Glycol Management Paper

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Aqueous - Based Quench Fluid Control

Introduction:

Water-based polymer solutions are being used in an increasing amount in the metal industries for both safety and environmental reasons. In addition, the aqueous polymer solutions give superior results in many cases. The use of polyalkaline glycol (PAG) solutions to minimize quenching distortion in the aluminum industry is an excellent example. With proper control the new solutions can also be as or more economical than the older formulations. In order to be effective and economical, aqueous polymer solutions require proper maintenance to perform as advertised.

In this sections specific topics that users need to understand and control in order to maximize the performance of these solutions will be presented. They are:

- Concentration Control
- Bath/Solution Conditioning
- Reclamation
- Equipment
- Benefits/Economies

In what follows these are discussed in order.

Concentration Control:

Concentration control is accomplished using densitometers, refractometers, and viscosity meters. The concentration of the polymer in the quench bath has one of the most significant influences on the finished product. The cleanliness of the bath directly influences the accuracy of the measurements. Several of the instruments require frequent calibration, which adds to the maintenance burden in the factory. The refractive index monitor with remote sensing and optional connection to a PLC has proven to be very stable if the solution is conditioned and filtered. The accuracy levels we have experienced are within +/- 0.5% over time.

With the use of PLC and operator interfaces, concentration changes tailored to the product can be carried out accurately and quickly. The use of fully automatic systems has proven somewhat impractical since trouble shooting becomes difficult. For example, the status of the filling and draining operations are hard to monitor. Semiautomatic systems where an operator initiates each phase have proven more robust and less troublesome. Savings due to elimination of straightening cost following PAG quenching can be up to 60% for aluminum solution heat treatment.

Conditioning:

Bath conditioning consists of filtering and tending to the control of any biological impurities in the solutions.

Any bath that is used in an industrial environment will eventually be contaminated with dirt and debris from the parts that are being heat treated. This, of course, includes scale in the steel industry. Quench performance over time will be affected by alterations of the total chemistry of the bath by these impurities. Filtering the solutions with cartridge or bag filters using 5-10 micron filter media has proven sufficient to keep the bath in a condition where concentration measurements are accurate. The next step of conditioning consists in controlling the bioburden in the bath.

Bioburden:

Aqueous solutions will experience bacteria and algae growth if there are no biocides present. Bacteria growth can cause corrosion of parts (MIC, Micro Induced Corrosion) and can detrimentally affect membranes used for separation in reclamation systems. The bacteria can also reduce the sodium nitrate in the bath if they are anhydrous bacteria. Algae will coat the insides of the tanks and piping and will result in incorrect concentration data. Biocides are used with various successes. Biocides with Glutealdehyde are the most commonly used. They last from 10-21 days in the bath and must be replenished periodically to remain effective.(Figure 2. shows typical injection system.) Shop test procedures that check for bacteria and fungi will tell the operators of the need to treat the bath. Small paddle sticks such as those shown in Figure 1. are used for this testing with satisfactory results. An occasional change of biocide will keep the bacteria from becoming resistant to the product.

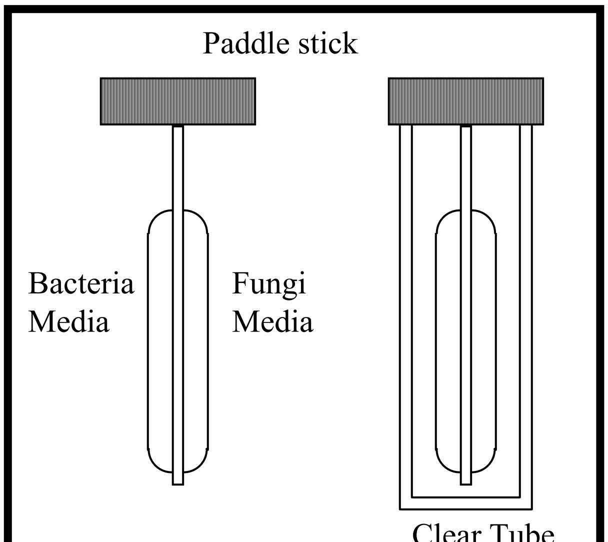

Figure 1 Showing Paddle stick tester

Chemical control:

The basic chemistry of new PAG changes very little over time when used in the quench bath. The pH level can change and must be maintained by adding buffers per the manufactures recommendations. The use of reverse osmosis (RO) membranes require special modifications to the PAG. Mainly the pH value is lowered slightly to increase membrane life. The pH must, however, not be lowered too much since the PAG becomes unstable at pH values less than 6-6.5. A low pH value can cause corrosion of aluminum parts during quench.

