Extending the Life of Polymer Quenchants: Cause and Effect of Microbiological Issues

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Abstract

Polymer (aqueous) quenchants have been utilized for many years in the heat treatment process of both ferrous and non-ferrous materials. Although the quenching process takes only a few seconds of the total production time for a component, care and maintenance of the proper quenchant is crucial to avoiding inadequate metallurgical properties, distortion or scrapping of costly machined components. It is important to establish methods and mechanisms to measure and control polymer concentration; identify contaminants from solids, pre-heat treatment process fluids, microorganisms, or dissolved materials (all of which can reduce quenchant life); and determine any possible degradation in service. Properly selected polymer quenchants and a properly operating quenchant system can combine to deliver reliable and consistent service, as well as performance benefits.

This paper will review a short history of biostable technology in metalworking fluids and more specifically the introduction of biostable polymer (aqueous) quenchants for heat treatment applications. The advantages of a biostable polymer quenchant versus a traditional polymer quenchant in-use regarding microbiological issues, pH, and heat extraction capabilities will also be reviewed.

Introduction

The prevailing mindset of both vendor and end-user was simply that wherever one had water and a food-source (which is what most process fluids are) you were destined to have biological issues with bacteria and/or fungus. Once the bio-population got a foothold in a metal processing system, it was controlled via the use of appropriate biocides and/or fungicides to varying degrees of success.

The use of sump side biocides then and now is still considered undesirable due to handling issue concerns, but accepted best practice to control biological populations. For the last several years Houghton has chosen to engineer metal processing fluids, including polymer quenchants to be inherently biostable first, and then build-in the required performance features which enable customer to manufacture the best quality part at the lowest possible cost.

This research and development mindset and effort began with a metal removal product to the metal working industry back in 1997. To do this, the choice of ingredients had to be changed. The traditional chemistries being used at the time simply could not measure up to the new self-imposed criteria. So work began formulating fluids with different building blocks and
ingredients that did not easily change in time and use. This meant these new ingredients had to remain unchanged in use from the biological challenges, the physico-chemical conditions, and the process conditions.

The design began with choosing individual constituents that met the above requirements, and putting them together so the sum of the parts gave the intended purpose of the fluid. Interestingly enough, the research and development stages that some metal processing fluids did not change much at all under a variety of chemical and biological stresses, but didn’t fulfill their intended purpose. Over time, we became judicious in the choices and found material that did not change easily in time, is use, and still provided the primary intent of the fluid. In a sense we worked backwards and this made formulations very complex.

Fluids that break down can produce bad actors ranging from biological conditions that change the chemistry and produce an unhealthy environment to chemical changes that detract from the stability of the fluid in use. If one must dump a fluid frequently, it also creates an environmental impact; waste treatment concerns, and is wasteful of water. Many of the molecules chosen existed as natural products or could be modified from natural products. This is also a type of sustainable development.

Contamination by bacteria and fungus is a common occurrence in the heat treating shop, especially with induction hardening applications. In these applications, parts are often taken directly from the machining center directly to the automated induction hardening operation. Often, no cleaning operation precedes the heat treatment of parts. Metal fines, chips and pre-heat treatment process fluids (coolants, cleaners and rust preventatives) are often dragged into the induction hardening operation. The metal working fluid is often contaminated with a broth of bacteria and fungus. This can impact the quenching operation and can contribute to “Monday Morning Stink”.

The source of the smells often attributed to polymer quenchants are anaerobic bacteria and fungus. These bacteria thrive in oxygen depleted environments and feed on the metal fines and the quenchant itself. Bacteria and fungus contamination can be controlled by the careful use of biocides and fungicides. However, proper application of these biocides must be performed by properly trained personnel, with proper personnel protective equipment, like full Tyvac suits, face shields, and safety glasses. Double gloving in latex is also recommended. Very small quantities of biocides are required. One manufacturer recommends just 1-2 ounces of biocide/fungicide per 1000 gallons. Since most induction hardening systems are small (less than 300 gallons and often about 150 gallons), the measurement and proper dosage of biocide can be problematic.

