The quenching operation is a critical part of the heat treatment process. The cooling characteristics of a quenchant will change during its working life. Improper quenching parameters and the drifting of the cooling characteristics can cause unforeseen costs if a malfunctioning component necessitates additional operations, e.g. straightening, machining, rework, or even rejection.

For a polymer quenchant the cooling characteristics are influenced by, inter alia, concentration, agitation, temperature, thermal degradation, contamination and drag-out. In this study tests have been performed in order to study how the ageing and contamination of polymer quenchants influence the cooling characteristics. Polymers used for induction hardening in showers as well as in quench baths have been evaluated with regard to e.g cooling curves, refractive index and kinematic viscosity after ageing. Quenchants used in industrial applications have been evaluated.

Cooling curves have been evaluated by using the ivf SmartQuench™ system. This is a tool for testing quenching media, primarily against the current ISO and ASTM standards for hardening oils and polymers. A large number of characteristics are recorded or calculated, such as cooling times to certain temperatures and cooling rates at these temperatures.

**Key words:** quenching, quenchants, cooling curves, polymers, ageing
INTRODUCTION
The cooling characteristics of a quenchant will change during its working life due to e.g. contamination, thermal degradation, evaporation and drag-out. In order to study these effects a pre-study was performed at Swerea IVF focusing on polymer quenchants. The aim was to gain a better understanding of why and how a quenchant’s cooling characteristics change due to e.g. ageing and contamination, and how the control and monitoring of quenchants can be improved to guarantee production quality.

A benchmark study was performed on polymer quenchants used in production. Samples of different polymer quenchants were collected from nine different manufacturing facilities in Sweden. The quenchants differed in type, concentration, application method, charge sizes and time used in production. All samples were evaluated with regard to cooling curves (which were analyzed by using the ivf Smart Quench™ system), concentration and viscosity. A new/fresh quenchant with a corresponding concentration was used as a reference.

After the benchmark study one quenchant was selected for a subsequent study to investigate thermal degradation.

POLYMER QUENCHANTS
Polymer quenchants consist of polymer solutions in water. A polymer quenchant contains bactericides and additives such as corrosion inhibitors and defoamers to control properties and cooling performance and prolong service life. The polymer is further diluted before use. The cooling characteristics of a quenchant depend on the type of polymer, the degree of agitation, the polymer concentration and the temperature.

The following are examples of different polymer quenchants: PAG (polyalkylene glycol), ACR (sodium polyacrylate), PVP (polyvinyl pyrrolidone), PEO (polyethylene oxazilone) and Amide (polyacrylamide). PAG is one of the most widely used polymer quenchants.

QUENCHANT ANALYSIS
The quenchants were analyzed with regard to cooling curves, concentration, viscosity, and, for selected samples, molecular weight distribution.

The ivf SmartQuench™ system was used to measure and evaluate the cooling curves (see Figure 1). The equipment consists of a registration unit, a furnace, a handle and a test probe. The software includes evaluation and analysis features which make it possible to interpret cooling curves from several different viewpoints.

The test probe used was in accordance with ISO 9950 (the same probe is used in ASTM D 6200 and ASTM D 6482 for testing oils and polymers respectively). The probe is made of Inconel and has a diameter of 12.5 mm and a probe body length of 60 mm. A Type K thermocouple is positioned at the centre of the probe body. The tests were performed by using the Tensi agitation unit as specified in the ASTM 6482 standard (Figure 2).
The concentration as stated by the companies was cross-checked by using a Brix refractometer in connection with the measurement of the cooling curves.

Steady shear viscosity (equilibrium) at various shear rates was measured with a rotational CS rheometer (Nova, Reologica Instrument AB, Sweden) by using a 25 mm bob/cup measuring device.

**QUENCHANTS USED IN PRODUCTION**

Samples of three different kinds of polymer quenchants were collected from nine different heat treatment facilities in order to compare quenchants that are in use to each other and to new solutions (see Table 1). All companies provided information on how and when the quench bath is replaced, how monitoring is performed, what the process parameters are and, when applicable, the quantities of steel that have been quenched.

