention, a strong base such as caustic soda may be used and nitric acid is the preferred acidic material.

It will, therefore, be seen that there has been provided by this invention an apparatus and method by which the various objects hereinbefore set forth, together with many practical advantages, are successfully achieved.

As various possible embodiments may be made of the features of this invention, all without departing from the scope thereof, it is to be understood that all matters herein set forth or shown in the accompanying drawing are to be interpreted in an illustrative and not in a limiting sense.

What is claimed is:

1. A method for controlling pH in an acidic aqueous chromate coating bath in which the acidity continuously decreases as the coating operation proceeds, which comprises continuously measuring the acidity as pH of the bath by means immersed therein, introducing replenishing acid to the bath at a point spaced from the point at which the acidity as pH is measured, the introduction of the acid immediately commencing when the measured pH attains a predetermined maximum upper value not substantially greater than a predetermined optimum operating value and thereafter proceeding at a rate slow enough to assure such abrupt terminating of the acid feed when the measured pH is reduced to a predetermined minimum lower value not substantially less than said aforesaid optimum value whereby the acid feed is prevented from being excessive at any time to objectionably influence the coating bath, and agitating said bath adjacent said point of introduction of acid to the bath.

2. A method according to claim **1** wherein the bath contains a compound yielding a fluoride ion, said compound being selected from the group consisting of fluosilicic acid and salts thereof.

3. A method according to claim **2** wherein the salts of fluosilicic acid are selected from the alkali metal and alkaline earth metal salts thereof.

4. A method according to claim **2** wherein the means immersed in the bath is an electrode assembly and wherein the electrolyte in the reference electrode of said electrode assembly is selected from the group consisting of ammonium chloride solution up to saturation concentration, potassium chloride solution up to one normal concentration and sodium chloride solution up to saturation concentration.

5. A method according to claim **1** wherein the acid is nitric acid.

6. A method according to claim **1** wherein the flow rate of replenishing acid is adjusted to a value between about 1.5 and 5 times the rate of addition required to

compensate for said continuous decrease in acidity, whereby introduction of said replenishing acid to the bath occurs only during about 20 to 67% of the actual operating time.

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