Bacteria and fungus in polymer quenchants can be controlled without the use of biocides or fungicides. Cleanliness and oxygen content are the key factors. The solution should be kept well agitated, and minimize food sources. Cleaning of part prior to heat treating is always recommended. However, this advice is not always followed because of cost, space and process reasons.

The purpose of this paper is to demonstrate a new formulation of polymer quenchant that is damage-tolerant to the presence of bacteria and fungus, and does not have the down-side of biocide additions to the sump. Personal protective gear requirements are only those normally used for polymer quenchants.
Procedure

Two polymer quenchants of similar type (PAG) and molecular weight are compared for pH stability over a period of time. Samples were inoculated with typical metal working coolants to simulate typical induction hardening practice, where parts are hardened immediately after machining, without an intermediate cleaning operation. Results showing the stability of the polymer quenchants when exposed to fungus and bacteria are examined.

A study was conducted based on ASTM D3946 “Standard Test Method for Evaluating the Bacteria Resistance of Water-Dilutable Metalworking Fluids”. This method was modified to include testing of fungus resistance. Two polyalkylene glycol quenchants were examined; each having identical physical characteristics such as molecular weight and polymer composition were tested. These quenchants were Aqua-Quench 140 and Aqua-Quench 145, each typically used in induction hardening applications. Each quenchant was prepared at a 5% dilution commonly used for induction hardening applications.

Bacteria

The submitted samples were tested based on the regime presented in ASTM D3946. For bacteria, a contaminated metalworking fluid was mixed in equal portions with Soybean Casein Digest broth (Tryptic Soy broth) and allowed to grow for approximately two days prior to study initiation to prepare the inoculum. Ten grams of metal chips and 100 mls of inoculum (approximately 10% of the total volume of the test system) was added to a 1 liter French Square Bottle, each filled to the brim with the test fluid, Aqua-Quench 140 or Aqua-Quench 145 respectively, at 5% concentration. Each French Square Bottle was equipped with a holed cover for the establishment of aeration which was supplied from an aquarium air pump through a cotton-plugged sterile pipette. Standard plate count analysis for bacteria was done using Tryptic Soy Agar and standard counting and sterile dilution techniques with incubation for ≥ 48 hours at approximately 35°C.

Fungus

ASTM D3946 was modified to test fungus since the procedure was written for use with bacteria only. Fungus growth can also be a problem in metalworking fluids. For fungus testing, a concentrated spore suspension of Aspergillus niger, a resistant mold (fungus) species, was added directly to 100 mls of Sabouraud’s dextrose broth, a medium designed to propagate yeasts and molds. This medium contained 2 g/l Chloramphenicol to retard bacteria growth. Ten grams of metal chips and 100 mls of the fungal preparation (approximately 10% of the total volume of the test system) was added to each 1 liter French Square Bottle and filled to the brim with the test fluid, AQ 140 or AQ 145 respectively, at 5% concentration. The French Square Bottle was equipped with a holed cover for the establishment of aeration which was supplied from an aquarium air pump through a cotton-plugged sterile pipette. Standard plate count analysis for fungus was done using Sabouraud’s Maltose Agar and standard counting and sterile dilution techniques with incubation for ≥ 3 days at room temperature.
Testing Regime

The testing regime followed ASTM D3946. Bacteria and fungus testing was done separately in separate French Square Bottles. The regime was as follows:

- The inoculum was tested prior to introduction of the test fluid. Testing included physical properties and cooling curves ASTM D 6481 (Standard Test Method for Determination of Cooling Characteristics of Aqueous Polymer Quenchants by Cooling Curve Analysis with Agitation (Tensi Method)).
- After mixing of the metal chips, inoculum, and test fluid a sample was removed prior to the start of aeration for plate count testing and pH analysis as an initial test (5 minutes). Additionally, a cooling curve was performed per ASTM D 6481 to examine the effects of inoculating the polymer quenchant with bacteria and fungus.
- After approximately 5 days of aeration, another sample was removed for the same testing as in step 2 (5 day test) and the aeration was stopped for approximately 2 ½ days.
- After the 2½ day un-aerated period, another test sample is removed for the same analysis (8 day test) and aeration resumed for an additional 5 days.
- At the end of this 5 day period a final sample (13 day test) is removed for the same analysis as above. A final cooling curve was then performed to examine the effects of exposure to the bacteria and fungus.

