Proper Care of Quench Oil Leading to Consistent Part Quality

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Abstract

This paper will discuss the effect of contamination, including sludge, oxidation, products, and other debris on the performance of quench oil. Further, methods of reducing the contamination by filtration will be illustrated. By proper filtration, oil life can be extended, while reducing part staining.

Introduction

Cleanliness demands of customers are becoming increasingly stringent. It is imperative that parts be clean prior to shipment. Staining, especially after heat treatment, is difficult and expensive to remove. The most common sources of stained parts are contaminated or oxidized quench oil [1] [2] .

There are various sorts of contaminants in a quench oil. This include soot, scale water and oxidation products. These contaminates lead to problems with part cleanliness, increased maintenance costs and increased cleaning costs.

Oil Degradation

The life of quench oil is dependent upon its thermal stability. Thermal stability is a function of the quality of the base oil, the antioxidant package used, and the presence of heat and catalysts. 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 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.

The degradation of quench oil is aggravated by residues on parts, washer residues from oil reclaimed from washers; high energy density heater or radiant tubes, and excessive peak temperatures. The addition of robust additive packages prolongs a quenchant life and provides for repeatable quenching.

Oxidation of quench oil is caused by exposure to oxygen. As operating temperatures increase, the kinetics of oxidation approximately double with each 10°C. This is especially true with martempering oils because of their elevated temperature use.

Thermal degradation is from exposure to temperatures that cause the base oil and additive package to change. This results in the formation of insoluble products of reaction that can cause deposits on parts and sludge the quench tank.

Contamination can be from many sources. Water, dust, scale, and soot are not the direct result of oil degradation, but can contribute to other degradation issues. For example, soot can act as nucleation sites for thermal degradation products, and can mimic oxidized oil.

Additive depletion is normal and expected. The anti-oxidants are consumed as part of their function. Anti-oxidants are replenished as make-up oil is added.

Oil degradation is manifested by a viscosity increase, acidity increase (as measured by Total Acid Number), varnish and lacquer deposits, sludge, and changes in the quench speed [3]. Examples of staining of parts are shown in Figure 1.

Figure 1. Deposits on ring gears due to severely degraded quench oil.

There are many papers covering the mechanism of oxidation of oil and the function of antioxidants [4] [5] [6] [7]. There are three primary steps in the oxidation of oil: Initiation; Propagation; and Termination (Figure 2).

During Chain Initiation, the presence of iron and copper catalyze the reaction. In this reaction, free radicals are formed. These reactions are slow at room temperature, but become increasingly faster as the temperature increases.
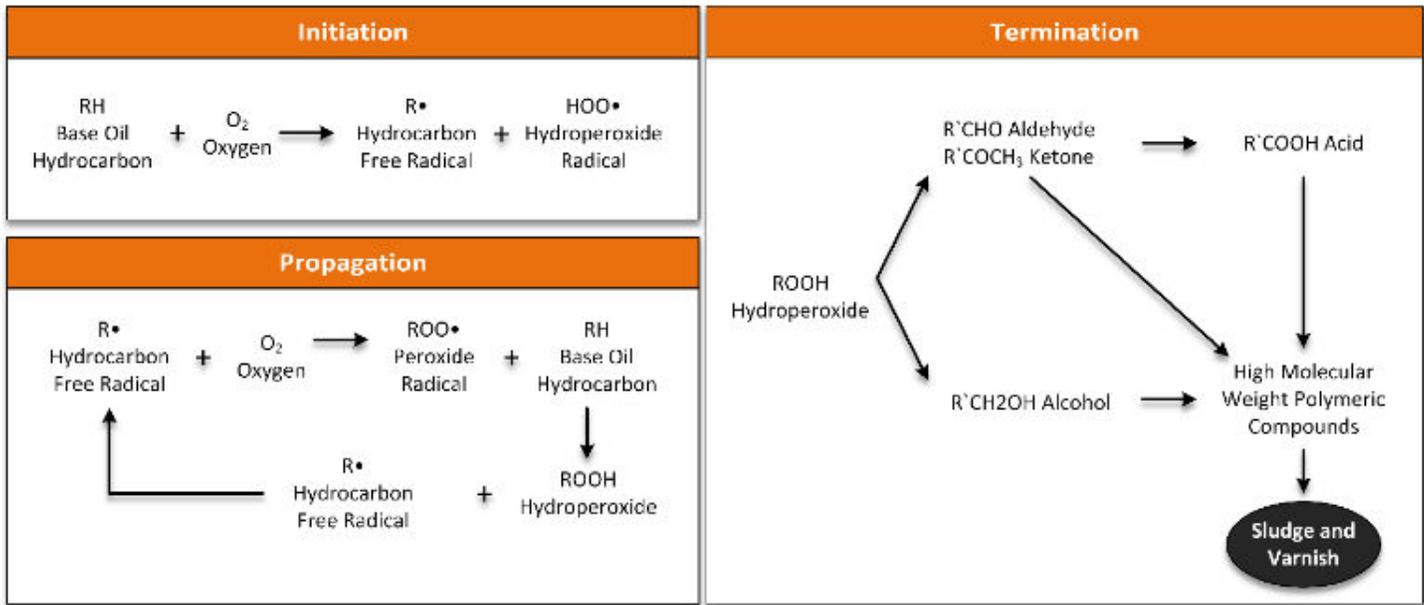
Figure 2. Overall schematic of the oxidation of quench oil [4].

