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TESTING AND CONTROL

The ABCs of pH Measurement in Metal Finishing

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pH is a measure of the acidity or alkalinity of a liquid solution. It is the measure of the hydrogen ion concentration of a solution.

Across the full spectrum of metal finishing operations from pretreatment, through plating, to wastewater treatment, pH is a critical indicator of the chemical processes. In several processes, pH level ranks among the critical values that influence plating rate and throughput. In others, such as environmental regulation, accurate pH monitoring is absolutely essential to documenting regulatory compliance. Surprisingly, many individuals responsible for ensuring product quality, resource efficiency, regulatory compliance, and plant profitability, may simply take pH testing for granted. In fact, pH measurement may not be well understood by those who actually perform the work — particularly as advances in pH metering have long surpassed those traditional chemical methods that many of us learned in school.

The need for pH control for improved cost control, product quality, and environmental compliance suggest that it is important to understand a few basics about pH and to take a snapshot of currently available measurement tools and technology.

pH AND PROCESS CONTROL

As mentioned above, there are many different applications for pH measurement in metal finishing. The most common applications for measuring and controlling pH all revolve around consistency. Accurate pH measurement is essential to making up baths that function as expected. Equally importantly, it is essential for the optimal replenishment of individual bath chemistry components to deliver consistent operation hour after hour, day after day. Timely and accurate pH monitoring enables the most tightly controlled replenishment strategy, helping to avoid wild swings in bath composition and avoiding the risk of "poisoning" a bath from adding too large a quantity of a particular chemical.

The criticality of maintaining proper pH varies with the plating operation. In electroless nickel, for example, it is a critical controller of plating rate and needs to be controlled extremely narrowly to a range of only plus or minus one-tenth of a unit. In the rinse tank for a wide range of plating operations, extreme pH values can result in a product that is undesirably spotty or uneven in finish, color, or texture.

ENVIRONMENTAL ISSUES

While pH control has a major impact on product quality, strict local or federal standards may require documented pH control of the wastewater treatment system. Although recent trends have somewhat slowed growth in new regulations, pH is still the single most common measurement used to characterize industrial wastewater today.

Metal Plating and Wastewater

Regulations require that toxic substances be removed from plant effluent before discharge into the environment or public water treatment system. Frequently, this involves the oxidation of cyanide and removal of heavy metals such as chrome. Treating chemical solutions that contain hexavalent chromium — with its well-known toxicity to plants, animals, and humans — is a critical step in wastewater treatment. We are all acutely aware of the environmental and regulatory concerns raised by the presence of sizable amounts of the various metals in our wastewater.

Chrome removal from the wastewater involves the use of chemical reactions to produce a separation of chromium from the liquid process. Once separated, the chrome is removed through filtration or flocculation before the wastewater is discharged into the environment. Previously, it was sufficient to chemically reduce hexavalent chromium to the trivalent state before discharging the effluent. Today, however, trivalent chromium is also considered toxic and must be removed.

Effective chrome removal processes require pH control. If the pH level is correct, chrome reacts almost immediately. If the pH level is too low, the chemical reaction is so slow that the wastewater must be held up in larger tanks before discharging (see the accompanying sidebar, “The Role of pH Testing in Removing Hexavalent Chromium From Wastewater”). Because metal finishing plants can be held liable for the chemical contents of their effluent, pH readings are best monitored on a continuous basis to verify that regulatory standards are met — and met consistently.

MEASURING pH

Traditional Grab Sample Analysis

Metal finishing processes have historically measured pH by extracting a grab sample and “sending the sample to the lab” — either internal or external. Chemists in the lab would use pH indicator papers that change color based on the stream pH and compare the color produced to a color chart.

Titration

When the sample is very concentrated, the chemist relies on titration to determine the concentration of acid in the process. In this titration, a known concentration of caustic is added drop-by-drop into the grab sample until all of the acid has reacted. The point at which all the acid has been reacted is called the equivalence point. This point can be determined by measuring the pH during the titration and noting when the largest change occurs. It can also be determined by adding an indicator dye to the sample and noting when the color changes. Titration (or electrical conductivity) is frequently used for measurements at extreme pH values where small changes in pH result in large differences in acid (or base) concentrations. For instance, control of 1 to 3% hydrochloric (HCl) acid would be difficult with pH since the pH would only range from 0.56 to 0.08. The 3% HCl solution, however, would require about three times as many drops of caustic to neutralize it, making the measurement much more precise.

