

# Care and Maintenance of Quench Oils

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## Abstract

Quenching, and quench oil, is a critical part of the manufacturing process for a heat-treated part. In this paper, the effects of many common issues with quench oils are illustrated. These include contamination, soot, and filtration.

## Introduction

It is not known how long oils have been used in the hardening of ferrous alloys. It is known, however, that before the discovery of petroleum oils, fish and animal oils were sometimes used in the quenching process. It is also known that in 1880 researchers at E. F. HOUGHTON & CO., Valley Forge, PA, developed the first non-animal, petroleum-based quenching oil. Since that time oil and water-based quenchants have been the backbone of the heat-treating industry.

Although polymer quenchants have replaced oil in many settings, for some applications oil is the only option. And quench oil is some thing often taken for granted by heat-treaters. But in today's quality and environment-conscious world, selection and maintenance of quench oil deserves renewed attention.

Indiscriminately dumping quench oil and recharging a quench tank or system is a thing of the past. The use of quench oil must be optimized because of the increasing problems of disposal and the increasing cost of petroleum. By using quenchants that contain additives, implementing proper filtration and circulation systems, and contracting with suppliers who conduct audits and cooling curve analyses, a heat treater can effectively guard against contamination and ensure oil quality and long tank life.

A wide range of quenching characteristics can be obtained with oil- based quenchants through careful formulation and blending. A high- quality quenching oil is formulated from refined base stock with a high paraffinic content. Selected wetting agents are added to the base stock to ensure proper quenching rate. Along with the wetting agents, a complex antioxidant package is added to maintain the oil's quenching speed, and viscosity, for long periods of continued use.



**Figure 1 - Typical integral quench furnace used in many heat-treating operations.**

Tank life, which is another way of saying resistance to oxidation, is an important property of quench oil. With short tank life, oil is less productive and more expensive.

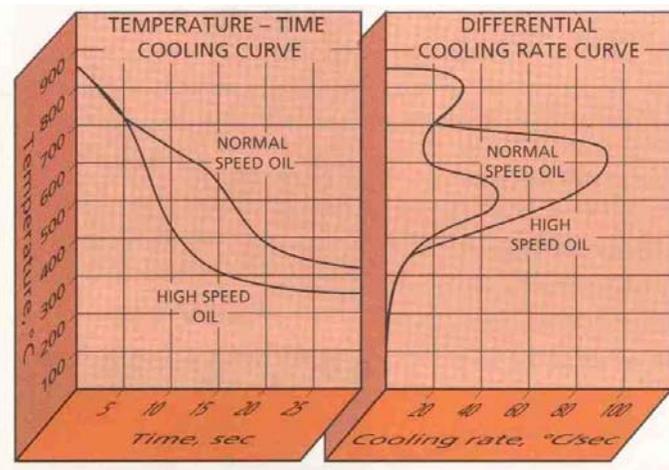
When oils oxidize they form asphalt materials, commonly known as sludge. This sludge can cause system-wide problems such as clogging the heat exchangers used to cool the oil. When heat exchangers become clogged, the temperature of the oil rises. The result can be excessive fuming, and possibly, a fire.

In addition, sludge and other products of oil oxidation cause unsightly stains on quenched work-pieces; these are difficult to remove by normal cleaning methods. With the increased emphasis on quality work, appearance can be a factor in the quenching. Finally, oil oxidation increases viscosity, which, in turn, increases consumption and costs.

### Understanding Quench Rates

Quenching oils can be divided into several categories, depending on their functional characteristics. Two such characteristics are quenching rate and operating temperature.

Quench rate for oils can be divided into normal, medium and fast speed. This classification is based on the General Motors (GM) quenchometer speeds (nickel ball) test in seconds at 80°F. Normal speed oil has a 13 to 20 second range, a medium-speed oil has a 10- to 12-second range, and a fast oil ranges from 7 to 9 seconds. These classifications based on GM quenchometer speeds also correlate well with the maximum cooling rates based on cooling curve analysis (Figure 2). It is important to understand the quench rates and cooling curves for each classification normal, medium and fast oils.



**Figure 2 - Comparison of high-speed and normal-speed quench oils.**

Normal-speed quench oils have relatively slow rates of cooling. Normal-speed oil has a 13-20 second GMQS quenching speed. These oils are used in applications in which the hardenability of the ferrous alloy is high enough that maximum mechanical properties are obtained even with a slow cooling rate. Tool steel hardening, for example, is an application that would use a normal-speed quenching oil.