The Chain Propagation and Branching step involves the reaction to produce additional radicals that propagate the oxidation sequence. Alkyl radicals (R•) react with oxygen in the oil and create peroxy radicals (ROO•). These peroxy radicals react with additional hydrocarbon molecules to produce hydroperoxides (ROOH) and additional akyl radicals.

As the oxidation increases, the acid levels from the formation of carboxylic acids increase. This increase leads to further oxidation because the carboxylic acids promote oxidation. This is why, once oil starts to oxidize, it does so in an exponential fashion, with the oxidation rapidly increasing. Carboxylic acids are formed by the oxidation of aldehydes and ketones. This is measured by ASTM D664. It is a measure of the amount of organic acids present in the oil, and is useful for determining when staining is likely, or if the oil is reaching the end of its useful life. For most oil quenchants, when the TAN (Total Acid Number) is greater than 1.5-2.0, it is indicative of a high potential for staining or deposits on parts during the quench.

As oils become increasingly oxidized, whether in the quench tank, or in oxidation tests, the viscosity increases. This occurs by condensation reactions that become important as the levels of aldehydes and ketones increase. These reactions are known as Aldol Condensations [8]. It is this reaction that causes varnish on parts and sludge in quench tanks.

The condensation products described in the above section have a limited solubility in the quenchant. These are high molecular weight oligomers. These are molecules that have a few monomer units, in contrast to a polymer that can have an unlimited number of monomers. As oil oxidizes the amount of carboxylic acids will increase. These acids are very effective catalysts for Aldol condensation reactions [8]. These then convert the low molecular weight carbonyl compounds into higher molecular weight oligomers.

As the reactions progress, chemical changes in the oligomers will result in making them insoluble in the quench oil. At this point the insoluble oligomers will precipitate from the quench oil and create sludge on the bottom of the quench tank, and deposits on the hot metal part.

The higher kinetic rate of aromatic group oxidation increases sludge and deposits. Because paraffinic oils have fewer aromatic groups than naphthenic oils, paraffinic oils are preferred for quenchants. Metal scale and soot, base oil sulfur, additive sulfur can also promote the formation of sludge and deposits. Soot can also act as a nucleation site for the formation of oligomers formation, resulting in oligomers coated soot particles. These accumulate at the bottom of the quench tank in low velocity areas, and are deposited on parts.

These oxidation by-products change the heat transfer characteristics of the quench oil [9] [10]. This contamination can lead to increased distortion and cracking; part cleanliness and plugged heat exchangers. Reduction of heat exchanger efficiency can increase cycle times.

