Oil quenchants are used throughout the world as a method for hardening steel parts. This article discusses how the base oil composition affects quench-oil performance and the effects of oil degradation on oil performance, as well as methods to counteract this degradation.

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When a hot component comes into contact with a liquid quenchant, there are normally three stages of quenching. There are exceptions to this, which will be explained as we cover each stage. Three stages of quenching are:
1. Vapor stage (Stage A, or vapor blanket stage)
2. Boiling stage (Stage B, or nucleate boiling stage)
3. Convection stage (Stage C)

The vapor stage is encountered when the hot surface of the heated component first comes in contact with the liquid quenchant. The component becomes surrounded with a blanket of vapor. In this stage, heat transfer is very slow, and occurs primarily by radiation through the vapor blanket. Some conduction also occurs through the vapor phase. This blanket is very stable and its removal can only be enhanced by agitation or speed-improving additives. This stage is responsible for many of the surface soft spots encountered in quenching. High-pressure sprays and strong agitation eliminate this stage. If they are allowed to persist, undesirable microconstituents can form.

The second stage encountered in quenching is the boiling stage, where the vapor stage starts to collapse and all liquid in contact with the component surface erupts into boiling bubbles. This is the fastest stage of quenching. The high heat extraction rates are due to carrying away heat from the hot surface and transferring it farther into the liquid quenchant, which allows cooled liquid to replace it at the surface. In many quenchants, additives have been added to enhance the maximum cooling rates obtained by a given fluid. The boiling stage stops when the surface temperature of the component reaches a temperature below the boiling point of the liquid. For many distortion-prone components, high boiling-temperature oils or liquid salts are used if the media is fast enough to harden the steel, but both of these quenchants see relatively little use in induction hardening.

The final stage of quenching is the convection stage, which occurs when the component reaches a point below that of the quenchant’s boiling temperature. Heat is removed by convection and is controlled by the quenchant’s specific heat and thermal conductivity, and the temperature differential between the component’s temperature and that of the quenchant. The convection stage is usually the slowest of the three stages. Typically, it is this stage where most distortion occurs. An example showing the three stages of quenching is shown in Fig. 1.

Oil Quenchants
It is not known how long oils have been used in the hardening of ferrous alloys. Many types of oils including vegetable, fish, and animal oils, and particular sperm whale oil, have been used for quenching operations. The first petroleum-based quenching oils
properties are required. Dependable, consistent metallurgical high hardenability applications where intermediate quenching characteristics are widely used for medium to low rates of heat extraction, and are used in applications where the material being quenched has a high hardenability. Highly alloyed steels such as AISI 4340 or tool steels are typical examples of steels quenched in normal speed oils.

Medium-speed quench oils provide intermediate quenching characteristics and are widely used for medium to high hardenability applications where dependable, consistent metallurgical properties are required.

High-speed quench oils are used in applications such as low hardenability alloys, carburized and carbonitrided components, or large cross sections of medium-hardenability steels where high rates of cooling are required to ensure maximum mechanical properties. A comparison of the quenching speeds of the different types of quench oil is shown in Fig. 2.

Mar-quenching oils are a special case where the part is quenched into a quenchant at elevated temperature, typically 100 to 200°C. The workpiece is held in the quenchant until temperature equilibrium is established throughout the section, and then air cooled to ambient temperature. During mar-quenching, components are quenched to an intermediate temperature close to the Ms temperature, and held at this temperature. This eliminates the temperature gradients across the surface, and consequently, during subsequent slow cooling after removal from the hot oil, transformation to martensite occurs uniformly throughout the section. This minimizes the generation of internal stresses and reduces distortion.

Since mar-quenching oils are used at relatively high temperatures, their formulation and physical properties are different from cold quenching oils. They are formulated from very carefully selected base stocks with high oxidation resistance and thermal stability. They have high flash points and viscosities, and contain complex anti-oxidant packages to provide long life. Selection of the mar-quenching oil is based on the operating temperature and quenching characteristics. A minimum of 50°C should be maintained between the operating temperature of the oil and its flash point.