<table>
<thead>
<tr>
<th>No.</th>
<th>Polymer</th>
<th>Type</th>
<th>Facility</th>
<th>Conc.</th>
<th>Comments / Fig</th>
<th>Service time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Aquaquench 365</td>
<td>PAG</td>
<td>A</td>
<td>10%</td>
<td>Induction shower / 2a</td>
<td>1 year</td>
</tr>
<tr>
<td>2</td>
<td>Aquaquench 365</td>
<td>PAG</td>
<td>A</td>
<td>13%</td>
<td>Induction shower / 2b</td>
<td>8 months</td>
</tr>
<tr>
<td>3</td>
<td>Aquaquench 365</td>
<td>PAG</td>
<td>G</td>
<td>5%</td>
<td>Induction shower / 2c</td>
<td>1 year</td>
</tr>
<tr>
<td>4</td>
<td>Aquatensid BW/RB</td>
<td>PAG</td>
<td>D</td>
<td>16%</td>
<td>Induction shower / 2d</td>
<td>2 weeks</td>
</tr>
<tr>
<td>5</td>
<td>Aquatensid BW/RB</td>
<td>PAG</td>
<td>D</td>
<td>16%</td>
<td>Induction shower / 2e</td>
<td>1.5 month</td>
</tr>
<tr>
<td>6</td>
<td>Aquatensid BW/RB</td>
<td>PAG</td>
<td>D</td>
<td>17%</td>
<td>Induction shower / 2f</td>
<td>2.5 months</td>
</tr>
<tr>
<td>7</td>
<td>Aquatensid BW/RB</td>
<td>PAG</td>
<td>E</td>
<td>17%</td>
<td>Induction shower / 2g</td>
<td>4 months</td>
</tr>
<tr>
<td>8</td>
<td>Aquatensid BW/RB</td>
<td>PAG</td>
<td>F</td>
<td>16%</td>
<td>Induction shower / 2h</td>
<td>2 months</td>
</tr>
<tr>
<td>9</td>
<td>Aquatensid BW/RB</td>
<td>PAG</td>
<td>G</td>
<td>13%</td>
<td>Induction shower / n.i</td>
<td>3 months</td>
</tr>
<tr>
<td>10</td>
<td>Aquatensid BW/RB</td>
<td>PAG</td>
<td>H</td>
<td>13%</td>
<td>Induction shower / n.i</td>
<td>8 months</td>
</tr>
<tr>
<td>11</td>
<td>Feroquench 2000</td>
<td>Amide</td>
<td>B</td>
<td>8%</td>
<td>Bath / n.i</td>
<td>?</td>
</tr>
<tr>
<td>12</td>
<td>Feroquench 2000</td>
<td>Amide</td>
<td>B</td>
<td>14%</td>
<td>Bath / n.i</td>
<td>?</td>
</tr>
<tr>
<td>13</td>
<td>Feroquench 2000</td>
<td>Amide</td>
<td>C</td>
<td>12%</td>
<td>Bath / 2i</td>
<td>4 months</td>
</tr>
</tbody>
</table>

Irrespective of application method – i.e. bath or induction shower – the time used in production and the applicable process parameters, the cooling curves for all samples were measured at a temperature of 30 °C and at an agitation rate of 0.3 m/s.
Figure 2 shows cooling curves for quenchants that are used in production compared to new solutions. It should be noted that no conclusions can be drawn regarding the quality of a specific quenchant as the background information is incomplete. The purpose is to show how the cooling characteristics can differ between quenchants that are in use and new solutions.

![Cooling Curves](image)

- a) Aquaquench, 9-10%
- b) Aquaquench, 13-15%
- c) Aquaquench, 5%
- d) Aquatensid, 15-16%
- e) Aquatensid, 15-16%
- f) Aquatensid, 15-17%
- g) Aquatensid, 15-17%
- h) Aquatensid, 15-16%
- i) Feroquench 2000, 12%

Figure 3: Cooling curves of some of the quenchants in the benchmark study – a comparison between new solutions and solutions that are in use.

It is obvious that the behaviour of the different quenchants is affected by their usage. With the exception of g) the overall trend is that the cooling rate accelerates at lower temperatures, around < 400 °C, during usage. Regarding the curves shown in g), where the cooling rate decelerates over the complete temperature range, a possible explanation could be that the quenchant solution is contaminated with oil or oil emulsion from e.g. cutting fluids. This assumption is also supported by the presence of vapor phase tendency.

The effect of usage on the cooling rates at higher temperatures varies a lot and there is no marked tendency. This may be because the total effect of usage at higher temperatures depends on a combination of several factors, e.g. different types of contamination, thermal and mechanical degradation and oxidation, which can be more or less predominant depending on the local conditions at each facility. At lower
temperatures, however, the effect may instead be determined by only one factor, e.g. thermal degradation.

**STUDY OF AGEING BY THERMAL/OXIDATION DEGRADATION**

One of the quenchants in the benchmark study – Aquatensid BW/RB – was selected for a study on how thermal/oxidation degradation influence cooling characteristics.

Thermal degradation occurs due to the exposure of the quenchant to high temperatures during the quenching process. An accelerated test was developed to isolate this effect as much as possible. The test was performed by using an induction heating equipment with a quench bath (see Figure 4). A 75 mm long cylinder made of Inconel 600 and with a diameter of 25 mm was heated up and quenched in a 3-litre bath of 10% Aquatensid at a temperature of 20 °C. A Brix refractometer was used to verify the concentration. No additional polymer concentrate had to be added to maintain a constant concentration.