Medium-speed quenching oils are blended to provide a quenching rate to ensure martensitic transformation in ferrous alloys with medium to high hardenability. These are oils with a GMQS of 10 to 12 seconds at 80°F. Medium-speed quench oils are used widely for applications in which dependable, consistent metallurgical properties are required: leaf and coil springs of SAE 5160; small-diameter fasteners (screws, bolts) of AISI 1080 and 4140; roller bearings of SAE 52100 and 3310 carburized; oil harden wire SAE 1080; automotive and power transmission gears made of SAE 4140.



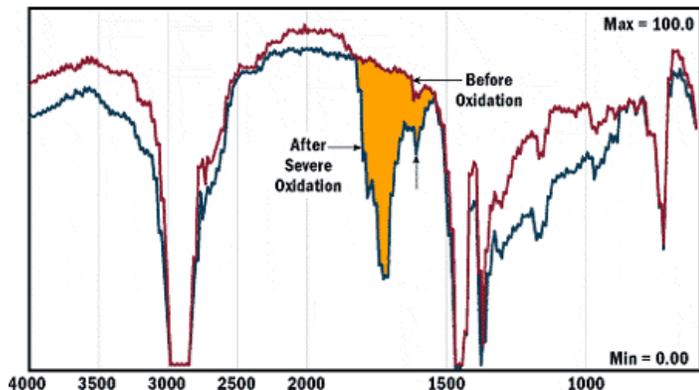
**Figure 3 - Typical components heat treated in quench oils.**

There are applications such as low-hardenability alloys, carburized and carbonitrided components, or large cross-sections of medium hardenability ferrous alloys, for which a fast rate of cooling is required to ensure maximum mechanical properties. Fast oils used in these situations have a quench speed of 7 to 9 seconds at 80°F. Fast quench oils contain selected accelerators or wetting agents to provide this maximum rate of cooling. The maximum cooling rate of normal, medium and fast oil is based on oil in the agitated condition, and at normal operating temperatures of 140°F to 160°F.

### Oil Chemistry and the Deterioration Process

Premium, quality heat-treating, quenching, and martempering oils are formulated from refined base stocks (usually paraffinic) of high thermal stability with additives to improve performance and increase tank life. These additives are a combination of specially chosen ingredients compatible with the base oil; in particular, carefully selected and tested antioxidants, which retard the aging process.

Petroleum oils are subject to two kinds of deterioration: oxidation and thermal cracking. Petroleum oil at high temperatures and in contact with air or oxygen is oxidized at relatively high rates. Oxidation results in the buildup of organic acids and the formation of insoluble materials or sludge. Sludge causes the fluid viscosity to increase.



**Figure 4 - Example IR Spectra of severely degraded quench oil.**

Thermal cracking occurs when petroleum oils are exposed to high temperatures. Thermal cracking results in the formation of new materials, some of which are light, relatively volatile products as compared to others that are heavy, less volatile products. The more volatile products lower the flash point of the oil, and the heavier products increase the oil's viscosity.

During the deterioration process or oxidation of petroleum oil, new materials not original to the oil can be formed. These new materials, or "radical species," are very reactive organic fragments that undergo a variety of chemical reactions. These chemical reactions can be with other radical species, with the organic materials that are components of the oil itself or other additives used to maintain the physiochemical and physical properties of the quenching oil (Figure 4).

For example, most oils have a composition of several hundred components even after refining. It is the nature and type of components that determine the oil's usefulness as a quenching or martempering fluid, and even small amounts of a detrimental element or compound can be enough to set off a disastrous chain of events.

Three descriptors can be used to define the changes in properties experienced by oil in use: chemical changes (oxidation), physiochemical changes (dispersant action and quenching speed), and physical changes (viscosity and flash point). Other than the presence of oxygen, the following factors influence the formation of "radical species" that start the oxidation process: temperature, metal, light (UV/sunlight), and contamination.

However, premium grade quenching and martempering oils are formulated to counter these negative factors that cause oil deterioration. What premium compounded quenching oil cannot always do, though, is counteract the effect of outside contamination.