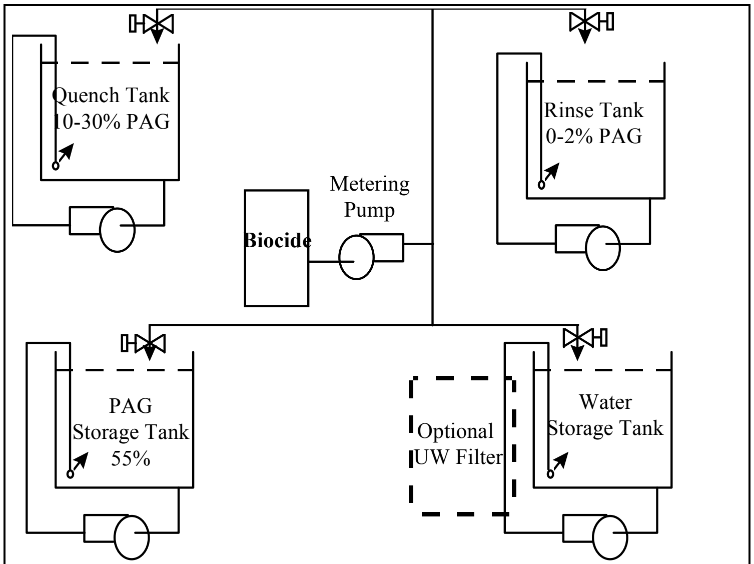

Figure 2. Typical biocide injection system

The corrosion inhibitor used in PAG is commonly sodium nitrate. This salt will be depleted over time and must be replenished to protect piping, pumps and other equipment. Sodium nitrate is also one of the first products that migrate through a worn RO membrane and create high electrical conductivity in the permeate water. This can be used as an indicator for tracking the condition of the membranes over time.

Equipment choices:

The choice of equipment to monitor, filter and re-concentrate the PAG solution must be done carefully after a full evaluation of the production environment and economics of the system has been made. The cost of PAG is about $9-$10 a gallon. With the development of fully closed loop systems with variable concentration control and conditioning, the costs of PAG replacement have drastically decreased in comparison to previous practice when rinse water was flushed to a drain causing dragout from the quench tank to be lost.

The capital cost of installing these systems must be compared to the savings in PAG replacement cost. The reduction of fire hazards and environmental concerns in connection with the quench process are also items to be considered. Waste water reduction is also a major factor especially in areas where water is a treasured commodity .

Major factors in the selection of equipment include final properties of the parts, level of distortion and amount of cracking.

There are basically three (3) ways of separating the PAG from the water after it has been diluted to the concentration the user needs.

1. **Heat separation**. By heating a tank, as illustrated in figure 3, to about 165-185^{0}F the PAG will settle out to the bottom unless there are considerable amounts of salt present in which case it settles to the top. The water is then siphoned off and a new batch can be mixed.

Figure 3

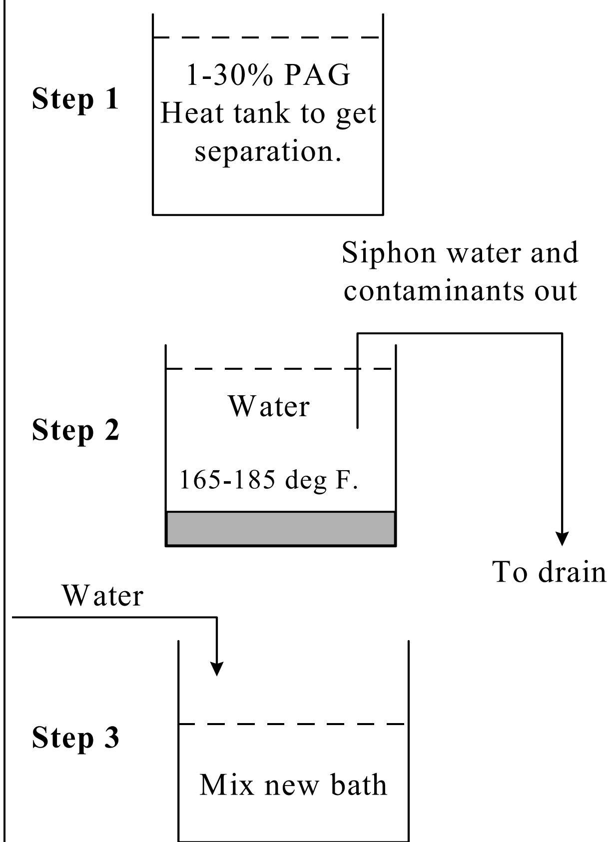

Figure 3. Batch heat seperation of PAG

2. **Membrane separation using Reverse Osmosis (RO) technology.** Figure 4 illustrates a typical closed loop RO system. With this method the PAG is separated from the water using membranes that allow the water to pass but reject PAG and salt which stay on the process side of the membranes. The water (Permeate) is stored in a water tank for later use or sent to drain. This technology does not work well in conjunction with salt baths or steel heat treat since the salt concentration in the PAG will increase during the concentration cycle. Salt is not desired in the quench bath since it can cause corrosion on the parts. Steel scale and free iron will damage the membranes and must be removed from the solution before it reaches the RO machine.

