General Guidelines for Maintaining Alkaline Cleaning Tanks

Aqueous cleaning tanks that must last several weeks, months, or more than a full year require careful monitoring to avoid mishap during their extended time frame. Tanks containing alkaline cleaners can be problematic due to changes in pH, cleaner carry-out rates, type of water used to make-up/maintain the tank, and the sensitivity of the alloys being cleaned. A variety of cost and time effective tests can be run on tanks that must provide long life. Following these basic testing guidelines when maintaining aqueous alkaline cleaning tanks filled with alkaline cleaners will help to ensure the longest possible tank life for a given application.
Aqueous cleaning tanks that are changed out fairly rapidly (1-day to 1-week range) typically require little or no maintenance because of the limited time for anything to go wrong. On the other hand, tanks that must last several weeks, months, or more than a full year require careful monitoring of the things that can go wrong over an extended time frame. Alkaline cleaners can be the most problematic due to changes in pH and detergent concentration, cleaner carry-out rates, type of water used to make-up/maintain the tank, and the sensitivity of the alloys being cleaned. Straight forward bath monitoring and maintenance tests can be very cost effective in providing long tank life.

The following are basic testing guidelines that BHC recommends for operating and maintaining aqueous alkaline cleaning tanks filled with alkaline cleaners. It mainly addresses operation of tanks using alkaline detergents.

1. pH

This property is important because the ability to remove soils can degrade as the pH drops; animal fats, esters, glycerides, rosin flux residues, and asphaltum-based soils are good examples of this behavior. General studies suggest that keeping the pH at $>9.0$ for non-aluminum, $>9.5$ for aluminum will prevent problems from arising with these pH-dependent soils. This property is also important because corrosion inhibitors have a pH-dependent solubility curve; the lower the pH, the lower the solubility.

Inhibitor concentration must be adequately maintained or corrosion/discoloration problems on aluminum and other soft metal alloys can result. Cleaning performance may also deteriorate if too much inhibitor precipitates out of solution; some corrosion inhibitors aid in soil removal. Inhibitors may begin to drop out of solution around pH 10.2 – 10.3 but the level doesn’t begin to get dangerously low until the pH falls below 9.5. The inhibitor level will definitely drop below the minimum threshold amount required to protect aluminum at a pH of 9.0. Precipitation is partially reversible if periodic pH adjustment is performed, preferably with potassium hydroxide solution. Add-back of the concentrated detergent does not provide sufficient pH buffering capacity to be effective for pH adjustment in tank maintenance.

Some maintenance programs attempt to adjust pH into the target range, as opposed to simply monitoring pH for remaining in range. Should a customer wish to have a pH adjustment program in place, BHC recommends controlling the pH to a range of 9.5 – 10.5; most of our customers who do this have been using a narrower range of 9.8 – 10.5 with excellent results. BHC provides a separate document on this procedure and the pitfalls that can occur with the process upon request. Adjusting pH, typically with a caustic solution (such as 45% KOH), will artificially increase the total alkalinity in the bath and this in turn will falsely increase the concentration reading from titration. To account for this, a new correction factor must be generated after each and every pH adjustment. As a result, a pH maintenance program requires considerable investment in equipment and in training personnel. A potential candidate for the pH maintenance program must take these costs and skillsets into consideration before proceeding.

**BHC Recommendation:** The bath pH should be measured and recorded every shift. But adjustment of pH is not normally recommended unless you have qualified on-site analytical resources.

For those companies that do not have the budget to acquire and operate pH meters, BHC has found certain narrow-range pH papers sold by Thermo Fisher Scientific to be sufficiently accurate. A tank sample must be taken in a capped jar, cooled down to room temperature, then the pH paper strip is dipped in the sample and the color compared to a chart. The part numbers with descriptions are as follows:

**Catalog#:** M95873  
**Description:** EM colorpHast pH Strips, covers 7.5 to 14 with a sensitivity of 0.3 – 0.5 pH units, 1 pkg can run 100 tests
Catalog#: M95833
Description: EM colorpHast pH Strips, covers 6.5 to 10.0 with a sensitivity of 0.2 – 0.3 pH units, 1 pkg can run 100 tests

Thermo Fisher Scientific can be reached at 1-800-766-7000 (U.S.A.).

Limitations of the Test: The pH test is purely qualitative; it will not tell the operator how much cleaner is present, only its general condition. Measuring pH directly in a hot tank with an “in-tank” pH probe is unreliable; contaminants and alkalinity attack the pH probe and will skew calibration quickly. The pH value is also a highly temperature dependent property. It is impossible for BHC to measure all the combinations of tank strength and temperature on our products to provide guidelines for in-process pH measurement. Measuring pH on samples cooled to room temperature with a laboratory pH meter provides superior control and reliability for both BHC and the customer. Any pH values provided/disclosed by BHC are at room temperature unless otherwise noted.

