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Performance of Vegetable Oils as a Cooling Medium in Comparison to a Standard Mineral Oil

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Immersion quenching is the most widely used quenching technique today and is usually one of the last steps in heat treat processing. Improper hardening to incorrect cooling is generally a great loss and causes a great percentage of manufacturing costs. To avoid a failure in cooling, researchers are committed to describing the cooling effect as precisely as possible.

The cooling of immersion cooled workpieces or probes is generally characterized by the process of wetting. Evaporable fluids exhibit the three well known stages of cooling: vapor blanket stage, boiling stage, and convective heat transfer. Therefore cooling behavior is influenced by a wide variety and depends on a number of parameters, that is, type of quenchant used, bath temperature, rate of agitation, and the physical and chemical properties of the quenched parts.

Environmental pollution has caused the search for new products in hardening and shock cooling of steels. The use of soybean oils as quenching fluids is new, and compared with standard mineral oils, there are many advantages mainly concerning the environment and the health of workers.

Keywords convection, cooling curves, cooling velocities, hardness distribution at the probes' surface, quenching media vegetable oils, wetting behavior

1. Introduction

Although mineral oils have traditionally been one of the most commonly used quenching media, unlike water, they are being subjected to ever-increasing controls due to increasingly stringent governmental regulations regarding their use. Routine disposal and inadvertent release into the environment, especially into the soil where they may leach into drinking water aquifers, is being increasingly regulated by governmental agencies (Ref 1, 2). Improper disposal, even if it is incidental, may be the source of large penalties or even litigation (Ref 2).

European studies have shown that mineral oil based fluid leakage, such as hydraulic fluids, is one of the primary sources of ground water pollutions (Ref 3). This has been followed by a worldwide effort to identify fluids that exhibit reduced environmental and toxicological impact upon incidental contact with the environment (Ref 4, 5). Additional impetus has been provided by the use of national labeling criteria. One of the first and most stringent environmental labeling procedures is the German "Blue Angel" label (Ref 6). Although a focus has been on mineral oil based hydraulic fluids, similar regulations are in place for oil quenchants (Ref 7).

Thus far, the most commonly cited basestocks for the formulation of environmentally friendly quenchants are vegetable oils including canola oil (Ref 7) and soybean oil derivatives (Ref 8). Most recently, a crambe oil derived fluid has also been reported as a potential quenchant (Ref 9). However, one of the earliest references to the quenching behavior of vegetable, animal, and fish oils was provided by Tagaya and Tamura (Ref 10, 11). However, although these authors have discussed general properties such as quench severity or, in some cases, general cooling curve behavior, the fundamental cooling mechanism of vegetable oils relative to the better known mineral oil quenchants has not been described to date.

The fundamental mechanism of the immersion quenching process is best characterized by surface rewetting characteristics (Ref 12-18). Vaporizable quenchants are characterized by the well-known stages of cooling: vapor blanket (full film boiling), nucleate boiling, and convective cooling stages. Therefore, the cooling behavior is influenced by a number of variables including type of quenchant with fluid viscosity, vapor pressure or boiling point, bath temperature, and rate of agitation as well as the physical and chemical properties of the quenched parts.

The objective of this article is to provide for the first time a comparison of the fundamental quenching performance of two vegetable oils (ABIL Laboratory, University of Northern Iowa) and a conventional mineral oil (QH 10 from Fuchs, Germany).

2. Principle of Measurements

At present, various methods of comparing the cooling effects of fluids are used around the world (Ref 16, 17). The Scientific and Technological Aspects of Quenching (STAQ), a committee in the International Federation of Heat Treating (IFHT), has taken steps to prepare international standardized proposals. The experimental testing procedure discussed was performed according to International Standard Organization (ISO) 9950, "Industrial Oils—Determination of Cooling Characteristics—Nickel Alloy Probe Test Method."

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According to Ref 19 the cooling behavior of austenitic stainless steel probes is very similar to that of INCONEL 600 probes, but they have the advantage of a very low variance of measurements (because of its tendency of passivation) and a better similarity to hardenable steels. Thus, the following probes were used. The tested probes were cylinders made of the transformation free austenitic steel X 6 CrNiTi 18 10 and the hardenable unalloyed steel Ck 45, tightened on a tube that was part of a mechanical transfer system. The austenitizing heat treatment and the automatic submerging into the quenchants was done under protective argon gas atmosphere. Table 1 shows the chemical composition of the steels used.