For example, the same antioxidants do not always work with all oils. The compositions of oils, although similar, are not chemically identical, and this difference is enough to set off a series of reactions that would be detrimental to the performance and tank life of the oil. This is what occurs when tramp oils, hydraulic oils, and other materials get into quenching or martempering oil. Also, certain components of

these tramp oils can reduce the effectiveness of antioxidants in the quenching or martempering oil, further reducing their overall performance.

Some of these chemical events are catalyzed by metals, particularly copper and lead and, to a much lesser extent, iron. Iron in a steel heating operation is always present and is unavoidable. Copper and lead can be eliminated in the construction of the heat-treating equipment.

Another source of concern is light. Sunlight/UV light is a catalyst of sorts and delivers a bundle of energy that can produce effects similar to metals. In most instances this is usually not a concern, since most quench tanks are inside, undercover, or enclosed in a furnace (integral quenching furnaces).

The effects of base oil selection, temperature, and contamination can be tested in a laboratory situation by using a modified ASTM D 943 accelerated oxidation test.

Change in viscosity of the tested oil indicates oxidation and thermal degradation. The oil's viscosity will increase as the oil degrades. Neutralization or acid number during the test measures the amount of organic acids formed in the oil during oxidation. As the oil becomes more oxidized the neutralization number increases. Precipitation number in the test is a measurement of high molecular weight compounds present in the oil that are not yet classified as sludge. This number is an indicator of the extent of oxidation or degradation of the oil. Quenching or martempering oils with high precipitation numbers may cause staining of quenched parts.

**Table 1 - ASTM Methods for Testing Quenching Oils**

Test	ASTM Method
Viscosity	D 445
Flash point	D 92
Fire Point	D 92
Water	D 95
	D 6304
Neutralization Number	D 974
Ash	D 484
Conradson Carbon Residue	D 189
Precipitation Number	D 91
Sludge	D 91
Specific Gravity	D 287
Quenching Speed (GMQS)	D 3520
Quenching Speed (Cooling Curve)	D 6200

### Flash Point, Fire, Viscosity

The flash point and the viscosity of oil are of great importance in quenching operations. The lower the viscosity, the more easily an oil can dissipate heat from a quenched part. A "thermo-siphon" effect distributes heat rapidly enough through the less viscous oil so that oil at the hot-metal/air interface does not reach or exceed its flash point.

Oils with higher viscosities cannot distribute heat as efficiently, because this more viscous oil film in contact with hot metal moves more slowly, becoming hotter as it flows

upward. Such oil may even arrive at the air / oil interface with its temperature hotter than the flash point. In this case it catches fire immediately. While oils having higher flash points are desirable, oils with lower viscosities are desirable, too. Viscous oils can be heated to decrease their viscosities, which also decrease the likelihood of fire.

### Water in the Oil - A Major Problem

Experience with poorly functioning quenching oils indicates that in at least half the cases water gets into the oil, causing cracking, uneven hardness and soft spots. Water can enter the oil in a number of ways, and the sources must be tracked down and eliminated. A leaky cooler might bring water into the oil, or water may drip into the tank from the roof. A tiny amount of water (about 0.1 %) can cause a bath to foam excessively and greatly increase the danger of fire.

Qualitative analysis for water in the oil can be made with the "crackle test." A test tube, one-third filled with oil sample, is heated. If audible crackling occurs before the oil smokes, there is water in that oil.

The quantity of water in the oil can be determined by xylol distillation. Equal parts of oil sample and xylol are placed in a condensation flash unit with trap and condenser, and heated. After distillation, the concentration of water can be calculated by volume or by weight.

Other factors being favorable, water can be removed, and the oil retained for additional service. Water settles on the bottom of an unagitated tank, where it can be drained away. Heating the oil to 250°F and agitating the bath until all bubbling and foaming at the surface cease can evaporate any moisture remaining after draining.

### Neutralization Number

The characteristics of quenching oils from different sources may vary. Oils can be alkaline or acid. Or they can vary due to additive content, refining procedures or deterioration during service. These differences are represented by a neutralization number determined by ASTM Method D-974.

Neutralization tests provide a check on the consistency of oil quality. These tests also serve as a guide for a change in the operating conditions or a determination of the product deterioration in used oils. Increased oxidation is generally indicated by a rise in the neutralization number. In quenching oils in service, a rising neutralization number suggests a greater tendency toward sludging.