2. Titration

This test is measuring total alkalinity, which is a measure of how much pH buffering capacity is present in the detergent solution. It is used to determine the concentration of the bath solution (commonly known as tank strength). The test involves adding an acidic reagent to a known volume of tank solution until a defined pH endpoint is reached. The simplest version of this test is done by counting drops of acid delivered from a bottle to the tank solution, to which a dye has been added, and which changes color at the pH endpoint. The drop-counting method is crude and subject to considerable variations if the operator is not properly trained (for example, to recognize the color change of the pH endpoint). Variations can be significantly reduced by using precision lab glassware and a pH meter but that requires much greater capital investment and training of personnel.

Nonetheless, the drop-counting method is useful for maintaining tank strength with a +/- 2% tolerance from the target concentration, which is adequate accuracy for the majority of process cleaning applications. Titration using precision lab glassware is needed if the application requires a tolerance tighter than +/- 2%.

Look for relatively constant tank strength over time. If the bath concentration drops over time, inappropriate use of air bubbling for agitation, cleaner carry-out, leaks in the system, overly aggressive oil skimming, pH degradation by contaminants, or excessive raw material stripping from using a micro/ultrafiltration unit are among the most likely suspects. If tank concentration increases over time, excessive add-back of cleaner or presence of water-soluble metal working fluids are typically the cause.

BHC Recommendation: Bath concentration measurement via titration should be tested and recorded every shift. The tank should be controlled within +/-2% of the target concentration. If the wash solution is outside this limit, add concentrated product to raise the concentration, or add water to lower the concentration.

Limitations of the Test: Not all ingredients in the cleaner will be detected by this test; it simply correlates tank strength to the underlying alkalinity of the alkaline solution. However, there is no one test that can detect all the ingredients in complex aqueous cleaners. Nonionic surfactants and solvents will not be detected by Total Alkalinity. In some cases, Total Alkalinity cannot discriminate between cleaner and soil. Nearly all water-soluble or self-emulsifying lubricants contain additives that have pH buffering capacity which will skew the pH. If the soil loading gets too high, titration test may indicate incorrectly that tank strength is increasing. The test could also indicate that tank strength is remaining constant when it is actually dropping the soil loading interfering in the analysis.

3. Assorted Performance Tests

Measuring pH and titrating the tank is very useful and often meets the needs of many manufacturers. The problem is that some customers have a unique set of conditions that call for some form of complementary performance testing to validate soil-removal or corrosion inhibition performance.
BHC recommends performance testing as a vital part of verifying the tank is operating to the expectations of the customer.

Which test(s) is required depends on the application. Here are some examples of simple complementary performance tests:

**A. Water Break Test**
This is the oldest and most traditional cleaning performance test. A flat panel made of the same/similar alloy and coated with same/similar soils as found in the manufacturing process is cleaned and rinsed in the process tank under the same control parameters. The panel is then immersed in a container of ambient temperature, overflowing tap water. The panel is removed from the container and allowed to drain for a minute while looking for breaks in the film of water as it sheets off the part. An early break in the film is evidence of hydrophobic contamination (oils and/or waxes). Be careful to note if the break is caused by mechanical surface imperfections as this is not evidence of remaining soil.

This is only a Pass/Fail test but part of the interpretation will be based on elapsed time until observation of a break in film; water break eventually occurs even on clean surfaces. ASTM F22-65 describes a semi-quantitative version of this test with measurement of how long it takes for a break in the film to occur. There is a variation of the water break test that uses a spray atomizer to coat the parts with water. This test can be more sensitive than the basic “dip in water” method but it is also more susceptible to operator error. The spray atomizer method is covered in ASTM F21-65.

**B. White Glove Test**
The name “white glove” is misleading since a glove is not typically used. The basic idea of the test is to wipe a metal surface with a white cloth/tissue after it has been cleaned. The evidence of residue on the cloth would indicate the presence of residual contamination on the part. One or more strokes can be used in the test with moderate-to-heavy pressure. This test is very useful in applications where smut removal (particulate contamination) from aluminum or steel is the task. The test is not quantitative and there can be difficulties with reproducibility due to variation in how each operator runs the test.

**C. Fluorescence (Black Light) Test**
This test looks for contamination by using a black light to search for residue that fluoresces. The advantage of this test is that it is a quick Pass/Fail test. The test sensitivity is pretty good when using a high-intensity black light (~ 100 watts). Workers must be properly trained when using high-intensity black lights because the ultraviolet radiation is damaging to eyes and skin without proper protection. The disadvantage to this test is that most mineral and animal-based oils do not fluoresce. There are several machining oil manufacturers that make metal working fluids containing fluorescent dyes to assist customers that wish to use the black light test.