Limitations of Grab Sample Analysis

There are limitations to grab sample analysis. One is response time. For example, if a sample is analyzed and the reading indicates the process solution does not meet specifications, there is no way to confirm exactly when or how long the problem occurred. Grab sample analysis merely provides analysis of the particular batch of process liquid collected at that particular moment. As a result, if a reading indicated pH levels were off, all products processed since the last scheduled measurement interval are suspect. One option is to reduce intervals between measurements; however, this requires more human intervention and thus higher labor costs.

Additionally, because liquid analysis is performed manually, results may vary depending on who does the analysis. Grab sampling affords no means of automatically keeping accurate and consistent records. Without excellent record-keeping, this may raise problems if a shop needs to demonstrate constant compliance with regulatory standards.

ELECTROMETRIC TESTING

Today, electrometric testing — the term given to the entire field of electronic pH meters — is the most common way of measuring pH. It overcomes many of the limitations of manual testing. However, electrometric testing must be understood in order to suit the sensors, equipment, and calibration techniques to the specific task at hand. It is also important to know when and how to check that the equipment continues to produce accurate measurements.

Continuous On-line Measurement

Continuous on-line measurement of pH using an online sensor and analyzer is generally the most suitable method of pH control in metal finishing because it provides the highest level of accuracy, ensures proper conditions for quality products, and can provide the documentary evidence to verify that environmental standards are being met.

pH sensors (see Fig. 1) consist of a pH-sensitive electrode, a reference electrode, and a temperature

THE ROLE OF pH TESTING IN REMOVING HEXAVALENT CHROMIUM FROM WASTEWATER

As mentioned in the accompanying article, one of the most critical applications for continuous pH measurement is in verifying the effectiveness of our wastewater treatment systems. This brief overview illustrate the part that pH testing plays in removing outlawed hexavalent chromium in a real-world, wastewater treatment scenario.

Step 1: Reduction of Hexavalent Chromium

Wastewater flows to the first reaction tank, where the pH is measured and sulfuric acid is automatically injected until a pH value of 2 is achieved. This pH setpoint of 2 is generally chosen as the most cost-effective compromise between speed and chemistry costs. While a lower pH would deliver an even faster reaction, it would require considerably more acid. At the same time, the oxidation reduction potential (ORP) of the solution is measured, and sulfur dioxide (SO_2), sodium sulfite or sodium metabisulfite is automatically injected until an ORP value of approximately 280 mV is achieved. Reactions occur that reduce hexavalent chromium to trivalent chromium (Cr^{+6} to Cr^{+3}).

Step 2: Chromium Hydroxide Precipitation

In the second tank, the pH is raised to 8.5 by the addition of an alkaline solution such as ammonia or caustic (NaOH). Chromium and other metals, form hydroxides that do not dissolve well in water, so a precipitate is formed. The precipitate, although heavier than the water, does not drop to the bottom due to agitation in the tank. The mixed slurry flows to a settling tank, where the trivalent (Cr^{+3}) chrome settles to the bottom and the clear chromium-free water flows over the tank for further treatment. Chemical coagulant are sometimes added to the second reaction tank to help form larger particles and aid in sludge removal.

element that provides a temperature signal to the analyzer. Using a specially formulated pH-sensitive glass in contact with the liquid solution being monitored, the pH electrode develops a voltage potential that is dependent on the pH of the solution.

The reference electrode is designed to maintain a constant voltage potential and serves to complete the pH measuring circuit within the solution by providing a known reference potential for the pH electrode. The difference in the voltage potentials of the pH and reference electrodes provides a millivolt signal that depends linearly on the pH of the solution. It is important to remember, then, that the pH meter is not actually measuring pH directly, but is interpreting a voltage that that generally — but not exactly — mirrors changes in pH. Because the variations in the voltage do not vary absolutely exactly proportionally to changes across the full pH scale, meters need to be periodically recalibrated to assure the overall accuracy and repeatability of electrometric pH testing.