Table 1 Chemical composition of Ck 45 and transformation free austenitic X 6 CrNiTi 18 10 steel

	Composition, %		
Chemical components	**Minimum**	**Maximum**	**Actual value**
Ck 45			
C	0.42	0.50	0.48
Si	0.15	0.35	0.25
Mn	0.50	0.80	0.59
P	…	0.035	0.023
S	…	0.035	0.017
Cr	…	…	0.050
X 6 CrNiTi 18 10			
C	…	≤0.08	0.086
Si	…	≤1.00	0.26
Mn	…	≤2.00	1.56
P	…	≤0.045	0.028
S	…	≤0.030	0.019
Cr	17.0	19.00	12.90
Ni	9.0	12.00	9.20
Ti	≥5 × C, %	≤0.80	0.45
Mo	…	…	…
V	…	…	…

Table 2 Physical properties and acid contents of soybean oils

Properties	Normal crude	Hydrogenated winterized
Viscosity, cSt	43.86	24.18
Density at 25 °C, g/mL	0.92	0.92
Freezing point, °C	–10 to –16	–9
Flash point, °C	296	328
Fatty acids, %		
Palmitic, 16:0	11	9.5
Palmitoleic, 16:1	0.1	NA
Steanic, 18:0	4.2	4.0
Oleic, 18:1	23.4	37.5
Linoleic, 18:2	52.5	42.31
Linolenic, 18:3	8.8	4.75

NA, not applicable

Table 3 Physical properties and acid contents of mineral oil

Properties	Mineral oil
Density at 15 °C, g/mL	0.845
Viscosity, mm^2/s	23 at 20 °C 11 at 40 °C 3 at 100 °C
Flash point, °C	156
Freezing point, °C	–14

The probe diameter after finish grinding was 15 mm with a length of 45 mm. The thermocouple was located in its geometric center and inserted into a hole of 1.1 mm diameter, as shown in Fig. 1. The used temperature sensor was a metal-sheeted NiCr/Ni (chromel/alumel) thermocouple of insulated junction type with an outer diameter of 1.0 mm. The virginal austenitic probe was conditioned by conducting three "dummy" quenches in a referencing fluid (distilled water at 60 °C) from 850 °C, until a continuous oxide film was formed around the probe surface and reproducible results were achieved (passivated surface).

The probe was inductively heated to 850 °C (1562 °F) in a protective gas atmosphere (argon) and after 5 min subsequently transferred into a fixed volume of quenchant being tested. The agitation rate of the tested quenchant was 0.3 m/s with 40 °C bath temperature. The change of temperature in the sample center of the probe was measured, and the portion of the wetted surface area was determined from a photo sequence and from measurement of the electrical conductance (Ref 12, 13, 16). The cooling rate in the probe center was calculated by a numerical differentiation from the measured temperature-time curve.

2.1 Quenchants

The vegetable oils used were crude expelled and partially hydrogenated and winterized soybean oils (Ref 20); the conventional mineral oil was QH 10. Table 2 gives a summary of the fatty acid content and physical properties of the vegetable oils, and the physical properties of the mineral oil are given in Table 3.

