Cost, cleanliness, carbon footprint affect quenchant

Weighing the application of vegetable-based quenchants for heat-treating applications.

Vegetable oils are seeing increased interest as quenchants for steel because of low carbon footprint, a renewable resource, and the ability to reclaim/recycle into bio-fuels. There are many different types of vegetable oils, and considerable research has gone into the viability of these oils for applications in quenching [1] [2] [3]. Vegetable oils are extracted from plant matter, usually seeds. The most common methods are mechanical, chemical, or distillation. Extraction by high pressure CO2 has been investigated. Mechanical means, using a hydraulic press, are the most common, but chemical means using solvents and specific enzymes are also being used. Once the vegetable oils are extracted they are degummed, which removes the phosphatide content common in some crude oils (soybean, sunflower, rapeseed). Often, the free acids present are neutralized by alkali. Using a “winterizing” process, some oils such as sunflower will present an unpleasant turbidity at low temperature. This can be removed by eliminating components such as waxes which solidify at low temperature. Some fat is present in the vegetable oils. This fat is the result of low and high melting temperature fractions. The fractionation process separates both the low temperature and high temperature fractions, in order to obtain a liquid fraction that remains limpid (remains clear) at room temperature. Finally, a hydrogenation process is used to saturate the oil with hydrogen for stability.

Chemically, vegetable oils are triglycerides, as either esters of glycerol or glycerol and fatty acids. A typical structure of a vegetable oil as a glycerol and fatty acid is shown in Figure 1. Typical fatty acids are shown in Figure 2. Typical fatty acid composition of vegetable oils are listed in Table 1.

Mineral oil quenchants are second only to water in use to harden steel. It is used in a wide variety of applications of alloy type and quenching systems. However, mineral oil has poor biodegradability [4]; flammability, and it is not renewable [5]. It produces smoke which can condense and leave a film of oil on machine surfaces. This produces a cleanliness issue as well as an environmental issue.

Multiple advantages apply to vegetable oil-based quenchants. First and foremost, they are readily biodegradable, meaning they are greater than 75 percent biodegradable. As determined by the European CEC Test, the biodegradability of vegetable oil is 80 to 100 percent, in contrast to 10 to 40 percent for mineral oil. These quenchants also possess lower toxicological hazard potential, as well as high flash and boiling points. Last, but not least, they are a renewable resource with consistent and expandable supply.

Despite these significant advantages, there are concerns with vegetable oil quenchants, including: hydrolytic stability, oxidative instability [6], low-temperature properties, and a narrow viscosity range [7]. Cost is also higher than mineral oil. In order to be a viable alternative, quenchants must have even heat extraction, be stable during use, be usable for a long or indefinite time, be environmentally friendly, and achieve the desired quenching performance.

The physical properties of a typical mineral oil quenchant and a vegetable oil quenchant are shown in Table 2. A comparison of cooling curves are shown in Figure 3 and the specific cooling curve data in tabular form is in Table 3.

For vegetable oils, viscosity is not an absolute guide to thermal stability. The amount of link saturation must be taken into consideration, as the viscosity increases with molecular weight, but decreases with increasing unsaturation.

The flashpoint of a liquid like a quench oil is the lowest temperature at which it can vaporize and ignite in the presence of an ignition source. It is well correlated with the lower flammability limit. As temperature increases, the vapor pressure of the

Table 1. Fatty acid composition of common vegetable oils.
liquid increases. As this pressure increases, the concentration of the vapor increases. The temperature at which the vapors ignite in the presence of an ignition source is called the flash point. As a general rule-of-thumb, the vapor pressure for most liquids at the flash-point is approximately 4-7 mbar.

The flash point provides information on two different aspects of a quenchant. First, the flash point provides an indication of tendency for fires. Second, it also gives an indication of the vapor pressure, and the amount of fumes present.

The flashpoint of the mineral oil quenchant is approximately 168°C, while the flashpoint of the vegetable oil is approximately 323°C. This shows that the vegetable oil will have a lower tendency for fires and have lower fumes and smoke than the mineral oil.

The cooling curve behavior of the two quenchants, while similar in the maximum cooling rate, shows some distinct differences. The mineral oil quenchant shows a definite vapor phase, with the transition to boiling occurring at approximately 721°C, while vegetable oil shows no vapor phase. Boiling starts immediately upon quenching. Further, the transition from boiling to convection in the mineral oil quenchant shows a much lower transition temperature than the vegetable oil-based quenchant. This would indicate that the vegetable oil would likely have superior or equal properties while producing lower distortion than the incumbent mineral oil. Similar microstructures are obtained with both quenchants (Figure 4). Quenchants degrade for four primary reasons: thermal degradation, oxidation, contamination, and additive depletion. This is manifested by viscosity increasing, total acid number increasing, and varnish and lacquer deposits. For a mineral oil, the use of Total Acid number (ASTM D974) [8] and kinematic viscosity is adequate. However, because of the free fatty acids present in vegetable oils, viscosity is not an absolute guide to thermal stability. The amount of link saturation must be taken into consideration, as the viscosity increases with molecular weight, but decreases with increasing unsaturation.
acids present in vegetable oils, the use of the total acid number is misleading. The oxidation processes are similar in both cases, but in the case of vegetable oils, initiation is by fatty acid free radicals instead of hydrocarbon free radicals. In all cases, a varnish or lacquer deposit will form on the parts. In the case of vegetable oils, the deposits are very similar to that formed by burned-on vegetable oil on an overheated pan, and are very difficult to remove. The oxidation resistance of vegetable oils is inferior to that of mineral oils (Figure 5).

Additional problems with vegetable oils are cleaning and removing vegetable oils after quenching. Vegetable oils tend to emulsify, so enhanced splitting formulations are required to fully clean the oil from quenched parts. Removing the last vestiges of oil can be difficult.

Lastly, the last issue with quenching in vegetable oils is the smell. It often smells like French fries cooking, which may become objectionable over time.

CONCLUSIONS
Vegetable oils are a viable quenchant that produces less smoke than a comparable mineral oil quenchant. It has a much higher flash point, which reduces fire hazards. Further, the quenching characteristics are superior to a mineral oil quenchant, yielding equal properties, while improving distortion. It is also a low carbon footprint quenchant, with zero volatile organic content (VOC). It is renewable, and “green.”

On the downside, vegetable oil quenchants are more expensive than equivalent mineral oil quenchants. The price is often dependent on crop success, and competes with food sources. It is also more difficult to clean.

Additional research is needed to improve cleaning of these quenchants, and to improve the short thermal stability of these oils compared to mineral oil. Vegetable oils, once these problems are solved, will be an excellent quenchant, suitable for many heat-treating operations.

Should you have any questions regarding this article, or suggestions for further articles, please contact the author.

REFERENCES