MONITORING SENSORS

Figure 1. pH sensor.

Experience has shown that some pH sensors last years while others last only a few weeks. Some sensors need cleaning every month while others must be cleaned daily. This is because each process is a unique environment and pH sensors are not one-size-fits-all devices. Sensor life and performance are dependent upon the environment in which the sensor is used, and as mentioned earlier, their usage in metal finishing extends to monitoring some very highly caustic and acidic environments as well as being asked to operate at some high temperatures.

For example, a pH sensor in a high-coating wastewater environment may require cleaning much more often than the same model sensor in a plating rinse water application. The rinse water application, however, may contain heavy metal ions that reduce the lifetime of the sensor considerably. Plant operators can optimize performance by selecting the sensor best suited for each specific application — and to understand the inherent stresses and demands of the different applications.

Coating of the reference junction, however, remains the primary challenge to pH measurement in dirty applications. A coated sensor cannot adequately sense the process and will respond very slowly, if at all. In the metal finishing industry, this may occur in wastewater tanks where solids and liquids, such as grease, are frequently present. Dirty applications impact the bottom line by requiring more handling by personnel or by reducing the availability (and benefit) of the pH measurement.

EXTENDING SENSOR LIFE WITH NEW TECHNOLOGIES

As sensor technology has evolved, the industry has seen the emergence of coating-resistant sensors.

Today, for example, some manufacturers have designed sensors with a large surface area reference junction and extremely small pores that are too small for most particulates and suspensions to penetrate. This large surface area extends the time between required cleanings by providing many more paths for the reference junction to contact the process solution. Regular scheduled cleaning, however, is always recommended to assure accurate pH measurement.

Why Some Sensors Fail In The Metal Finishing Environment

Reference contamination is another challenge associated with pH measurement. The reference is typically a silver-silver chloride-based electrode that can be damaged when poisoning ions such as lead, iron, chrome, cyanide and sulfide enter the reference and react either with the silver wire or with the chloride solution. Since many metal parts are composed of alloys that contain these ions, reference poisoning is quite common in the metal finishing environment.

New technologies slow the onset of reference contamination by barring entry into the sensor, lengthening the path, or changing the chemistry involved. One such concept uses multiple barriers to prevent the poisoning ions from direct access to the silver reference. These sensors are called double or triple junction sensors since they have multiple junctions from one solution to another.

Some sensors are designed with long, helical reference pathways that force ions to travel a long, winding path to the silver-silver chloride reference. The objective of the helical pathway is to require a long diffusion pathlength without requiring a large unwieldy sensor. This concept works well in conjunction with a viscous gel internal fill solution that also slows down the ion diffusion rate.

Mechanical Concerns

Another hazard of pH measurement is physical damage to the glass due to impact or temperature cycling. This concern has led some manufacturers to offer sensors made with new glass formulations that are designed to resist cracking and to use materials with similar temperature expansion coefficients. Nonetheless, it is still good practice to prevent temperature shock by allowing sensors to cool slowly and to locate pH sensors away from direct impact by metal particles.

pH SENSOR CALIBRATION

The best way to verify the accuracy of a pH analyzer and sensor is by two-point buffer calibration. A buffer is a standard solution formulated to resist changes in pH caused by external contaminants. Two different buffer solutions, which are usually at least three pH units apart, are used in pH sensor calibration. This allows the pH analyzer to calculate a new slope (pH glass efficiency) and zero offset (reference offset) for use in calculating the pH from the millivolt potential and temperature measurements. The magnitude of the slope indicates the condition of the glass electrode, while the zero offset generally indicates the degree of reference poisoning. An ideal pH sensor would have a slope of 59 mV per pH unit and a very low zero offset. In practice, a slope of 57 or 58 and a zero offset of less than ±10 mV can be expected.