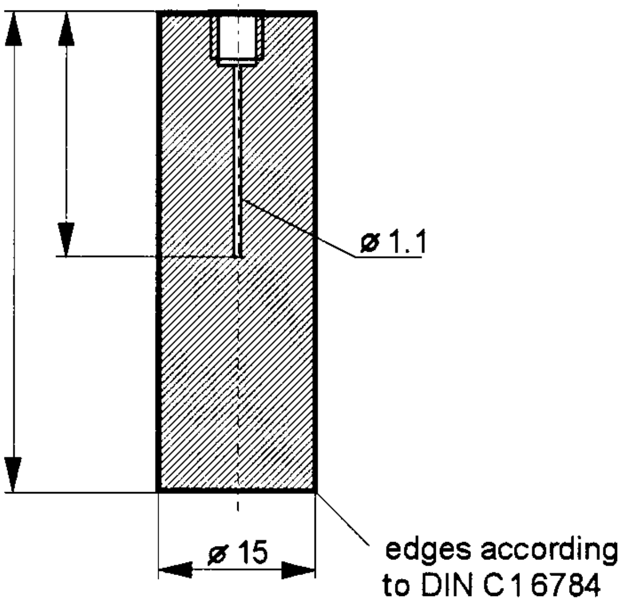

Fig. 1 The tested probe geometry with thermocouple hole and dimensions

Vegetable oils are typical natural occurring triglycerides with the generic structure shown in Fig. 2. Each vegetable oil is characterized by the particular type and concentration. Oil is removed from the vegetable beans (or seed) in an "expelling" process (Ref 20). Expelling can be performed by either pressing the bean (or seed) or, more commonly, by a solvent extraction process. Expulsion by solvent extraction is a three-step process: bean preparation, oil extraction and solvent stripping, and reclamation. To improve low temperature properties, soybean oil can be "winterized" (Ref 21). Winterization is a process that reduces the amount of solids, high melting saturated triglycerides, that are initially formed upon cooling. Winterization is performed by chilling the oil to a particular temperature at a specified rate, both of which are dependent on the end use of the oil, with the subsequent filtration of separated solids (Ref 21). A cooling curve comparison of the "crude-expelled" oil to an undefined parafinic oil was provided in Ref 9. However, until now, the important fundamental cooling properties of these oils have not been reported.

Fig. 2 Vegetable oil triglyceride structure

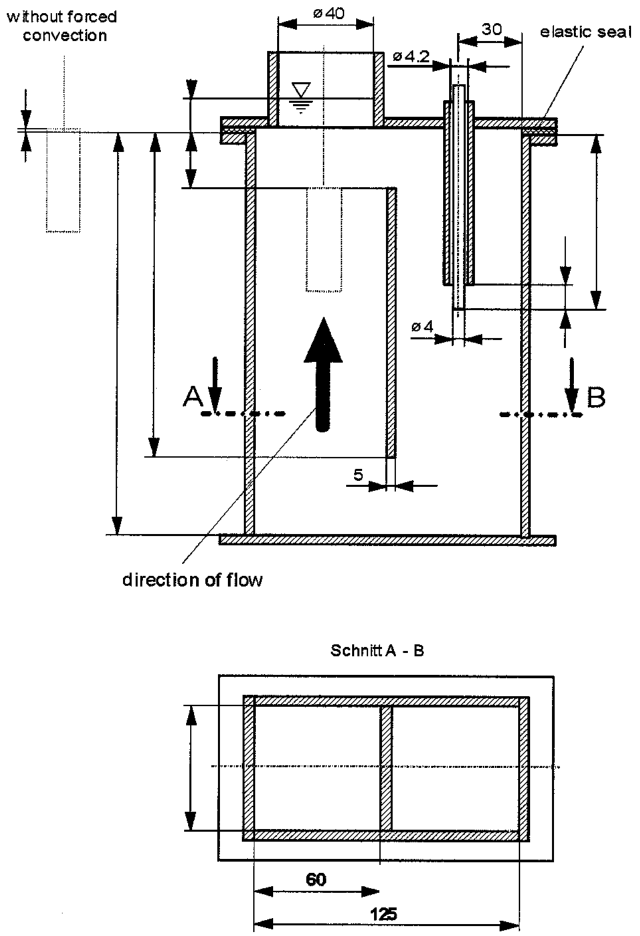

Fig. 3 The controlled agitation apparatus for generating a low-cost, single-phase, and spin-free fluid flow (Ref 15, 17). The quenching device can be constructed of glass or any other transparent and thermal resistant material and is the standardized quenching device according to ISO/DIS 9950. Dimensions in mm

2.2 Convection Apparatus

Figure 3 shows the convection apparatus and its dimensions (Ref 15, 17, and 18). The quenching vessel is rectangular with