Oil Composition

Engineered quench oil is governed by the desired quenching performance, the necessary thermal and oxidative stability, and final price or market considerations. Quenching performance is generally considered to be the heat transfer characteristics and the thermal stability of the oil. This includes having an acceptable flash temperature that is approximately 50°C above the expected use temperature, low sludge forming tendency, long life, and the necessary quenching speed. The best quench oils have the following characteristics:

- The maximum cooling rate to achieve maximum hardness and depth of hardening
- Minimal deposition of sludge
- Maximum thermal and oxidation stability (achieved through the additive package)
- Currently, this currently favors mineral oils.

The base stocks of oils used in the formulation of quench oils are complex. They contain various ratios of paraffinic and napthenic constituents, as well as numerous open chain and cyclic derivatives such as sulfur, oxygen, and nitrogen heterocycles. The specific composition of the base oil depends on the source of the crude oil. This means that the composition of the crude is different in the western U.S. than in the eastern U.S., Middle East, North Sea, Venezuela, etc. From a supplier’s perspective, this means that different additive packages or different ratios of thermal stability and speed improvers may be necessary to provide an oil that behaves similarly across the world. What this means to a heat treater is that there will be minor differences in quenching performance of a quench oil in different locations across the world because of differences in local feed stock.

As was inferred from the previous paragraph, the composition of quench oil affects the quenching performance. Because of local differences in composition, quench oil can exhibit a wide variation in thermal and oxidative stability, and a wide variation in quenching speed. When you add the thermal stability and speed improver additive packages, an even wider variation in cooling rates and thermal stability occurs.

Fig. 2 — Cooling curves for normal- and high-speed quenching oils.
The volatility of quench oil is inversely proportional to the flash point of the oil. The volatility decreases as the average molecular weight increases. As a general rule, the volatility decreases and flash temperature increases as the viscosity of the oil increases. This viscosity is related to the average molecular weight.

The quench severity of oil is directly related to the “wettability,” which is measured by the contact angle between the part and quench oil. As the viscosity increases, the contact angle decreases, which in turn decreases the cooling rate. The various additive packages available also change the wettability characteristics, which change the quenching performance.

Base oils are generally divided into two groups: napthenic and paraffinic grades. Napthenic oils have a high proportion of cyclic hydrocarbons. Napthenic grades contain very low portion of n-alkanes, which are chemical compounds that consist of only carbon and hydrogen. Alkanes are also known as paraffins. The low temperature behavior of napthenic oils is better than same-viscosity paraffinic oils, so the napthenic oils tend to have a lower pour point. The degradation products of napthenic oils tend to be more soluble in oil, which can contribute to greater staining. For the same viscosity, napthenic oils tend to oxidize at a faster rate and have a lower thermal stability. Napthenic grades, at the same viscosity as a paraffinic grade, also tend to have a lower flash temperature.

Paraffinic oils are oils that consist predominately of long chains of hydrocarbons, called alkanes. Because of these long chains, when compared with napthenic oils, paraffinic oils are widely used for lubrication base stocks. They are also the preferred base stock for oil-base quenchants. Comparing identical viscosities of napthenic and paraffinic oils, paraffinic oils have higher flash temperatures, superior cooling curves, and better oxidation and thermal stability. This means that they tend to stain less and last longer. There are many types of base oil used for quenchants including:

- Double hydro-treated mineral oils
- Refined paraffinic mineral oils
- Refined napthenic mineral oils
- Rerefiner mineral oils
- Reclaimed mineral oils

Double hydro-treated mineral oils are those that are treated with hydrogen to remove carbon-carbon double bonds. These double bonds can occur in aromatics and in impure paraffins. Because these double bonds are removed, they have greater thermal and oxidative stability. They have a higher flash temperature compared with other grades, and have a marginal improvement in the cooling curve for the same viscosity. These oils are generally clear to a very light amber. However, the color is not indicative of staining tendency—that is the function of the additive package. The primary disadvantage of double hydro-treated oils is availability and cost.