Usability of oil cannot be judged solely on its neutralization values. Therefore, these numbers should be considered together with the properties of the oil in question.

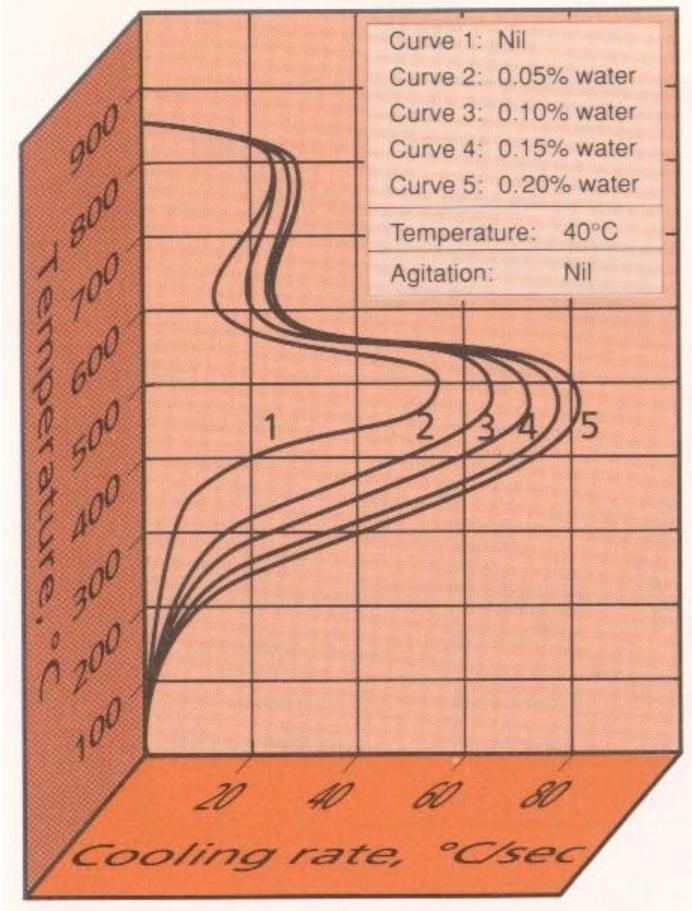


Figure 5 - Effect of water on the cooling curves of normal speed quench oil.

### Ash Content

The ash content of any quenching oil is a measure of the incombustible material that may be present. Ash content serves as a manufacturer's check on the formulation of new quenching oils formulated with ash-forming additives. If the ash in a used oil runs higher than the ash of a new oil, contamination with foreign metals such as scale from the quenched parts is suspect. If the ash runs low, this may be attributable to poor operating conditions. If a "soluble" quenching oil is not compounded with ash-forming additives, the ash content may indicate contamination.

### Carbon Residue

As noted in ASTM Method D 189, "carbon residue" is the carbonaceous residue formed after evaporation and pyrolysis of a petroleum product under conditions of insufficient oxygen. This residue is not compounded entirely of carbon, but it is in effect a coke, which can be further changed by pyrolysis.

## Quenching Speed

The Conradson carbon residue test, serves as an approximation of the tendency of quenching oils to form deposits under quenching conditions. This test has lost much of its original significance with the use of ash-forming or high molecular hydrocarbon additives in a majority of quenching oils. For example, while an additive may increase the carbon residue value of oil, it generally reduces the tendency to form deposits. Carbon residue tests, therefore, should be judged in conjunction with the additive content of the oils.

### Precipitation Number

The precipitation number of quenching oil is indicative of the presence of compounds, which will form sludge under operating conditions. This is a measure, like sludge, of the degree of aging in the oil.

### Sludge

Sludge is a result of the oxidation and polymerization of quenching oils in use. The presence of sludge probably causes more problems in quenching than anything except the presence of water. The higher the sludge content, the more the particular oil has aged.

New oils should have no sludge content. Some quenching oils, less stable than others, show a greater tendency to form sludge, although oils are often compounded with additives to resist and delay the formation of sludge.

Sludge clogs the coolers, reducing the efficiency of the entire quenching system. It can be filtered if the oil has not seriously degraded. Such degradation is readily visible with an increase in viscosity, saponification and neutralization numbers. A sludge content of 0.2% can be considered a high content if a bright metal surface is desired. Oil with 0.2% sludge content can be used, however, if other specifications are satisfactorily met.