Whether calibrating as routine maintenance or commissioning a sensor for the first time, there are a couple of common calibration errors that should be avoided. Both are related to temperature. Buffer solutions have a stated pH value *at a specific temperature*. The actual pH of many buffers will change with the temperature. The pH of the buffer solution at various temperatures is usually listed on the bottle, and the value at the appropriate temperature must be used to avoid errors in the calibration. For convenience, newer analyzers incorporate a buffer recognition feature that automatically corrects the buffer value for differences in temperature.

Failure to allow the sensor to reach a steady temperature is another common calibration error. Simply stated, if the pH sensor is used in a wastewater application of 90°F, the sensor shouldn't be calibrated with buffer that has just been in a refrigerator. This could lead to calibration errors and an erroneous pH reading. To prevent this, pH analyzers may feature a buffer stabilization setting that pre-

EXTENDING SENSOR LIFE

Whether cleaning sensors manually or on-line, it's important to clean the sensor with the mildest solution possible but at the same time, one that is appropriate for the application. Alkaline deposits can be removed with weak acid solutions. Acidic deposits may be removed with mild caustic solutions. Greasy coatings can often be removed with a detergent solution, such as liquid dishwashing soap. More tenacious coating may require the use of a solvent. Clean the sensor before it is badly coated for best results. Try not to allow coatings to dry or harden on the sensor. In all cases, a sensor's exposure to a cleaning solution should be minimized to protect the sensor from damage. Quick release cable connectors make cleaning easier by eliminating cable twisting when sensors need to be removed or inserted.

vents the analyzer from accepting a buffer pH reading that has not reached a prescribed level of temperature stabilization.

CONTINUOUS SENSOR DIAGNOSTICS

The lifetime and maintenance needs of a pH sensor vary widely depending on the application. In wastewater applications, for example, a sensor may need weekly cleaning, while the same sensor in a rinse water application might remain clean for months. Aging can occur slowly, as in the gradual effect of reference poisoning or suddenly in the case of a broken glass electrode. In any event, these problems may go undetected until the next routine buffer calibration. Newer pH analyzers continuously test the pH sensors to determine if the glass electrode is broken or the reference electrode is plugged due to coating. These tests are enabled by additional design features that turn the pH sensor into a multiparameter diagnostic device. For instance, a typical pH analyzer may continuously measure pH, temperature, glass impedance (to monitor breakage), and reference impedance (to monitor coating). Furthermore, digital communication over a standardized instrumentation bus allows transmission of all of these parameters to a remote location for viewing. These diagnostics serve as inexpensive insurance against the possibility of unknown failures leading to out of control processes and environmental problems.

The important lesson is that like all machines, electrometric pH meters can fail or, even more insidiously, degrade slowly and almost imperceptible over time. Their accuracy and performance can not be taken for granted — especially when being used in controlling critical bath replenishment. Smaller shops can simply schedule regular testing, calibration, and sensor replacement. Operations boasting larger laboratories can take advantage of the meter's diagnostic features that can be integrated into asset management software packages. These packages allow users to easily manage their plant operations, saving time and money by setting up and configuring analyzers, reading process variables and troubleshooting problems from a personal computer or a host anywhere in the plant.

CRYSTAL BALL

To improve accuracy and prevent downtime, very critical and difficult pH applications are frequently measured by two or more pH sensors. The trend toward smaller sensors and non-glass sensors may eventually lead to a multiple redundant pH sensor. Conceptually, a redundant pH sensor would incorporate multiple sensing heads within one sensor. This sensor would provide highly accurate readings and have increased life because internal logic would be programmed to average, for example, readings from the best three out of four sensors. Conversely, it could provide all the readings digitally and leave the interpretation to the pH analyzer. Currently, the issues of cost and mechanical design are limiting factors in the development of such sensors — but when they inevitably become "ready for prime time," you can say you heard about it first in *Metal Finishing*.

CONCLUSION

pH measurement, though sometimes regarded as something bordering on voodoo, plays an increasingly important role in metal finishing operations. Advances in sensor and analyzer technology have made installation and maintenance less of a mystery and more robust sensors are delivering much longer functional life than ever before. Improvements in the technology have brought the speed and accuracy of electrometric metering to even the smallest shop.

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ABOUT THE AUTHOR

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