Corrosion inhibitors are sometimes added after the cleaning process because brightness is a crucial factor in the metals industry. Problems may occur when the next manufacturing step prohibits inhibitors.

Alkaline Aqueous Cleaning Alternatives for Soft Metals

BY ADRIAN PULLEN

In metal parts manufacturing, the appearance of the final product is of paramount importance. In this competitive industry, the "brightness" of the part can make or break a bid regardless of the functional importance of appearance. As a result, a brightening step must often follow the actual cleaning of the part. This step is typically an acidic bath which, depending upon the part, may or may not contain an abrasive for physical buffing. The acidity (H+) serves to remove the oxide layer (MO) on the metal surface as shown in Equation 1.

Equation 1: Acidic Brightening

\[
\text{MO} + 2\text{H}^+ \rightarrow \text{M}^{++} + \text{H}_2\text{O}
\]

During the cleaning step, alkaline aqueous cleaners are often used. The alkalinity of these cleaners serves as a saponifying agent for fatty oils. The saponification reaction changes the insoluble fatty oil into soluble glycerin and soap (Eq. 2). This reaction is an extremely effective method for cleaning these types of oils in an aqueous medium.

Equation 2: Saponification Reaction

\[
\text{CH}_3\text{O} - \text{C} - \text{R} \quad \text{CH}_2\text{OH} \quad \text{Na}^+ - \text{O} - \text{C} - \text{R} \\
\text{O} \quad \text{O} \quad \text{O}
\]

\[
\text{CH}_2\text{O} - \text{C} - \text{R} + 3\text{NaOH} \rightarrow \text{CH}_2\text{OH} \quad \text{Na}^+ - \text{O} - \text{C} - \text{R} \quad \text{O} \quad \text{O}
\]

\[
\text{CH}_2\text{O} - \text{C} - \text{R} \quad \text{CH}_2\text{OH} \quad \text{Na}^+ - \text{O} - \text{C} - \text{R} \quad \text{O} \quad \text{O}
\]

Insoluble fatty oil Strong Soluble Soluble
alkali glycerin Soap

Although the reaction described in Equation 2 provides a very strong driving force for oil removal, there are four potential drawbacks with this type of processing, particularly when combined with sensitive metals.

Drawback #1: The cleaning process (the saponification reaction) is not applicable to all oils. Non-fatty, such as petroleum-based, oils will not be affected by this reaction. Such oils can be emulsified by the surfactant package and, to some extent, the alkaline boosters but this action tends to be somewhat oil specific in alkaline cleaners. This fact often requires the use of several cleaning lines, each using different chemistries, when different types of oils are used.

Drawback #2: The most important potential problem is the corrosive quality of alkaline solutions with some metals and metal coatings. To minimize this, a corrosion inhibitor is usually present in alkaline cleaners. Although this limits corrosion, subsequent acidic brightening is inevitably required. Also, there are numerous instances where the corrosion inhibitors are not sufficient to prevent substantial damage to metal coatings, bimetallics or soft metals such as copper, brass and aluminum.

Drawback #3: There are applications in the medical, aerospace and electronics industries where the presence of residues cannot be tolerated and the presence of corrosion inhibitors is unacceptable. Typically, these materials operate by forming a protective layer on the surface of the part. This layer is very difficult to remove and often remains on the finished part.

Drawback #4: There are associated health and safety problems with handling acids and bases in a plant. These problems can translate into hidden costs due to insurance and special handling.

Given these limitations of alkaline cleaning, plants that are processing soft metals often turn to neutral pH aqueous cleaning. In order for the process to be competitive and serve the customer adequately, any high performance, neu-
cessing agent amounts are reduced. This leaves a relatively uniform residual layer, which can be removed in plasma in a few minutes.