Sludge and tar deposits begin building up in quenching oil and in the heat exchanging equipment long before the quenching speed of the oil is affected. Such sludge deposits will cause frequent shutdowns for cleaning, otherwise the temperature of the oil increases to the point where either incomplete or non-uniform hardening occurs.

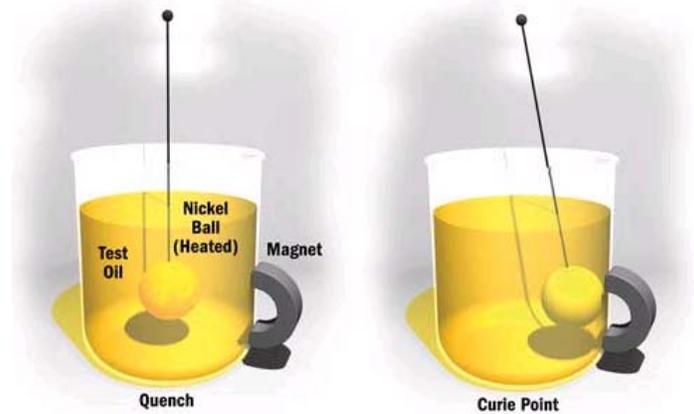
Sludge formation in quench oil accompanied by a cracking of the oil and the appearance of low-boiling-point petroleum fractions, which have low flash points.

High stability and low sludging characteristics of oil afford considerable savings in the direct expense of cleaning out oil lines, strainers, filters and cooling systems.

### Specific Gravity

Tests for specific gravity of quenching oils are not particularly helpful in examining used oil because the results provide little information on its usefulness for further quenching. Specific gravity tests on new oils, however, give a reading on the type of oil being used, what the base derivative was: naphthalenic; paraffinic; or aromatic, and hence a clue to the aging characteristics of the oil.

The convenient and informative General Motors Quenchometer test is available to relate metal hardenability or phase change to quenching speed of oil. This is schematically shown in Figure 6.



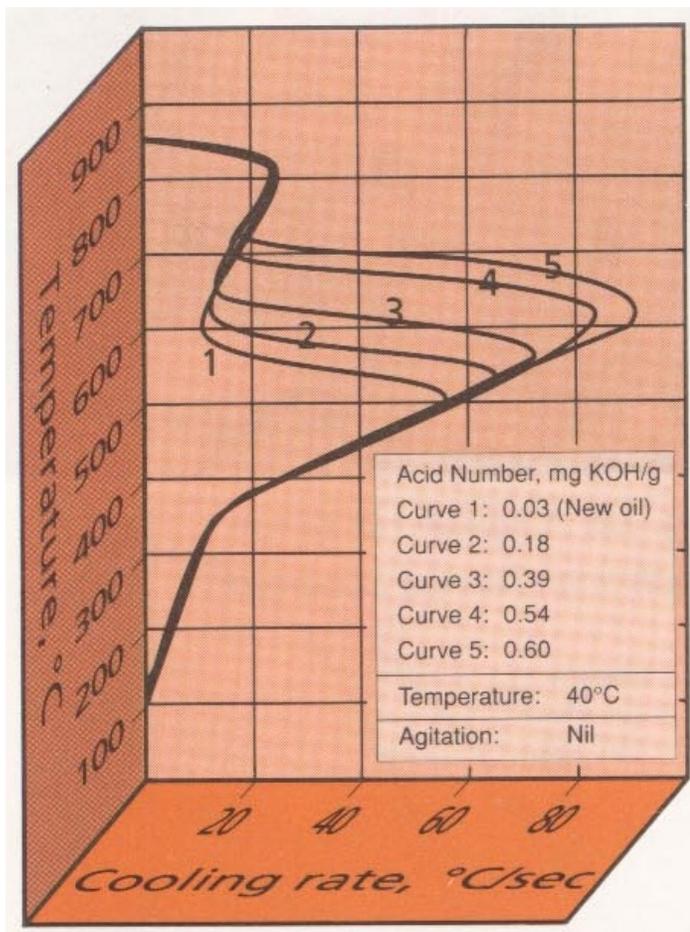
**Figure 6 - Schematic representation of the GM Quenchometer test.**

In the GM Quenchometer test (ASTM Method D 3520), a ball of nickel is heated to 1620°F in air, and then quenched in 200 ml of quenching oil. The time required to quench the nickel ball to 670°F, the Curie point at which nickel becomes magnetic, can be measured. Fast quenching oils can affect this change in 7 to 9 seconds; some quench times run as long as 32 seconds to drop the ball's temperature from 1620° to 670°F (slow martempering oils).