Removal of staining on a part can be an expensive process. It requires additional effort such as shot blasting to obtain a clean surface. If the parts are not properly cleaned, then surface appearance can be objectionable (Figure 3). Lack of adhesion for subsequent coating processes such as painting, nitriding or plating can become an issue.

Water is a common contaminate. Its presence must be minimized due to the risk of fire and explosion above 1000 ppm water. Contents below 500 ppm are generally considered safe, however can cause changes in the cooling curve (Figure 4).

Figure 3. Parts before and after filtration showing an improvement in part appearance.

Filtration Methods

Filtration is a common method to remove particulates, including oxidation products from quench oil. There are several methods, and they will be briefly discussed.

The dirt load, including particulate from oxidation products, ranges in size from very small (sub-micron) to very large. Particle size in general is inversely proportional to the amount of particulate present. In other words, there is a greater amount of fine particulate to be removed, than large particulate (Figure 5).

Bag Filters.

Bag filtration systems are common in the heat treating industry. They are an inexpensive method of particulate removal, but fall short in cleaning the oil to a level that would extend the oil life. Typically, bag filters are used at 10-20 microns. As can be seen from Figure 5, this size will only remove about 10% of the particulate present. Bag filters have the advantage of being inexpensive, but suffer the drawback of very limited particulate retention. This results in replacing the filter element at a very short interval, increasing maintenance costs. Replacement of the filters is a messy job.

While there have been improvements in reduction of pore size, poor dirt load retention results in rapid clogging of the filter. Often a manufacturer will spend the money on a filtration system, but maintenance will fail to replace the bags because of short replacement interval. Bags can also be replaced with a much bigger pore size to reduce the replacement interval. This is false economy, as the particulate that is responsible for part staining and sludge is very fine, and passes through the larger pore size.
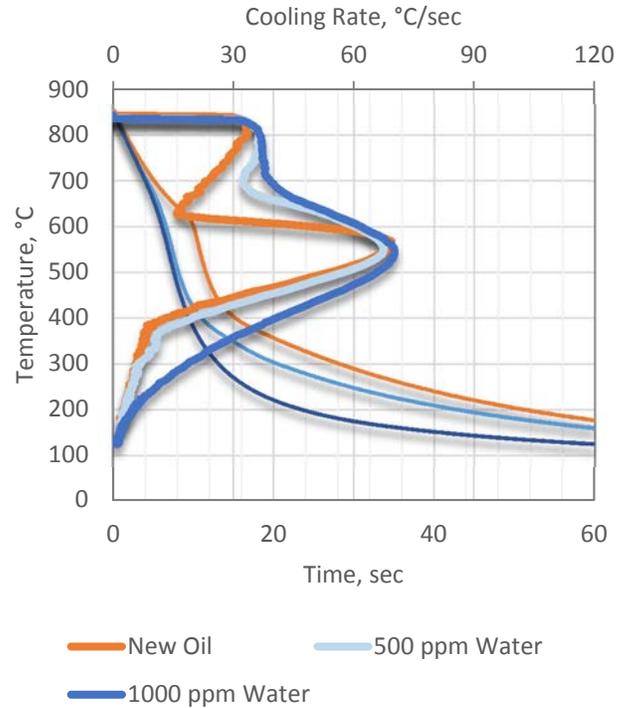