While the ASTM testing regime was not modified additional samples were taken to increase the amount of data generated during the test to better ascertain trends.

Results

The measurement of pH is an excellent indicator of the health of a polymer quenchant. It is proportional to the organic acids (primarily acetate, propionate, and butyrate) and the hydrogen-sulfide by-products of microbial metabolism. These compounds are formed as the anaerobic bacteria proliferate, resulting in a drop in pH. The results of exposure to bacteria are shown in Figure 1, while the exposure to fungus is shown in Figure 2.

Both of the polymer quenchants showed relative immunity to bacterial inoculation, with the pH staying at a relatively constant pH. However, because of the higher starting pH of AquafQuench 145 it is likely to be much more resistance to bacterial contamination. It will also offer better corrosion protection.

Examination of the exposure of the polymer quenchants to fungal contamination (Figure 2) shows a different result. In this case, Aqua-Quench 140 showed a significant drop in pH over the first 5 days before the pH became stable. Aqua-Quench 145 was stable throughout the length of the test. This would indicate that Aqua-Quench 145 is much more tolerant to fungal contamination than Aqua-Quench 140 in terms of pH.
Examination of the exposure of the polymer quenchants to fungal contamination shows a different result. In this case, Aqua-Quench 140 showed a significant drop in pH over the first 5 days before the pH became stable. Aqua-Quench 145 was stable throughout the length of the test. This would indicate that Aqua-Quench 145 is much more tolerant to fungal contamination than Aqua-Quench 140 in terms of pH.

Comparison cooling curves of the two products under each of the conditions were conducted per ASTM D6481. Conditions examined were the blank or control of the product at 5%; immediately after bacterial inoculation; after completion of the test (13 days); initial fungus inoculation and the final fungus result after the completion of the test. The resultant curves are shown in Figure 3. Summary data from the cooling curves are shown in Table 1 and Table 2.

The results of the cooling curve testing closely follow the results of the pH testing. For Aqua-Quench 140, there was an initial large drop in the maximum cooling rate due to the inoculation of bacteria. Subsequently, there was very little change from the initial drop in the maximum cooling rate due to bacteria. There was little change upon inoculation of fungus, however a slight decrease in the overall cooling rate occurred due growth of the fungus.

Aqua-Quench 145 showed very little change in the maximum cooling rate from the control. A slight increase was observed after inoculation with bacteria, and after the test was complete. However, these changes are not statistically significant. This result was repeated for the fungal inoculation, with the Aqua-Quench 145 showing little change due to fungal contamination.
Figure 2 - Comparison of responses to fungal contamination for two PAG polymer quenchants at 5% concentration.

Table 1 - Results of the cooling curve testing per ASTM A6481 for Aqua-Quench 140.

<table>
<thead>
<tr>
<th></th>
<th>Blank</th>
<th>Bacteria Initial</th>
<th>Bacteria Final</th>
<th>Fungus Initial</th>
<th>Fungus Final</th>
<th>Standard Deviation</th>
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<tbody>
<tr>
<td>Maximum Cooling Rate, °C/s</td>
<td>205.81</td>
<td>152.99</td>
<td>149.46</td>
<td>204.28</td>
<td>180.78</td>
<td>26.97</td>
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<td>Temp. at Max. Cooling Rate, °C</td>
<td>618.28</td>
<td>597.86</td>
<td>626.69</td>
<td>644.82</td>
<td>622.8</td>
<td>16.88</td>
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<td>Cooling Rate at 300 °C, °C/s</td>
<td>98.86</td>
<td>88.89</td>
<td>89.28</td>
<td>98.17</td>
<td>98.09</td>
<td>5.10</td>
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<td>Time to 600°C, s</td>
<td>2.32</td>
<td>5.82</td>
<td>5.14</td>
<td>1.58</td>
<td>3.47</td>
<td>1.80</td>
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<td>Time to 400°C, s</td>
<td>3.48</td>
<td>7.24</td>
<td>6.58</td>
<td>2.76</td>
<td>4.77</td>
<td>1.93</td>
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<td>Time to 200°C, s</td>
<td>5.85</td>
<td>9.84</td>
<td>9.17</td>
<td>5.12</td>
<td>7.18</td>
<td>2.05</td>
</tr>
<tr>
<td>Delta, °C</td>
<td>-52.82</td>
<td>-3.53</td>
<td>-1.53</td>
<td>-23.5</td>
<td></td>
<td></td>
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<tr>
<td>Delta, °C, from blank</td>
<td>-56.35</td>
<td>-25.03</td>
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Table 2 - Results of the cooling curve testing per ASTM A6481 for Aqua-Quench 145.