The refined paraffinic oils are the most commonly used base oil in quenchants. Besides the advantages cited earlier, they also have a wide range of viscosities available (70 to 2500 SUS). They are hydrophobic, which means that they displace water. This means better washing for the heat treater, and better splitting for improved reclamation. Unfortunately, refined paraffinic mineral oil is getting more expensive because of global demand, as well as local refinery shutdowns due to maintenance and other factors.

Refined napthenic base oils are readily available in a wide range of viscosities. Their primary advantage is cost. However, the reduced thermal stability, lower flash temperatures, and quicker thermal degradation tend to offset the advantages of cost. These oils are hydrophilic, which means that they tend to form a stable emulsion. This means that the oils do not split well in the washer, making recovery difficult. The oils also have a tendency to absorb water. It is also difficult to drive water from these grades. The cost advantage of napthenic base oils is decreasing because of the overall global demand for oils.

Re-refined paraffinic base oils are
those that are recovered and passed through a cracker and distillation column. Specific viscosities with a very narrow range are obtained from defined heights of the distillation column. These oils have all the advantages of paraffinic base oils, with an additional advantage of reduced light and heavy ends. This contributes to very predictable response. These oils are generally less expensive than virgin base oils, and are limited to the different types of viscosities available. There is a limited source of supply because the oils are considered “eco-friendly.” Unfortunately, increased local recycling reduces the supply and availability of feed stocks. These oils generally have a very limited viscosity range (100 SUS), with the cost advantage narrowing because of demand. In addition, the refiners tend to raise prices as crude prices increase.

Reclaimed oils are oils that are recovered from many sources, including coolants, motor oils, and greases. They are filtered and blended to give a specific viscosity. They may have an additive package thrown in to increase life. The primary advantage is that they are cheap. Because the source of the oil is unknown, the presence of heavy metals and other products can be a disposal nightmare. Typically, viscosity is the only requirement, and multiple grades of motor-oil greases, etc., are used to satisfy the viscosity requirement. These oils tend to have a poor life because the precursors to oxidation are already present as free radicals. Overall, the process cost is increased when these oils are used. More thorough cleaning is required, with increased staining. Because a greater percentage of heavy stock is used, these oils tend to have higher drag-out and reduced life. A big issue is the lack of process repeatability in quenching performance.

**Additive Packages**

Additive packages have two functions: to serve as a speed improver and to increase thermal and oxidative stability. These additives can have a dramatic effect on the quenching properties. The magnitude of the effect is dependent on the additive package. The additive packages are usually proprietary. Depending on the robustness of the additive package, they may tend to deplete during use. Some additive packages are prone to selective drag-out over time. It generally is not appropriate to mix additive packages from different quenchant suppliers because of the unintended consequences of precipitation; increased staining, and generally unpredictable response.

Speed improvers increase the quenching rates by increasing the wetability of the oil. There are different types of additives. The most common is the sulfonate-type. Barium sulfonate used to be the most common, but is no longer used by most quenchant suppliers, because the presence of barium can cause an issue with disposal and special precautions during disposal. Potassium and sodium sulfonates are commonly used. These sulfonates provide excellent speed improvement and can double as thermal oxidation stabilizers. Hydrocarbon-based additive packages are used in high-end quenchants. They are very robust and have a long life and are not prone to needing replenishment. The primary disadvantage is cost.

The other purpose of an additive package is to improve the thermal and oxidative stability of the base oil. These packages reduce the formation of sludge and minimize the formation of organic acids upon thermal aging of the oil.

**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 degradation. 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. Polymerization causes the fluid viscosity to increase.

Thermal degradation 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 (Fig. 3). 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, 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.

Conclusions

The choice of base oil and additive package has been shown to be critical in the performance of quench oil. The basic composition of the base oil chosen by the manufacturer plays an important part in consistent heat treating. Understanding local variations in feed stock also are important to ensure that the quench oil purchased in China is the same that is purchased in Brazil or the United States. 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 ensure quality parts and customer satisfaction.