Figure 4. Effect of small amounts of water on the cooling curve of a cold oil. Cooling curve per ASTM D6200, tested at 60°C.
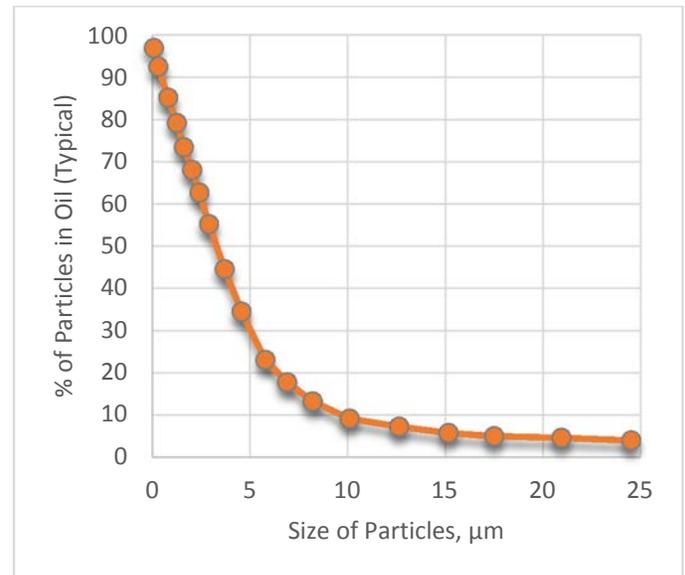

Figure 5. Typical distribution of particulate in used quench oil.

Pleated Filter Elements

Pleated filter elements are either cellulose or micro-fiberglass fiber. These filters have the capability to remove very fine particle removal, down to less than 1 micron. However, the problem with these filters is the amount of dirt that the filter can hold. An industry standard pleated micro-glass filter can only hold around 140 grams of dirt per filter element. With the high number of particles that are inherent in a quenching system,

these filters would not last very long and would be a very expensive solution to the problem. In addition, the micro-glass filters would only be able to remove particles and would have no impact on the water, acid, or soft contaminants (that lead to varnish). In the presence of water, the pleated cellulose elements will swell and become clogged very quickly. As an example, a commercial heat treater purchased and installed a pleated filtration system. The stopped using the system shortly after installation due to blinding of the filters, which had resulted in changing the filter elements on a daily basis. While the intent was there, and the filters were capable of very tight filtration, the system was just not economically feasible to use due to the low dirt retention of the filter system.

Online Depth Filtration

The best method for capturing and retaining fine particles, water and varnish, is by installing an offline depth filter. This system utilizes a dense cellulose filter medium capable of filtration down to 3 micron absolute or 0.8 micron nominal. The system circulates the oil continuously. Depth filters provides a large surface area to capture fine particles as well as soft contaminants and water. Debris is captured on the surface of the filter and in the interior filter material. This enables the depth filter to have the highest dirt holding capacity of any type filter insert or element. This high dirt holding capacity makes the depth filter the best solution for filtering quench oils with a high dirt load. Not only can the oil get to the cleanliness level necessary to prevent the sludge and carbon deposits, but this can be done with an insert that can hold several pound of contaminants. The high dirt load capacity will result in long filter change intervals. Depending on the cleanliness of the oil, and the size of the filtration system, filter change intervals can be extended to months between changes.

The typical dirt holding capacity for this type of filter is 4 liters of evenly dispersed solids (depending on size of filter element). The filtration element will retain approximately 4 kg of oxidation products, such as sludge and the oligomers from oxidation.   Wood cellulose is most commonly used filter material, and can retain up to 50% of the total retention capacity.

Experimental

A sample of used Mar-Temper 355 was received from a customer. The oil was badly oxidized (Table 1) and exhibited a cooling curve indicating badly oxidized oil (Figure 7).

Table 1. Table comparing new and as-received oil.

Property	New		Used
	Min.	Max.	
Viscosity (40°C), cSt	69	82	85.6
Flashpoint, °C	229		252
Water, %	-	0.10	0.02
TAN, mg KOH/g		0.1	3.0
Precipitation Number, %	-	0.05	0.4
Sludge, %	-	0.05	0.5

Figure 6. Deep Filtration Element used for cleaning quench oils to 3 μm absolute and 0.8 μm nominal. This means that 98.5% of all particles greater than 3 μm and 50% of all solid particles greater than 0.8μm.

The physical properties of the used oil exhibited severe oxidation. The viscosity had substantially increased. The Total Acid Number (TAN) had a value of 3.0 mg KOH/g. Oil is considered to be oxidized and prone to staining, if the TAN is greater than 1.5 – 2.0. The Precipitation number and Sludge were also nearly an order of a magnitude greater than new oil. This shows that the oil is badly oxidized, and contains considerable oxidation by-products, and potentially other contaminates.