<table>
<thead>
<tr>
<th></th>
<th>Blank</th>
<th>Bacteria Initial</th>
<th>Bacteria Final</th>
<th>Fungus Initial</th>
<th>Fungus Final</th>
<th>Standard Deviation</th>
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<tr>
<td>Maximum Cooling Rate, °C/s</td>
<td>177.37</td>
<td>187.88</td>
<td>191.11</td>
<td>174.4</td>
<td>166.35</td>
<td>10.11</td>
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<td>Temp. at Max. Cooling Rate, °C</td>
<td>628.84</td>
<td>614.75</td>
<td>598.76</td>
<td>584.67</td>
<td>633.85</td>
<td>20.56</td>
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<tr>
<td>Cooling Rate at 300 °C, °C/s</td>
<td>92.63</td>
<td>92.29</td>
<td>93.51</td>
<td>100.71</td>
<td>95.55</td>
<td>3.47</td>
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<tr>
<td>Time to 600°C, s</td>
<td>2.14</td>
<td>4.05</td>
<td>2.6</td>
<td>2.39</td>
<td>3.8</td>
<td>0.87</td>
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<tr>
<td>Time to 400°C, s</td>
<td>3.4</td>
<td>5.27</td>
<td>3.78</td>
<td>3.61</td>
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<td>Time to 200°C, s</td>
<td>5.85</td>
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<td>Delta, °C</td>
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<td>3.23</td>
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<td>Delta, °C, from blank</td>
<td>13.74</td>
<td>-11.02</td>
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**Discussion**

Quenching systems are dynamic systems that change over time due to the influx of contaminants from pre-heat treatment process fluids. This results in different quenching characteristics over an extended time frame. Previously, this would require dumping and recharging systems with new quenchant at specific intervals, usually measured in several weeks (4-6 weeks is not uncommon). These changes in the quenching characteristics also mean the potential of poor properties and improper case depths, resulting in rejected parts and increased maintenance time.

Proper maintenance of the quenching system and the polymer quenchant is critical for long life and repeatable properties. The use of bio-stable quenchants, such as Aqua-Quench 145 enables the customer greater freedom from the periodic dump, clean and recharge required using typical polymer quenchants.

**Conclusions**

What many clients have discovered (and now enjoy), is the fact that these metal processing fluids and related variations offer systems that typically do not sour. The client has to do their part and maintain recommended operating concentration, but will reap the reward of reduced biocide usage, reduced waste treatment costs, reduced down time and reduced consumption. The bottom line to our customer base is simply this; the implementation of this new technology in your plant will remove metal processing fluid related issues from the to-do list. A company will be able to focus upon manufacturing components and not deal with fluid related issues.

**Acknowledgments**

We would like to thank the following Houghton technicians for their work in completing this work: Joe Jankowski; Gloria Graham and Nan Burch. We would also like to thank our management allowing us to present this data and attend the 6th Quench and Control of Distortion Conference.
Figure 3 - Comparison cooling curves of Aqua-Quench 140 and Aqua-Quench 145 at 10%. Aqua-Quench 140 (Top): 1 – Blank; 2 - Initial bacteria; 3 - Final bacteria; 4 – Initial fungus; 5 – Final fungus. Aqua-Quench 145: 6 – Blank; 7 - Initial bacteria; 8 - Final bacteria; 9 – Initial fungus; 10 – Final fungus.