**Precleaning With Different Media**

For the above-mentioned reasons, precleaning may be required depending on the initial conditions. The medium used for preclean is inconsequential to the subsequent plasma cleaning results. It is safest to focus on the material to be cleaned and the chemical composition of the contamination. In the following examples, solvents in the form of cold cleaners, as well as glycol ethers and water, are used as cleaning agents. The part must be dry prior to plasma fine cleaning.

Plant design with the respective peripherals (distilling unit, water treatment and purification), in addition to the initial condition of the parts and the results that can be achieved, are on page 21.

**Examples and Results of Cleaning Procedures**

**Application:**
Degreasing of metallic part (Dragerwerke AG Lubeck)

**Case Description:**
Cleaning of brass, aluminum and steel parts prior to assembly.

**Cleaning requirements:**
Minimum grease level (low total residue carbon).

**Former cleaning process:**
Aqueous and CFC.

**Alternative solution:**
Aqueous precleaning and final plasma cleaning.

**Results:**
According to user, better than the process to be replaced (see specifics in Table 1 page 21 and Table 2).

The good cleaning results are confirmed by the quantitative measurements of adhesion of the cleaned parts.

Test setup: copper tube with 3mm diameter, glued into an aluminum block, both suitably cleaned; glue used: Gupalon 30, setting for four hours at 120°C.

**Table 2**

<table>
<thead>
<tr>
<th>Cleaning Method</th>
<th>Tear Strength (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous</td>
<td>531</td>
</tr>
<tr>
<td>Aqueous = Tri</td>
<td>642</td>
</tr>
<tr>
<td>Aqueous = Plasma</td>
<td>795</td>
</tr>
<tr>
<td>Test Site: Dragerwerke AG Lubeck</td>
<td></td>
</tr>
</tbody>
</table>

**About the Author**

Dr. Hermann Schmid received his doctorate at the Institute for Organic Chemistry, University of Tuebingen, Germany. He has been the manager of the Applications Laboratory at Technics Plasma GmbH (Kirchheim bei Muenchen, Germany) since 1989. Additionally, Dr. Schmid has published numerous papers in European magazines and trade journals. He may be reached at (49) 89 905030 or by fax at (49) 90503100. U.S. telephone (606) 647-0730 or via fax (606) 647-0737.
neutral pH cleaner must address each of the four drawbacks.

Addressing Drawback #1: Since the solution is pH-neutral, no saponification will take place. All cleaning will be performed by strong surfactant emulsification. As a result, the formulation must have good wetting characteristics so that it can penetrate deep, narrow crevices. It must also have good emulsification properties so that oil is brought quickly into the cleaning solution. This cleaning mechanism has the major advantage of being applicable to a wider range of oils. Thus, many cleaning processes can often be collapsed to a single cleaning line.

Addressing Drawback #2: Although the corrosion effect of neutral solutions is much less than that of alkaline solutions, corrosion inhibition is still important. However, in order to address drawback #3, traditional corrosion inhibitors cannot be used. Also, in order to avoid the acidic brightening step in drawback #4, the cleaner must not only inhibit corrosion but must also brighten the part.

Addressing Drawbacks #3 and #4: To avoid the use of both traditional corrosion inhibitors and the acidic wash, a neutral pH brightening agent must be included in the formulation. This material should not only prevent corrosion without forming a layer on metal surfaces, but must also brighten the part sufficiently to obviate the necessity for the acid bath. The photo above shows the effect of a neutral pH brightening agent on a brass valve block. These valves were processed at 160°F for four minutes.

Neutral pH cleaners which successfully address these drawbacks are currently available. These cleaners have the following attributes:

• Since the cleaning mechanism is strong surfactant emulsification, the cleaner is broadly applicable and many different types of oils can be cleaned.
• As the solution is neutral, both hard and soft metals can be effectively cleaned without corrosion problems, making the cleaner more widely applicable in the plant.
• With an effective brightening agent, the cleaning and brightening steps required for soft metals are now combined into one pH-neutral step.
• As the solution is neutral and contains a brightening agent, traditional corrosion inhibitors are not required.