In the cooling curve of the oxidized oil, the vapor phase of the oxidized oil is virtually non-existent. Further, the maximum cooling rate has increased substantially.   The fine suspended oxidation products are causing the initiation of nucleate boiling at a much earlier temperature. Further, the oxidation products also act as a speed improver, increasing the maximum cooling rate.   Staining of the cooling curve probe was also evident (Figure 8).

Once the physical properties and cooling curve were obtained, a 25 liter sample from the customer was filtered. The quench oil was filtered using a filter element consisting of bonded discs of four different types of cellulose fibers. Each type of cellulose fiber filters and conditions the oil. The large surface area of the cellulose fibers acts as a free radical scavenger, reducing oil degradation precursors and degradation products.

In this filter element, particles greater than 3 microns are removed by mechanical filtration, while particles less than 3 microns are removed primarily by Van der Waal forces and electrochemical forces. The degree of filtration of the filter element is [11]:

Figure 7. Severely oxidized oil showing change in cooling curve behavior.

Figure 8. Stained probe from quenching severely oxidized quench oil.

- 21 µm absolute > 99.9% of all solid particles > 21 µm
- 6 µm absolute > 99.5% of all solid particles > 6 µm
- 4 µm absolute > 99% of all solid particles > 4 µm
- 2 µm absolute > 80% of all solid particles > 2 µm

Resultant particle counts are shown in Table 2 and Figure 9

As evident from Table 2 and Figure 9, the initial as-received oil sample was saturated with very fine particulate with a size much smaller than 10µm. The customer had indicated that the oil was filtered to 20 µm. However, on further investigation it was determined that the actual filter size used was 50µm. The change was initiated by maintenance to reduce the frequency of filtering.

Table 2. Particle counts on filtered oil. Testing conducted to ISO 11171 using laser particle HIAC/ROYCO. Particle counts are based on 1 ml of sample.

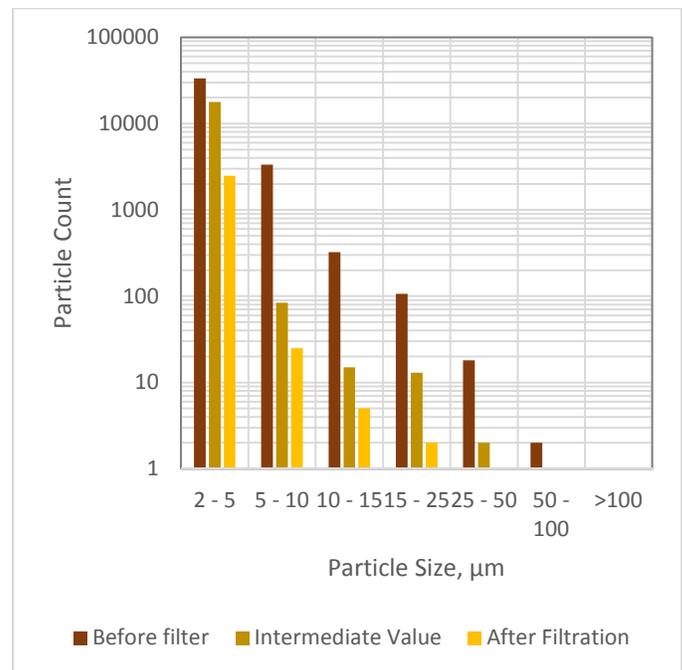| Particle Size Range (µm)	Before filter	Middle of Filtration	After FIltration
2 - 5	33275	17803	2478
5 - 10	3332	84	25
10 - 15	324	15	5
15 - 25	107	13	2
25 - 50	18	2	0
50 - 100	2	0	0
>100	0	0	0

Figure 9. Results of the filtration showing substantial improvement in reducing fine particulate in oil.