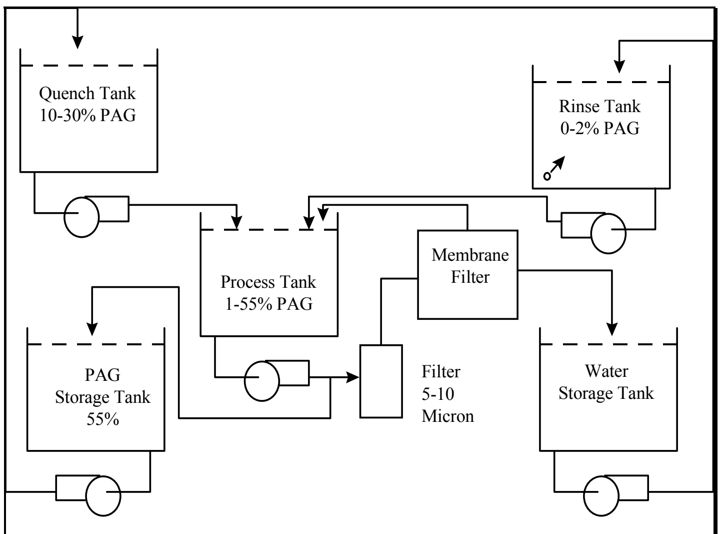

Figure 4. Reverse Osmosis Separation - Closed Loop System

3. **Membrane separation using micro or nano filtration.** These methods are similar to RO separation. However, small amounts of PAG will pass through the membranes with the water resulting in some waste of PAG. PAG will break down over time to smaller molecules as a result of mechanical and thermal action on the polymer.

4. **Heat separation in one pass through with heat recovery.** A new method has been developed and implemented that uses the heat separation concept but requires only a single pass through. Figure 5 shows the schematic for this system. Note that the process tank is optional compared to the RO system shown in figure 4. The heat separation method does not use membranes and is not sensitive to salt or iron in the bath. Production testing concentrated a 3% PAG solution into a 60% solution and clean water (Less than ½% PAG) in one pass at a rate of 5 gallons per minute. Other concentrations included 22% PAG where the recovery rate also proved to up to 60% PAG on the product side of the stream and "clean"(Less than ½% PAG) water on the other side. The system is very compact, robust and less costly than RO separation. At this time, this method is implemented at (5) locations throughout the country and more systems will be brought on line within this year.

Benefits/Economics:

Benefits of using aqueous based polymer quenchant solutions are many fold. Concentrations can be changed quickly and tailored to specific products. There are no fire hazards (in contrast to oil) and an economical recovery system can be put in place to cut the water and chemical costs of operating the systems. Based on experience in the aerospace industry, straightening costs can be reduced by up to 60% compared to using a water quench which adds directly to the bottom line. The cost of maintaining the systems has decreased. This is particularly true with RO systems since third generation control and hardware are now in place. These have proven to be reliable over time.

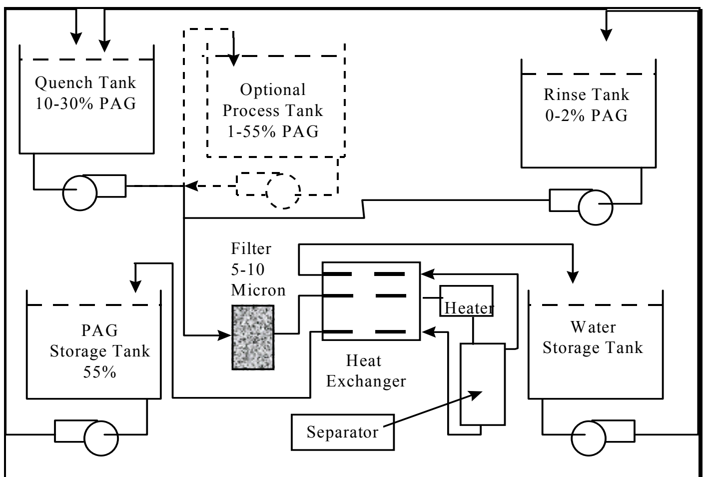

Figure 5. One Pass through Heat Separation

Future developments:

There is no doubt that more stringent environmental restrictions will be imposed on the industry which will make closed loop systems and recovery more attractive to the users. The development of single pass heat separation is imminent and will make it possible to recover PAG from systems that have iron in the quench bath. The ability to get better and more controlled quench rates and thus more control of the finished product will be a major factor in decisions to implement a PAG quench into a production process.

CEC offers all four systems described in the above and will be glad to help you select the most cost-effective system for your facility.