

# **The Application of Electrodeless Conductivity Measurement in Chemical Process Control for Surface Finishing**

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Conductivity measurements may be used to control the chemical concentrations of a number of metal finishing process solutions. This paper will discuss the basics of conductivity measurement, how it may be applied to specific process solutions, its limitations, and provide recommendations on how to determine if it can be applied to other process solutions.

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## Introduction

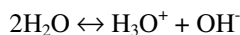
In the surface finishing industry, maintenance of the chemical concentrations of all of the various process solutions is one of the most critical quality control operations. In an ideal world, every constituent of every bath would be automatically measured and controlled, with an occasional laboratory analysis to double-check the accuracy of the automatic equipment.

In the real world, most surface finishing solutions are a complicated matrix of chemical components, reaction by-products, and contaminants, all of which influence the quality of the parts that are being processed. In addition, the chemical analyses are not easily and inexpensively automated. Direct measurement of even a simple 10% sulfuric acid solution would require an expensive titrator, which would cost tens of thousands of dollars to purchase and maintain. As a result, surface finishers must choose their battles, and only automate the control of the most critical chemicals.

For certain chemical solutions, lower cost options are available. If the square footage of parts process per hour is fairly consistent, an electronic metering pump can continuously dose replenishment into the bath. It is relatively rare that this will be sufficient. Another option is to use conductivity control as an indirect method of measuring the chemical concentration. There are different methods for measuring conductivity, and some are more applicable to certain chemicals than others. In general, the electrodeless method will be the most reliable.

## Basics of Conductivity Control

The first thing to consider in order to determine if electrodeless conductivity will work to control the process is to make sure that the chemical you want to measure is conductive. Pretty much any aqueous solution will be conductive to some extent. The chemical of interest must ionize once in solution. Typically, any organic constituents will not ionize, and therefore will not contribute to the conductivity of the bath. Ultrapure water is extremely non-conductive ( $0.055 \mu\text{S}/\text{cm}$ ) since the only contribution to the conductivity is the slight dissociation of water:



This reaction equilibrates at  $10^{-7}$  M concentration of hydrogen ions, which is pretty slight.

If you add a salt, such as potassium chloride, the conductivity will increase. Most salts dissociate completely until they reach saturation and the conductivity increases linearly until that point (see Figure 1):

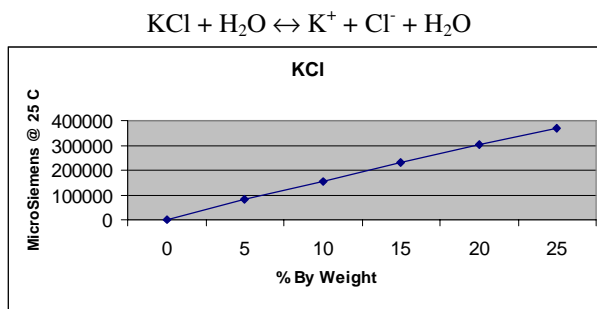
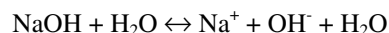


Figure 1<sup>1</sup>

Similar results occur when an acid or base is added to water. For example, for sodium hydroxide:



The dissociation is not as simple however, and at some point the addition of more acid or base pushes the reaction in the opposite direction. The solution conductivity depends upon ion mobility (as well as other factors) and with increasing concentrations, ion mobility is hindered. In the case of NaOH, at concentrations above 15% by weight, the conductivity actually decreases (see Figure 2).

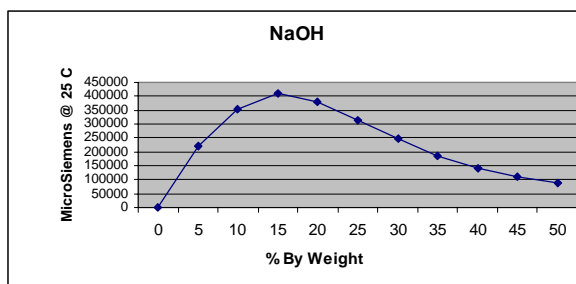


Figure 2<sup>1</sup>

It is evident from the graph in Figure 2 that the conductivity is pretty linear between 0 and 10% by weight, so automatic control in this range should be successful. Also note that if the concentration of your process can vary between 13 and 17% by weight, then automatic control will NOT be successful, since a decrease in conductivity could mean either an increase or a decrease in concentration. A typical cleaner solution will be under 5% sodium hydroxide, and can be controlled by conductivity.

You will also notice when comparing Figure 1 and Figure 2, that at the same concentration, sodium hydroxide has a much higher conductivity than potassium chloride. Some ions are more mobile than others, and therefore are more conductive at the same concentration.

There are two methods of measuring conductivity: contacting and electrodeless. The electrodeless technique is preferable in process applications for a number of reasons.

In a contacting conductivity system, the sensor consists of two metal electrodes that are in physical contact with the solution. A voltage is applied to one of them, and the solution to be measured acts as a resistor that connects the two. The voltage that is returned from the second electrode is proportional to the conductivity of the solution.

Because this type of electrode relies upon a direct electrical contact with the solution, it is sensitive to any coating on the metal surfaces. If any oil is present in the solution, it can coat the metal, insulate the electrodes from the solution, and the sensor will read near zero conductivity. The same thing can happen with any non-conductive material, such as an organic resist, algae, etc. Similarly, if the sensor can be coated with a conductive material, the two electrodes become shorted, and the sensor will read the conductivity way too high.