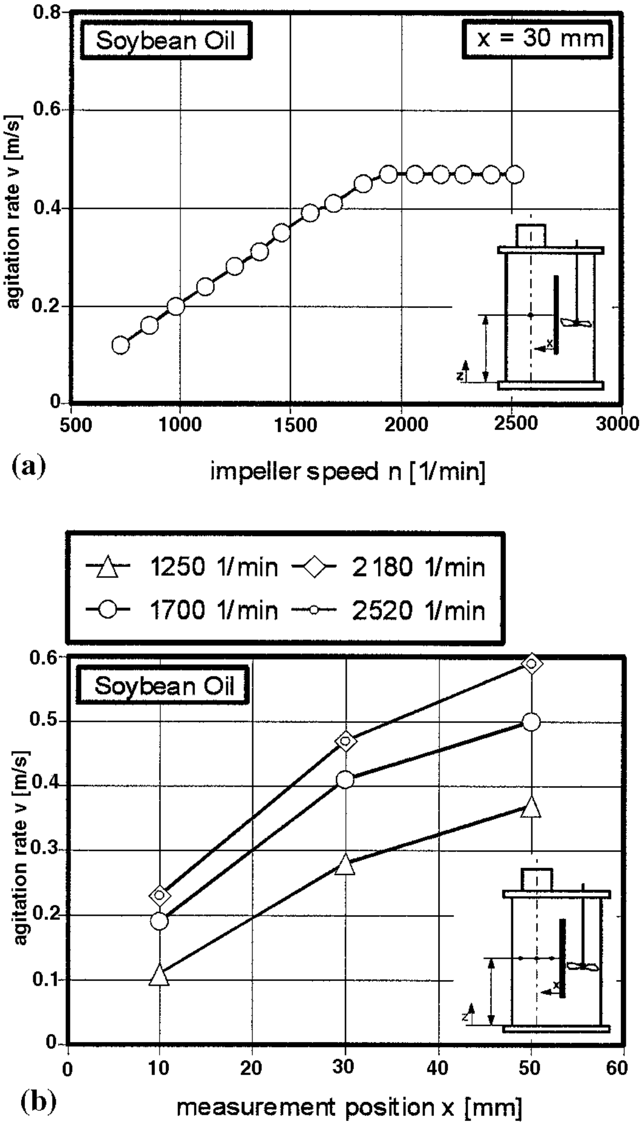

Fig. 4 (a)Velocity of flow versus impeller speed (rpm) in the center of the rectangular flow duct for soybean oil (bath temperature: 40 °C, $x = 30$ mm, $z = 110$ mm). (b)Velocity of flow over the cross section of the rectangular flow duct as a function of the impeller speed for soybean oil (bath temperature: 40 °C, $x = 10$ to 50 mm, $z = 110$ mm)

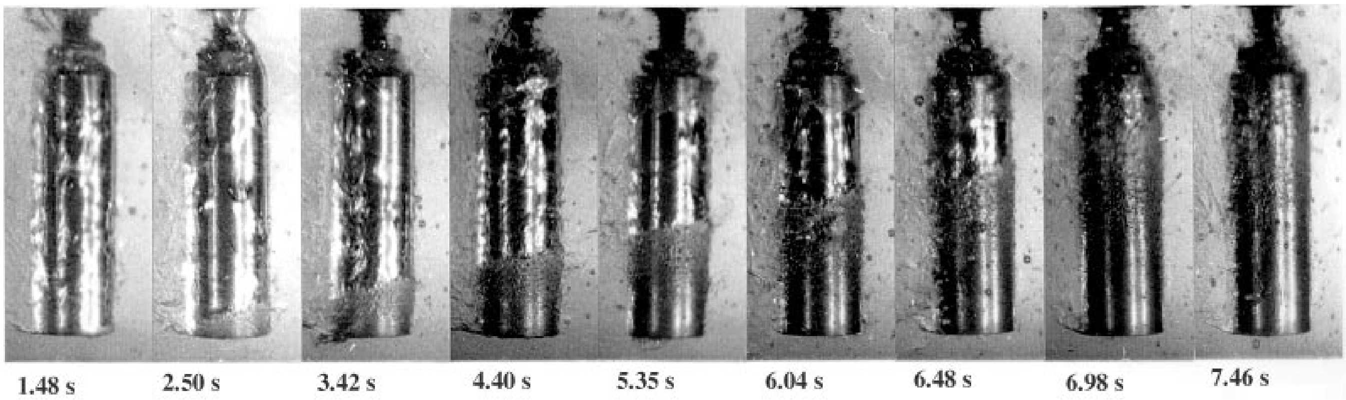

Fig. 5 Wetting process of a cylindrical Ck 45 steel sample (15 by 45 mm diameter) being quenched in partially hydrogenated and winterized soybean oil of 40 °C with 0.3 m/s agitation rate