Significant reduction of the particulate in the 2 – 5 µm size by almost 50% was accomplished during the initial pass. Nearly 2 orders of magnitude improvement was observed on particulate greater than 5 µm.

A much greater improvement in the residual particulate present after the final pass was observed. The very fine particulate was reduced by 92.5%, while the particulate in the 5-10 µm range was reduced by 99.3%. This substantial improvement significantly reduced probe staining during quenching and cooling curve testing.

The results of the physical testing and cooling curves on the initial and final filtering are tabulated in *Table* 4 and the resultant cooling curves are shown in Figure 11.

Particulate was also measured by the pore-blockage test. In this test, the sample is passed through a series of calibrated screens. As particles collect on the screen, the amount of flow decreases. The decrease in flow is measured and the particle count is obtained [12].

The methodologies are different in the two test methods, so the results cannot be compared directly. In a laser based particle count, the system will count everything that blocks the laser, such as wear products, water, varnish and other soft particles. Pore blockage only counts the captured particles. The pore blockage method is most suitable for oils that are dark. The results of the pore blockage tests are shown in Figure 10 and Table 3.
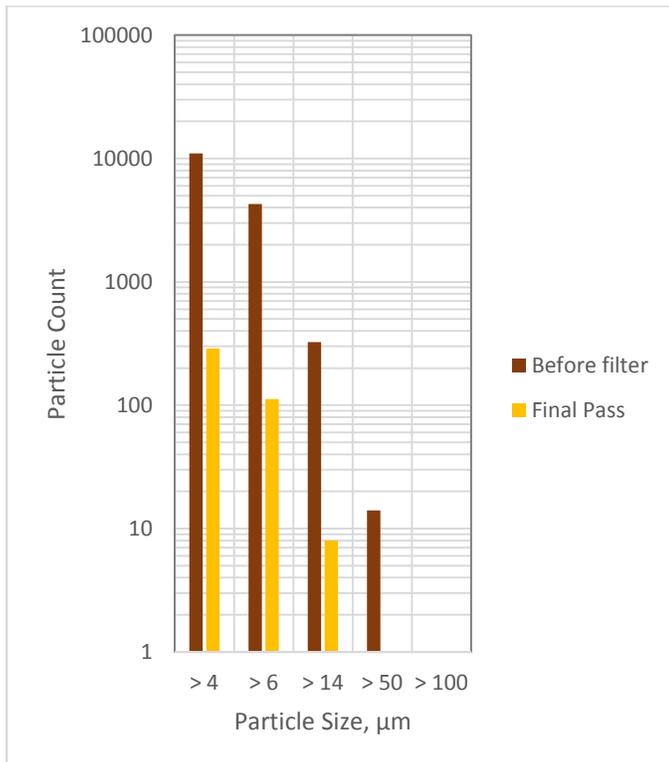

Figure 10. Pore blockage test results.

The resulting data shows that the oil has been cleaned six ISO codes and is substantially cleaner than before. This is evident in the cooling curve data, showing the reemergence of the vapor phase.

The initial pass of the severely oxidized oil showed a substantial improvement in the physical properties. The TAN was reduced from an extremely high value of 3.0, to a moderate value of 0.8 mg KOH/g. This is a large improvement. As a general rule, an oil that is oxidized and prone to staining would show a TAN greater than 1.5 – 2.0 mg KOH/g. After filtration the primary oxidation products and acids have been predominately removed from the oil.

The precipitation number, a measure of oil oxidation, was reduced from 0.4% (very high) to a value less than 0.01 after the final pass. This shows that the sludge and dirt load in the oil has been removed from the system. After the final pass, all physical properties met the requirements for new oil.

Table 3. Particle counts per Pore Blockage test (ISI 4406:2017)

Particle Size Range (µm)	Before filter	After Filtration
> 4	10973	288
> 6	4267	112
> 14	325	8
> 50	14	0
> 100	0	0
ISO Code	21/19/16	15/14/10

Table 4. Physical properties before and after filtering. After filtering, physical properties met manufacturing specifications for new oil.