Another important consideration is chemical compatibility of the sensor with the solution. Most contacting conductivity electrodes are made of 316 stainless steel. Attempting to control a solution that is intended to etch steel with this type of sensor will prove costly!

An electrodeless conductivity sensor functions without any electrodes in direct contact with the solution. This type of sensor consists of two coils (also known as toroids) encapsulated in plastic. A voltage is applied to one of the coils. The other coil picks up an induced voltage in proportion to the conductivity of the solution surrounding it. Since the coils are encapsulated in plastic, a thin layer of oil that would completely insulate the electrodes in a contacting type sensor only lowers the reading slightly with an electrodeless sensor. The magnitude of the error is similar with conductive coatings. Electrodeless sensors still require periodic cleaning, but the frequency of maintenance is much lower than that required for a contacting sensor. While a toroid generates a magnetic field, that field is entirely

contained within the coil itself, so magnetic particles will not be attracted to the sensor and foul it.

## **Application to Specific Process Solutions**

### *Cleaners*

A typical alkaline cleaner consists of a mixture of components, including sodium or potassium hydroxide, trisodium phosphate, wetting agents, etc. In most cases some proprietary formulation will be used. In general, however, it is a single liquid concentrate that is used to replenish the cleaner, added back based upon the results of a laboratory analysis (titration). It is the hydroxide component that will contribute the most to the conductivity.

An electrodeless conductivity controller may be used to automate this process. When the cleaner is at its optimum concentration, note the conductivity value and use this as your set point. This will generally fall in the 50-100 mS/cm range. Many controllers may also be calibrated to read directly in percent concentration.

There can be a slight drift in calibration if conductive soils build up in the solution, which can necessitate recalibration on a weekly basis. If the cleaner is designed to etch metal, then the contribution to the conductivity of the metal salts may overshadow the loss of hydroxide. In this case, conductivity control will not be possible.

A similar program may be implemented for acid or neutral cleaners.

### *Phosphating*

A typical phosphating bath will contain phosphate salts, phosphoric acid and one or more of many possible accelerators. While pH control is often used, some baths contain fluoride that will quickly dissolve the pH electrode's glass measuring surface. In high temperature baths, pH electrode life can be shortened to only a month or so.

An electrodeless conductivity sensor can be used, with much longer life of the sensor, and less frequent calibration. While sludge formation will not have a significant influence the solution conductivity, since it is not in the ionic form, it can tend to build up in the sensor. This will necessitate periodic cleaning. Orienting the sensor in a way that eliminates horizontal surfaces on which the sludge can settle can reduce the frequency of cleaning.

### *Rinse Tanks*

As a water conservation technique, conductivity measurement may be used to operate a solenoid valve to control the level of contamination of rinse tanks. In many cases, rinse water will flow through the rinse tanks to the wastewater treatment facility regardless of the workload, wasting water. If the line is shut down for the operator's break, and water flow manually shut off, it may not be turned back on when the break is over. To optimize water usage, note the conductivity of the rinse tank at its highest acceptable contamination level, and use that as your upper set point for conductivity control.

### **How to determine if it can be used in new applications**

If you are considering using an electrodeless conductivity controller for an unusual application, there are a number of things to consider. Your first step might be to consult with your chemical supplier to see if they have already tried (either successfully or unsuccessfully) this control method for that chemical process. You may also want to consult with a reputable manufacturer of the controllers. You will need to consider:

1. **Chemical compatibility of the sensor.** You need to select a plastic material that will withstand the chemistry.

2. **Temperature range.** The sensor must be able to withstand the operating temperature, and also be able to compensate for the temperature change when reading the conductivity.

3. **Conductivity range.** The system must be able to read the conductivity accurately in the range in which the solution operates. Most controllers can handle from 100  $\mu\text{S/cm}$  (fairly clean water) to 2,000,000  $\mu\text{S/cm}$ . The highest known chemical conductivity is 31% nitric acid, at 865,000  $\mu\text{S/cm}$ .<sup>2</sup>

4. **Non-Linearity.** The chemical of interest needs to have a linear (or near linear) conductivity curve at the operating concentration. It must certainly not be at a point on the curve where the conductivity can drop with either an increase or decrease in concentration. Some controllers will allow a multiple-point

calibration in order to correct for non-linearity. Since the point of automatic control is to maintain the chemical concentration very close to the optimum value, non-linearity is rarely a major stumbling block.

5. **Influence of other components.** If there is more than one chemical in the solution, the chemical of interest must also be the most conductive. If not, the concentrations of the other components must be constant using some other control technique. Even then, slight changes of the most conductive component may mask changes in the component of interest.

6. **Influence of by-products or contaminants.** Any by-products of the reaction, or contaminants that may be dragged into the solution must not change the conductivity too much. Sometimes the drift is slow enough, so that a reasonable frequency of calibration can correct for it. One way to test for this is to measure the conductivity of two samples of the solution at the same concentration of the chemical of interest; one that is freshly made up, and the other after it has been used for its normal life. If they are significantly different, you may be out of luck.

### **Conclusion**

The electrodeless conductivity method of chemical process control can be used in many surface finishing applications, to provide a low cost alternative to automatic titrators or other direct measurement techniques. It provides better accuracy than continuous replenishment based on assumed surface area of parts. Care must be taken in applying this method, to ensure the desired results.

### **References**

1. Technical Bulletin, "Conductivity Measurement Theory and Practice", Sensor Development, Inc., Santa Ana, CA
2. Technical Bulletin, "2000 Laboratory Products Catalog & Electrochemistry Handbook" Orion Research, Inc., Beverly, MA 01915 (1999)