Abstract

In this paper, examination of the problems associated with residual water in quench oil are discussed. Problems can include formation of organic acids, spotty hardness, and finally an explosion hazard. Methods to measure water content are reviewed, and ways to control the presence of water are further discussed.

Introduction

Water is quench oil can be roughly divided into two different forms, based on the concentration of water: water less than saturation; and water greater than saturation, where free water exists in the quench tank.

The effect of water differs based on the quantity of water present. The amount of water present in the oil can differ based on the additive package. As a rule of thumb, the saturation point of most conventional quench oils is on the order of 1000 ppm (0.1%).

The primary reason that the control of water in oil is so critical is because of the low boiling temperature of water. Water boils at 212°F (100°C). Once water turns to steam, it expands approximately 1600 times. In other words, one gallon of water creates 214 ft³ of steam, or the equivalent of 1600 gallons of steam. This expansion of steam also increases with the temperature of the steam. In other words, steam at 400°F will occupy a greater volume than will steam at 212°F. So in a 1000-gallon oil quench tank containing 1 gallon of water (0.1%), when a hot load is quenched, the free water can turn to steam, creating a severe fire and explosion hazard (Figure 1).

Sources of Water

Sources of water can either be external or internal to the furnace or quench tank. External sources include recovery of quench oil from washers; leaking roof; and contamination due to improper maintenance practices. Internal sources include: water to oil heat exchangers; water cooled doors, fans and bearings; fire extinguishers, and fire-resistant hydraulic fluids (when leaking).

Figure 1 - Results of a quench oil fire from excessive water.

When the water content of the oil is less than the saturation point, the oil exists as small droplets mixed with the oil. It can also exist as a light emulsification. When the water content is less than the saturation point, it can have some significant effects on the microstructure and distortion of heat-treated parts.

The cooling curve of oils containing minute quantities of water show very distinct characteristics:

- Increased stability of the vapor phase;
- Increase length of the vapor phase;
- Increase rate of nucleate boiling; and
- Decreased transition temperature between nucleate boiling and convection.

In extreme cases, the transition between nucleate boiling and convection can be completely suppressed.

These changes in the cooling curve behavior of cold quench oil can be observed in Figure 2. It can be observed that the vapor phase becomes significantly more stable, and the maximum cooling rates increase. Also the temperature at maximum temperature decreases as the water content is increased. At extreme water concentrations the convection phase disappears.
The effect on parts heat treated when water concentration is high, can manifest itself in several ways, including:

- Soft spots from a stable vapor phase;
- Improper microstructure from inadequate quenching;
- Increased distortion and risk of cracking due to the suppression of the transition between nucleate boiling and convection.

Internal investigations have shown that water concentrations of as little 250-400 ppm can cause improper transformation of low hardenability steels, resulting in localized bainitic transformation.

When the concentration of water exceeds the saturation point (approximately 1000 ppm or 0.1%), a new series of problems occur that increase the potential for catastrophic fire and explosion. In addition to the hazards to parts indicated above (soft spots, improper microstructure, etc.), there is a severe hazard for fire and explosion. This is due to the generation of large volumes of steam from small quantities of water and from the expansion of steam-laden froth into the work zone of the furnace.

Imagine a simple integral quench furnace, with 1000 gallons of oil. Because of leaking air cylinder, approximately 1 gallon of water (0.1%) is sitting at the bottom of the quench tank. The quench tank is being maintained at 170°F, and a 1000-pound load of parts in quenched from 1600°F. Immediately upon quenching, the bulk temperature of the oil increases approximately 50°F, resulting in the one gallon of oil turning completely to steam.

This one-gallon of water creates approximately 215 ft³ of steam. This steam immediately displaces the oil level up, spilling over the furnace hearth. The oil ignites, and expands further. The furnace outer door opens from the pressure, and the froth of the oil-steam mixture is explosively expelled all over the heat treat shop. Because the number of ignition sources in a heat treat shop, it is likely that this oil-steam froth is ignited, and a large fire ensues. Major property damage, and potential loss of life can result (Figure 3).

This simple scenario of a water-oil quench fire unfortunately has been repeated with disastrous results many times in the past several years. The source of the water varies, but has the same catastrophic results. Several heat treat shops have either closed, or experienced long expensive delays while their shop and equipment has been repaired.

The sources of water have often been due to poor maintenance, poor shop keeping, or a lack of understanding of the ramifications of water in the quench oil. In the balance of this paper, it will be attempted to illustrate the possible sources of water, and the methods required to measure, control and eliminate water in quench oil to properly avoid the potential of catastrophic quench oil fires.
In another case, the roof was leaking over a large continuous mesh furnace. A plastic tarp was placed over the quench tank. Unfortunately, small holes were present in the tarp. Over a period of time, the quantity of water increased to a point that fires were occurring on a daily basis. Only by testing of the oil for water was the heat-treat shop able to detect the source of the fires.