Property	Used	First Pass	Final Pass
Viscosity (40°C), cSt	85.6	79.6	77.7
Flashpoint, °C	252	248	250
TAN, mg KOH/g	3.0	0.8	0.7
Precipitation Number, %	0.4	0.1	0.01
Sludge, %	0.5	0.03	0.01

The cooling curves of the oil (Figure 11) showed a similar improvement. Specific locations on the cooling curve are shown in Table 5. In the oxidized oil, the vapor phase was practically non-existent. The oil showed an improvement in the vapor phase, nearing the value for new oil. The maximum cooling rate was also reduced to within the allowable range for Mar-Temp 355, and the expected variation of the cooling curve test [13]. The temperature at the maximum cooling rate was reduced to nearly the value of new oil.

While the severely oxidized oil, after initial filtering, did not meet the cooling curve for new oil, a substantial improvement was obtained. After final filtration, the oil would be considered to be acceptable for continued use, with moderate oxidation.

Without filtration, the oil would be considered to be in very bad shape. It would be recommended that the quench tank be dumped and recharged with new oil. With filtration, the oil was reclaimed and recovered. Additions of new anti-oxidant may be required to replenish depleted anti-oxidant in the oil.

Discussion

Once an oil is badly contaminated, or has a high TAN or precipitation number, it is often sent out for filtration. The oil can be filtered on-site by a service or the oil can be filtered by trucking the oil away. The cost of this process is expensive – usually about half the cost of new oil. The oil should be tested after filtration and prior to entering into service. This is to make sure that the cooling curve compares favorably with new oil,

and if any additive package is necessary to bring the oil back to near new condition. The oil should be tested for water to make sure that a new hazard is not introduced into the system.
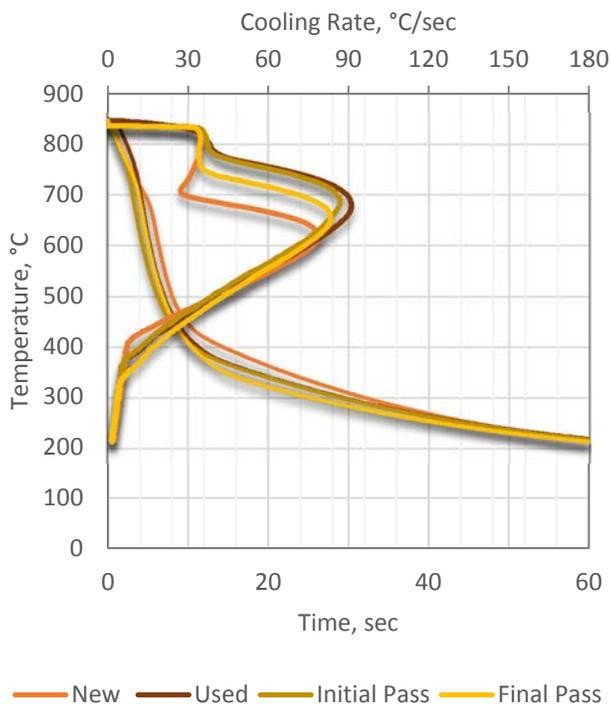

Figure 11. Cooling curves of new oil compared to the severely oxidized oil. Additional curves showing the improvement after initial pass and final filtration passes are shown.

Table 5. Specific values for the cooling curves shown in Figure 11.

	New	Used	Initial Pass	Final Pass
Max CR	78.8	91.0	86.8	83.2
Temp @ CR_{max}	613.2	682.3	682.9	656.8
Cooling Rate @ 704°C	28.3	89.2	85.5	72.9
Cooling Rate @ 600°C	76.2	74.1	85.5	71.6
Cooling Rate @ 500°C	40.3	41.0	37.7	42.5
Cooling Rate @ 400°C	7.3	13.2	11.8	16.4
Cooling Rate @ 300°C	4.3	3.9	4.1	4.0

However, this method produces a saw-tooth pattern of oil cleanliness. It is better, and more cost effective from a maintenance and production standpoint to filter continuously. This can be seen from Figure 12.