When determining the cooling curve based on ASTM Method D 6200, it measures the entire response of the quench oil. The effect of contamination on the various heat transfer phases (Vapor Phase, Nucleate Boiling and Convection) can be determined. Further, the effect of aging on the oil can be seen readily and compared to new quench oil (Figure 7).

### Oil Recovery

Quenching and martempering oils deteriorate during use, although most premium quenching oils can last more than 10 years when given reasonable use and care. Martempering oils, on the other hand, have shorter tank life, due to their higher operating temperatures. These temperatures are essential because parts are quenched to temperatures near but above those where transformation to martensite starts ( $M_s$ ) and held there until the center and surface equalize. Subsequent slow cooling and ultimate transformation minimizes internal stresses with resultant reduced distortion. However, the detrimental effect of higher oil temperature operation can be compensated, by methods of laundering or cleaning the oil, which extend its useful life.



**Figure 7 - The effect of oxidation on the quenching characteristics of normal speed quench oil.**

One such method is fine filtration. A bearing manufacturer using a 300 SUS martempering oil had a service life of about 8 to 12 months, but was able to increase the life to more than 21 months by changing the filter from a 10 micron to a 3 micron media. These filters are polypropylene bags and are changed about once a day. The filter media usage may have increased, but the lower downtime and cost of martempering oil pay for the filters.

In another actual example, a manufacturer of diesel engine components uses a 100 SUS quenching oil. After the oil was used for a time, the part became stained and the oil normally would be discarded at this point. However, in this case the oil was filtered through a 5-micron and then a 3-micron filter. The staining was eliminated and the oil's service extended.

Other filter media may be useful in reducing the organic acid present in the quench oil that cause staining. This filter media has been shown to be effective in reducing staining caused by the build-up of organic acids and oxidation. One caveat is that some filter media type may remove the anti-oxidation additives in the oil. The quenchant oil supplier should be consulted prior to the implementation of new filter media types. Table 2 shows the effects of different types of filter media on the removal of organic acids.

**Table 2 - Effect of filter media on the acid number of used martempering oil.**

Filter Media	Acid Number (mg KOH/g)
Used Martempering Oil	0.7
Activated Alumina	0.5
Attapulcite Clay	0.2
Bentonite	0.1
Kaolin Clay	0.2
Fuller's Earth	0.01

Recovery of oil from washers is not generally recommended, unless special precautions are made. The oil from the washers may contain soaps and cleaners from the washer, and this may have the tendency to increase staining of parts. Further, the oil from the washers is likely to contain water. This water must be thoroughly removed before the recovered oil is placed back into the quench tank.

In the case were multiple oils or different speeds or types (cold oils and martempering oils) are cleaned from parts using the same washer, the oil cannot be recovered. This is because the recovered oil will be too viscous for cold oil, and too low of a flash point to be used as martempering oil. It is always best to use different washers for each different type of quench oil. In this fashion, the oil recovered from the washers can be properly segregated.

The best practice is to capture the oil recovered from the washer into a separate drum or tank. This will allow the water to settle, and the water can be removed by draining the water from the bottom of the tank. However, this will not remove all the water in the quench oil. The use of a vacuum is the best way to remove residual water from the quench tank. Your quench oil supplier can make recommendations on qualified people to remove water from quench oil recovered from washers.

The recovered oil, after separation, should be thoroughly filtered. This will minimize any debris such as scale that was picked up by the skimmers.

The oil recovered from the washers should be tested to make sure that it conforms to the original specifications of the quench oil, and is suitable for continued use. Once the recovered oil has been approved for use, it is always best to mix this oil with new in a 50/50 mix. This insures that the anti-oxidant packages in the oil are not depleted, and that rapid premature oxidation of the oil will not occur.

### Conclusions

The effects of contamination and oxidation of quench oil can cause significant changes in the maximum cooling rate and temperature of maximum cooling. This can result in increased part distortion, cracking, and non-uniformity of properties. A control program to monitor and track quench oil performance is necessary to insure quality parts and customer satisfaction.