The primary method of remediation is the elimination of all sources of water. The use of air to oil heat exchangers is strongly recommended (Figure 4). A comprehensive operator and maintenance training program is also recommended. Routine facility inspections to detect and repair pneumatic lines, leaky roofs and other water sources are also recommended. Each operator should be empowered to inspect his equipment.

Remediation – Preventative Maintenance

There are multiple sources of water in a heat-treating shop. Some of the most obvious sources of water include:

- Leaking roofs;
- Water to Oil heat exchangers;
- Leaking pneumatic cylinders;
- Water cooled bearings and fans;
- Water cooled doors; and
- Operator error.

Just because a tarp has been placed over the quench tank does not mean that water will not get into the quench tank. Even double walled water to oil heat exchangers will eventually leak because of corrosion. Even if the pressure is higher on the oil side of the heat exchanger, water will find its way into the quench tank reservoir.

Transfer of quench oil into spare barrels that contain small amounts of water is a very common method of contaminating quench oil with water, as is accidentally adding the wrong barrel to the quench tank.

In one instance, during maintenance, the quench tank was emptied prior to cleaning the quench tank. The quench oil was transferred to spare barrels that were previously located outside, behind the heat-treat shop. No one inspected the barrels prior to transferring the quench oil to the barrels. Little did they know that one of the barrels had approximately 2 gallons of rainwater because the bung was left opened. Once cleaning of the quench tank was completed, the barrels were emptied back into the quench tank. When the first load was quenched, a low deep rumble occurred, and the resulting fire caused extensive damage to the heat-treating shop. No personnel were injured, because they ran at the onset of the deep rumble.

Remediation – Monitoring and Control

There are two primary methods to measure and control the presence of water in the quench tank. The first method is routine testing at periodic intervals (typically monthly or quarterly) by several different techniques; or my in-line monitoring of the quench oil. Each has its merits, and should be done to complement each other.

**Periodic Testing.** There are two primary tests used to determine if water is present in quench oil. One method, the “Crackle Test” (ASTM D-93) is qualitative, and involves taking a small quantity of oil and heating it up to above the boiling temperature of water. If bubbling or crackling of the oil occurs, then water is present in the oil. However, the oil will “crackle” only if water is present is quantities above the saturation point. Unfortunately, at this point, it may be too late.

A quantitative test method widely used to determine the quantity of water in oil is the Karl Fisher Test (ASTM D-6304). This test is based on the Bunsen reaction between iodine and sulfur dioxide. This method is very accurate for used oils, and can determine water contents to approximately 250 ppm. Measurements are less accurate in new oils, because of interference due to the anti-oxidant additive packages in new oils. It is based on a simple titration (Figure 5).

This periodic testing should also include viscosity, flashpoint, and precipitation number. All quality quench oil companies will provide this service free of charge, generally on a quarterly basis. A typical report is show below (Figure 6).
Figure 5 - Typical Karl-Fisher Apparatus (ASTM D6304).

Figure 6 - Typical quarterly quench oil report, with performance trending. All quality quench oil suppliers will provide this testing.

Typical Quench Oil Report

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Figure 7 - Sensor control box for determining percentage of water in oil (Courtesy SBS Corporation).

In-Line Testing and Monitoring. In-line monitoring is a more effective method of observing the water content in quench oil. The first method is really an alarm, which detects the presence of water in excess of saturation, and is typically interlocked with the furnace controller, and prevents quenching from occurring.

This method utilizes a type of spark plug, in which a voltage is impressed. When water is present, the gap in the spark plug is conductive, and continuity is made. An alarm is sounded, and an interlock is tripped, preventing quenching. However, this requires that the sensor is located at the bottom of the quench tank and that no sludge is present that may isolate the probe. The probe serves no purpose if it is lying next to the quench tank, not installed.
Whenever the sensor is energized, water is present in a concentration in excess of saturation. However, the presence of other contamination may cause this sensor to malfunction. It is possible that quenching result in fire and explosion before the probe has sensed the water. It would be far better if a sensor were available that would sense increases of water at levels below saturation, and alarm before the water concentration becomes free water at the bottom of the quench tank.

The second method utilizes technology adapted from the power generation industry, where the sensor detected water in large oil-filled transformers. This sensor works by measuring change in capacitance of a thin-film polymer as it absorbs water molecules. It only measures the percentage of water before saturation, so that the problem of water in quench oil is caught well before it becomes a fire and explosion hazard. This sensor can be set to alarm at preset points, such as 250 ppm, so that parts are not affected. It is effective in measuring water in quench oil to 5 ppm to the saturation point. Use of differential alarms can also sense the rise in water levels and alarm if water concentration is rising at an unacceptable rate. An example is shown in Figure 7.