**D. Stock Loss Test**
This test requires an in-house laboratory with an analytical balance, ovens, drying chambers, and trained personnel. A clean, dry, preweighed coupon (better to do three for statistical purposes) is immersed in the tank for a predetermined amount of time, then thoroughly rinsed, dried, and reweighed. Etch rates are calculated and any visible signs of discoloration or pitting are noted. This is a quantitative Pass/Fail test for evaluating corrosion inhibition performance based on the maximum stock loss allowed for the application. Evidence of staining or pitting may also be a qualitative Pass/Fail portion of the overall test.

**E. Metal Staining Test**
This is somewhat of a modification of the stock loss test and is only useful with alloys readily susceptible to discoloration or flash rusting, i.e., high-silicon diecast aluminum, 2024-T3 and 7075-T6 and -T7 series aluminum, brass, bronze, copper, high-chrome steels. This test is a qualitative method for evaluating corrosion inhibition performance. The operator takes a clean panel and immerses it in the cleaning tank for a period that is longer than the normal cleaning process. The panel is then removed, rinsed, dried, and compared to a clean, unused panel to detect signs of unacceptable discoloration or rust. Another variation of this is to place a strip or two of electrical tape on the panel before immersion, perform the cleaning-rinsing-drying steps, then remove the tape and compare the protected region to the area exposed to the cleaner. Processes
that require no change in color and/or luster of the substrate can benefit from this test. By exposing the test panel for a duration much greater than normal, the operator may begin detecting discoloration. As the tank gets older, discoloration or rust may appear sooner on the substrate. This test can be used to determine when to adjust or dump the tank.

Care must be taken in maintaining consistent tank temperature; wild variations can invalidate the test. If the panel is processed through more than one tank before inspection and discoloration/rusting is detected, the test should be repeated on individual tanks to determine which one is causing the failure.

**BHC Recommendation:**
In addition to maintaining the tank strength and monitoring pH, cleaning and corrosion performance should be monitored and be used as the ultimate criteria for determining the tank life end point. Cleaning performance (Water Break, White Glove, Black Light, or other custom-validated methods) should be tested and recorded every shift. Corrosion performance (Stock Loss, Metal Staining or other custom-validated methods) should be tested and recorded weekly or at an extended interval acceptable to the customer. Due to the large variations of substrates, soils and purposes of cleaning, there are no standard cleaning and corrosion tests and they have to be custom-tailored to each application and need.
4. Conductivity

This test measures how readily the solution is willing to conduct electricity. Conductivity is very effective in controlling acidic and caustic cleaners but is not effective in controlling pH-neutral and mild-to-moderately alkaline cleaners. When an acid or caustic cleaner is used, the acid/caustic chemical is consumed and water is generated as a by-product. The conductivity of water is negligible compared to the acid/caustic. Thus, decreases in acid/caustic strength generate large decreases in conductivity which allows this test method to work effectively.

Mildly alkaline and pH neutral cleaners do undergo some chemical consumption but the main by-product is usually another ionic species, not water. Fresh pH-neutral and mildly alkaline cleaners do not have high conductivities relative to acids and caustics. As soil loading and dissolved trace metals build-up in the tank, the conductivity of these cleaners tends to increase, not decrease. Conductivity is very effective as a control parameter to charge a fresh cleaning tank but it is not effective at maintaining mild pH cleaners with long tank life. Conductivity can also fail on acidic/caustic cleaners if the tank life is pushed too far through chemical add-backs; soil-loading eventually does affect even these cleaners but it takes much longer for it to become apparent. Conductivity is good at detecting excessive cleaner carry-out on mildly alkaline products.

**BHC Recommendation:** Conductivity method is not recommended for controlling wash tank strength. It can be a useful test for monitor rinse tank water quality.

5. Soil Loading

There are tests for determining the amount of emulsified oil present in a cleaner but BHC has found these to be ineffective in most cases. The oldest version of these tests involves adding concentrated sulfuric acid or sodium sulfate solution to a sample then setting it aside to allow the oil to separate to the surface. The problem with this test is that it usually does not work with cleaners that already split oils. This test was developed back when most cleaners were based on simple fatty acid emulsifying surfactants. Today’s synthetic detergents generally do not respond to this test.

**BHC Recommendation:** There is no standard soil loading method we can recommend at this point.

Final Comments

This paper does not cover all possible test methods and operating guidelines; it is meant to be a starting reference point that covers the most basic pitfalls and testing scenarios. A good reference book on industrial cleaning that covers chemicals, equipment, and testing in greater detail is: “Practical Guide to Industrial Metal Cleaning” by David S. Peterson, Hanser Gardner Publications, 207 pages, Copyright © 1997.