It is also appropriate to start filtration when the oil is new. If filtration is started once the oil is already dirty, then the filter media will clog rapidly, resulting in short media life and frustrated maintenance personnel. Filtration is best when it is continuous. The goal is not to clean to a minimum level and let the oil become dirty again, but to maintain the oil in "like new"

condition. It is in this condition that the oil (and the filter element) will last the longest.
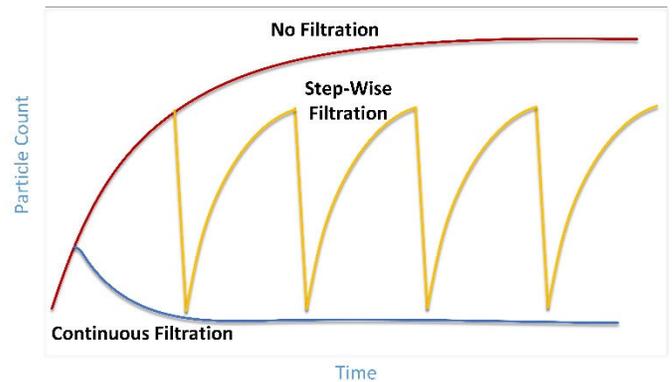

Figure 12. Schematic comparison of step-wise filtration and continuous filtration. The average particle count for step-wise filtering is much higher than continuous filtering.

It is also recommended to filter heavily contaminated oil, with large amounts of sludge and large particles, by starting off with a coarse filter, then gradually decreasing the pore size. Once the filtration interval is satisfactory, the filtration pore size is stepped down and the process repeated. This will clean the system in a gradually, without having system interruptions. In the case where the oil condition has been neglected, then sometimes the only alternative is to outsource the filtration one time, and then implement a continuous filtration system. Alternatively, if the existing oil is beyond redemption, then recharging the system with new oil is the only choice. Continuous filtration should then be implemented to obtain the longest life of the oil.

A good filtration system should capture all the contamination (sludge, soot, scale and water) found in a typical quench system. It should be capable of filtration to at least 5μm. While many people filter to 20μm, this is only capturing a small amount of the total dirt load (Figure 5). The greatest percentage of particulate in quench oil is less 5μm. To achieve proper filtration, the system should be capable of filtering to around 3μm or less. It should be capable of capturing sludge, and have a high load capacity (Figure 13).

Conclusions

Test results of a study described herein showed:

- Initial oil, received from the customer, was severely oxidized, and contained high particulate.
- The physical properties of the oil showed severe degradation and did not meet specifications for new oil. Excessive TAN, Precipitation number and %Sludge indicated severe degradation.
- The cooling curve showed an excessive maximum cooling rate, and a nearly absent vapor phase. These are all signs of a badly degraded quench oil.

Figure 13. Typical high capacity filtration system designed for high capacity dirt loading and fine filtration.

The oil was filtered using a high density wood cellulose filter element with a 3 μm absolute and 0.8 μm nominal filtration system. After filtration, the oil exhibited much improved physical properties and cooling curve:

- The TAN decreased from 3 to 0.7 mg KOH/g. This is a substantial improvement, and staining was significantly reduced.
- The Precipitation Number and Sludge in the as-received oil was very high, with values of 0.4% and 0.5% respectively. After filtering, the Precipitation number and %Sludge was reduced to 0.01% each. This is nearly a fifty-fold improvement.
- The cooling curve showed a much improved appearance. The curve went from representing a badly oxidized oil to that of a moderately oxidized oil. While the cooling curve did not meet new manufacturing specifications, it was considered to be acceptable for continuous use.

The use of a continuous filtration system capable of very fine filtration will extend the life of the oil and reduce the potential for staining. It would avoid the expensive outsourcing of oil filtration, with extended furnace down time.

Acknowledgements

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