**Remediation and Control – Recycled Quench Oils**

Because of the cost of new oil, and the cost of disposal of quench oil, many companies are looking at recovery of quench oil from washers. This has several cost advantages – including reduction of operating costs, and substantial reduction of disposal costs. Quench oils can be recovered effectively, but several precautions must be taken to insure safe operation. The basic steps involved with recovery and recycling quench oil are shown in Figure 8.

**Collection.** Quench oils are typically recovered from washers immediately after the quench tank. It is important that the skimmers used are effective in removing the oil because inefficient skimmers will recover excessive amounts of water. This makes recovery of the quench oil less efficient, with lower yield. Typical skimming operations are shown in FIGURE. Oils recovered from the pre-wash and post-quench washer should never be mixed, as it can contaminate the recovered quench oil. This contamination, at best, can cause significant staining of the heat-treated parts. At worst, it can present a significant fire problem.

**Segregation.** As indicated earlier, it is important that the collected oils from the pre-wash not be mixed with the collected quench oils. It is also important that different kinds of quench oils not be mixed. Specifically, martempering oils and cold quench oils should not be mixed. Each type of oil should be segregated to ensure that no contamination occurs. For instance, typical Mar-Tempering oil, Mar-Temp 355 has a viscosity of approximately 300 SUS, and a flashpoint of 440°F, while Houghto-Quench G (a common medium speed cold oil) has a viscosity of 100 SUS, and a flashpoint of 355°F. Because of the differences in flashpoint, these oils should not be mixed. If combined and not segregated, eventually, the oils will mix and result in oil that has the average of all the properties. This could result in cracking, distortion, and potentially a fire hazard due to the lowered flash point.

These oils should be segregated into separate holding tanks of adequate size. The holding tanks should be sized to capture and hold at least the quench oil from approximately 3 months of recovery. This minimizes the amount of labor and physical testing necessary to ensure high yield and a quality recovery.
Filtration. Particulate from soot can act as a catalyst for the creation of organic acids. Scale and refractory can also become catalysts for the formation of organic acids. This particulate can also clog heat exchangers, and damage pumps or impellers. Quench oil with large quantities of particulate can also have altered quenching properties because of early initiation of nucleate boiling. Filtration removes this particulate.

The size of filtration varies with application. Typically, initial filtration is accomplished using a 50-75µm filter, and is followed up with additional filtration at 10-15µm. Depending on the particulate and the quantity, filtration can be accomplished at 2-5µm effectively. It is often an economic decision regarding how often the filters are changed (and the cost of the media) and the expected extension of the oil.

Use of other filter media like Fuller’s Earth, activated alumina, or Kaolin Clay can be effective in reducing the organic acids present in quench oil. However some filtration media (such as Fuller’s Earth) can also remove the remaining anti-oxidation package. After testing, it may be necessary to add additional anti-oxidants or speed improvers to compensate for those removed during filtration by Fuller’s Earth.

Dehydration. Dehydration of the quench oil is the removal of water. Much of the water present can be removed during collection by simply draining off the bottom water layer. However, water at concentrations less than 1000-ppm still remains. Water can be removed by heat, and driving off residual water. This is slow and energy intensive. Many hours at temperatures above 212°F are necessary before the water is driven out of the quench oil.

Air stripping of water from oil is an effective method of removing water. In this method, finely dispersed air (or dry nitrogen) is passed through oil heated to 80°C. The air immediately heats, and absorbs the moisture from the oil. With air stripping, the temperature of the oil and the amount of airflow determine the rate of water removal. An airflow rate of 5 ft³/min with an oil temperature of 160°F degrees will remove one gallon of water per hour. This method is only capable of removing water that is below the saturation point (about 1000 ppm). Once the water is saturated, the efficiency of the process rapidly deteriorates.

The final method takes advantage of the different vapor pressures of water and oil. Water has a significantly higher vapor pressure than water; so water can be taken out preferentially from quench oil by the use of a vacuum. This method is effective in drying out to 20 ppm, but suffers from slow thru-put.

Regardless of the method chosen, dehydration of oil is necessary to prevent the formation of organic acids, and the prevention of soft spots, cracking and increased distortion.

Testing and Analysis. Finally, once the recovery and recycling process is complete, the oil should be tested to ensure that the oil satisfies the specifications for new oil, in terms of performance and water content. Should any anomalies be detected, immediate corrective action should be taken, based on the laboratory recommendation.

Conclusions

In this paper the dangers of water contamination were illustrated. Two types of oil contamination were described: below saturation (1000 ppm) and above saturation. Methods to eliminate sources of water were described. Remediation of oil that has been contaminated with excessive water was also described. Test methods to determine water content in the laboratory and shop floor were discussed. The necessary procedures to effectively recycle quench oil were described.