Overall, the product must also have minimal environmental impact and be considered essentially non-toxic. With these attributes, neutral pH aqueous cleaning can provide, in a simplified single-step process, the same excellent cleaning results of saponification with acid brightening, a two-step process. Also, both hard and soft metals can be cleaned by a wide variety of oils in the same cleaning operation. In plants where both different oils and soft metals are used, neutral pH cleaning can offer tremendous process simplification.

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CLEAN with Alconox
For the difference you can see...

and the difference you can’t see:

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Using an activated carbon fiber gives the element a higher adsorption capacity relative to granular carbon.

Recovering and Recycling Chlorinated Solvents

BY ROBERT E. KENSON, PH.D.

Recovery of corrosive and/or reactive solvents has been risky using conventional granular carbon adsorption technology. There is now available a technology using an activated carbon fiber, which has all of the solvent adsorbing micropores at the carbon surface. This gives the carbon high adsorption capacity relative to granular carbon as well as providing rapid adsorption/desorption rates. When used in a system designed for short adsorption and desorption cycles (10-15 minutes), the carbon fiber adsorption system provides advantages over conventional granular carbon systems for recovery of corrosive chlorinated solvents such as chloroform, trichloroethylene and methylene chloride. Higher quality of recovered solvent, less system corrosion and less wastewater treatment problems are some of the advantages shown in numerous installations of activated carbon fiber-based solvent recovery systems worldwide.

Chlorinated Solvent Recovery

The recovery of chlorinated solvents has had mixed success when granular carbon technology is used. During carbon regeneration, the presence of steam and the catalytic action of the heavy metals (Fe, Cu, etc.) present in the carbon at the carbon regeneration temperature (250-300°F) hydrolyzes a small portion of the solvent to form hydrochloric acid and corrosive organics.

The acid, in the presence of condensed steam, causes stress corrosion cracking when alloy steels are used for system construction. Protective polymeric liners over the steel have been tried, but liner adhesion or integrity cannot be guaranteed with the alternate heating/cooling cycles to which the adsorption vessels are subject.

Some users have found that more exotic alloys are the only suitable materials for vessel construction where corrosive chlorinated solvents are to be recovered. The resulting high capital cost of such alloys have discouraged their use when the cost-effectiveness or payback period of the solvent recovery systems was examined.

Even if the system integrity can be maintained when granular carbon systems are recovering corrosive chlorinated solvents, the quality of the recovered solvent is usually poor. The activated carbon fiber adsorption system, because there is far less solvent decomposition during steam desorption, allows the reuse of the recovered solvent without repurification in many cases.

Activated carbon fiber-based solvent recovery systems have been applied in the precision cleaning industry with a high degree of success. A number of installations have shown some of the advantages of this unique activated carbon form and system operating cycle.

First, the activated carbon fiber contains 1/2 to 1/10 the heavy metals content of granular carbons, so that catalysis of solvent decomposition by heavy metals is inhibited. Second, the system desorption cycles with the carbon fiber are 10 to 15 minutes, whereas more than 60 minutes is required to regenerate a granular activated carbon bed satisfactorily.

The result of these two differences is that the quality of solvent recovered with activated carbon fiber adsorption is far better than that from granular carbon systems. A side benefit is that system corrosion is less because of the reduced concentration of hydrochloric acid formed, so that in many cases, vessels, valves and piping can be made of readily available stainless steel rather than exotic alloys.

Table 1 shows data from a typical application of an activated carbon fiber system for recovery of trichloroethylene at high removal efficiency and with direct reuse of the recovered solvent. Table 2 (page 28) shows a comparison of the quality of recovered trichloroethylene from the activated carbon fiber adsorption system and from granular carbon solvent recovery systems. The activated carbon fiber adsorption system, in this case, has shown itself to be capable of recovering trichloroethylene which meets new solvent specifications.