Irrespective of polymer type, parameters such as bath temperature, agitation and the concentration of the polymer have a strong influence on the cooling characteristics. In order to focus on the degradation effect on the polymer, the bath temperature and agitation rate were kept constant.

The probe was heated up during 25 seconds. The surface temperature was measured to 1050 °C and the calculated temperature at the core was approximately 900 °C. After a holding time of 1 second the probe was immersed in the quench bath. This was repeated in up to 400 cycles. After every 100 cycles the quenchant was analyzed with regard to cooling curve and concentration and a sample was collected to measure the viscosity.

The aim was to simulate the quenching of 9000 crank shafts, total quenched weight 310 ton, in a 8000-litre quench system. The quench bath of the test rig had a volume of 3,5 litres.

*Figure 4  Experimental set-up for thermal degradation tests.*

Figure 4 shows the temperature/oxidation degradation effect on Aquatensid BW/RB. The ageing of the quenchants results in a higher cooling rate at all temperatures, in the upper as well as the lower range.
EVALUATION OF VISCOSITY

The chemical structure and molecular weight of the quenchant influence its cooling characteristics. Most polymers used for quenching applications have a linear structure. One of the primary factors controlling heat transfer in the convective cooling phase is the ability of the polymer to transfer heat either by convection or conduction through the film. In this context, the viscosity of the polymer solution is an important factor. An increased viscosity is expected to result in a decrease in heat transfer, implying a slower cooling.2

The chemical structure of the polymer influences its cooling characteristics. The film strength is influenced by the molecular weight of the polymer and therefore by the duration of the vapor blanket stage, which affects the heat transfer2.

MOLECULAR WEIGHT DISTRIBUTION

The T CP/GPC method were used to arrive at a qualitative determination of the molecular weight distribution in three of the quenchants (PAG, new, used in a facility 2,5 months and artificially aged at Swerea IVF). The T CP/GPC method showed that the solution used in a facility had a significantly lower molecular weight distribution, while the artificially aged solution only had a slightly lower distribution. This suggests that despite the fact that the objective was to make the artificial ageing as similar as possible to the ageing in a facility, the thermal degradation was much more severe in
the real-life case at the facility. The molecular weight is also influenced by other factors despite thermal degradation. The quenchant used in the facility has been, despite thermal degradation, also exposed to air for a longer time (oxidation) as well as influenced by contaminants and bactericides.

THE INFLUENCE OF CONTAMINATION
The quenchant can be contaminated by several different sources, e.g. corrosion inhibitors, lubricants, oxide scales, cutting fluids and detergents. In this project the contamination caused by detergents and cutting fluids was studied (see Figures 7 and 8). Contamination was achieved by adding a 3% detergent solution and a 5% cutting fluid emulsion to Aquatensid 15%. Cooling curves were measured at a contamination level of 0.5%, 2% and 5% respectively.

The detergent had no significant influence on the cooling curve at concentrations of up to 2%. At a contamination level of 5%, the maximum cooling rate tends to be lower. No influence could be shown at lower temperatures.

The cutting fluid had no significant influence on the cooling curve at concentrations of up to 2%. At a contamination level of 5%, the maximum cooling rate is lower, while the cooling rate below 400 °C is higher. A higher cooling rate at lower temperatures was also observed at a contamination level of 2%.

A Brix refractometer was used to measure the concentration in all solutions. The measured value was between 14.3% and 14.6%.

Figure 9.: Cooling curves, Aquatensid 15%, 30 °C, contaminated with 0-5% detergent (3% solution).

Figure 10.: Cooling curves, Aquatensid 15%, 30 °C, contaminated with 0-5% cutting fluid (5% emulsion).
CONCLUSIONS

This pre-study shows the importance of careful monitoring of quenchants in use. To only measure concentration by refractometer is not sufficient, other tests are also needed, e.g. cooling curve measurements.

To gain a full understanding of how quenchants are degraded and how this affects the quenching performance a combination of different analyse methods must be used. Further work is needed to explore suitable ones.

Laboratory ageing of a PAG polymer results in markedly higher cooling rates, and lower viscosity, at all temperatures. However, the result was less clear-cut regarding quenchants used in production facilities, due to interactions of other factors.

Contamination of a PAG-polymer with cutting fluid emulsion results in a higher cooling rate below 400 °C and a lower maximum cooling rate.

While some of the effects on the quenchants in the benchmark study can be explained by the above, the contradictory behavior observed was also due to the influence of other factors, chemicals and contaminations that were not studied within the framework of this project.

FURTHER WORK

It is our intention to continue to study the degradation of polymer quenchants during their usage, including the effect of different types of contamination. This will be done on a polymer chemical and molecular level in order to establish how changes affect cooling performance, cooling curves and hardening results, e.g. hardness, microstructure and residual stresses. Different viscosity measurements will be tested to arrive at a qualitative and quantitative determination of the molecular weight changes. The emphasis will be on quenchants that are used for induction hardening.

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