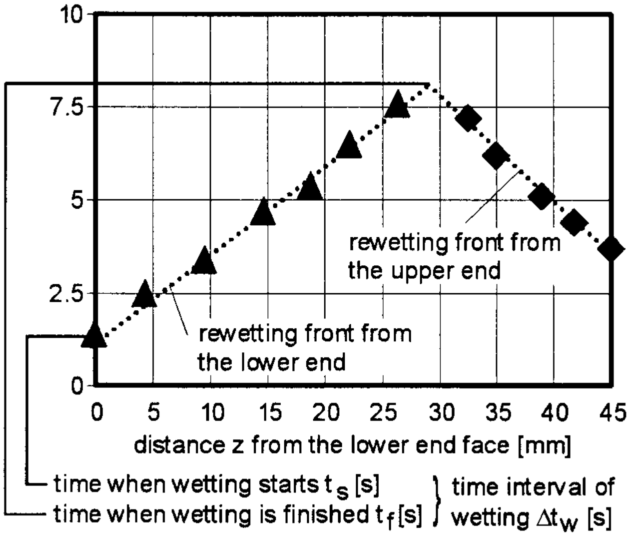

Fig. 6 Wetting characteristics, t_w, t_s, and t_f (determined from a photo sequence), versus distance, z(mm), from the lower end of a cylindrical probe, quenched in partially hydrogenated winterized soybean oil at 40 °C and 0.3 m/s agitation rate. Tested material: X6CrNiTi 18 10

the dimensions 125 by 60 by 60 mm. The volume of the bath is approximately 1.5×10^{-3} m^3. The bath can be constructed from glass or any other transparent and temperature-resistant synthetic material. Thus foaming of the fluid and apparatus cleanness are easily observed. In addition, the overall quenching process can be observed and controlled. Defined levels of forced convection (agitation) are produced by an impeller (diameter, 50 mm; number of blades, 3; pitch setting, 42 mm) (Ref 15, 17).

The bath can be heated outside the convection apparatus, for example, in a water bath or with an immersion heater. The use of a cooling coil is the preferred method of cooling. During heating or cooling, no foreign substances are allowed to be brought into contact with the fluid. The convection apparatus was cleaned prior to its initial use. Sufficient cleaning to assume that no residues or detergents remain in the apparatus was performed. With each charge of fluid, the complete apparatus was washed with water at least three times.

The correlation between the rotational speed of the impeller and flow velocity in the center of the flow duct and over the cross section of the flow canal for the investigated soybean oil is given in Fig. 4(a). The flow velocity is directly dependent on the viscosity of the fluid used and varies according to the bath temperature. If the construction rules for the convection apparatus are observed, the reference graph shown in Fig. 4(b) can be used for fluids with sensitive viscosities as a first approximation.

3. The Rewetting Process

During immersion cooling in vaporizable fluids, such as vegetable oils, the heat transfer coefficient changes its value by more than one order of magnitude, due to the sequence of the three known stages of cooling: vapor blanket stage (or film boiling stage), nucleate boiling, and convective heat transfer (Ref 22, 23). To illustrate the three cooling stages, a photo sequence of the quenched sample was taken during the immersion cooling process. The direct influence of some physical and chemical parameters of the fluid and the probe material on the rewetting process are given in Ref 12.

Immediately after immersion of the probe into the tested fluid, a vapor film (its stability is quenchant dependent) forms around the entire sample surface. Heat transfer from the cylinder surface into the surrounding fluid is very low because of the high thermal resistance of the vapor film. The surface temperature, at which the vapor film breaks down and wetting occurs, is the so called Leidenfrost temperature (TL). An ascending wetting front results in different wetting temperatures along the length of the probe (Ref 1, 13, 14, 23). The subsequent nucleate boiling stage is the region exhibiting the highest heat transfer rates during immersion cooling. After the surface temperature reaches the boiling temperature of the quenchant, nucleate boiling stops and convective heat transfer starts. Heat transfer during this cooling stage is mainly influenced by free and forced convection and is comparatively low.

Figure 5 shows a typical example of the rewetting process during quenching in vegetable oil (partially hydrogenated winterized soybean oil).

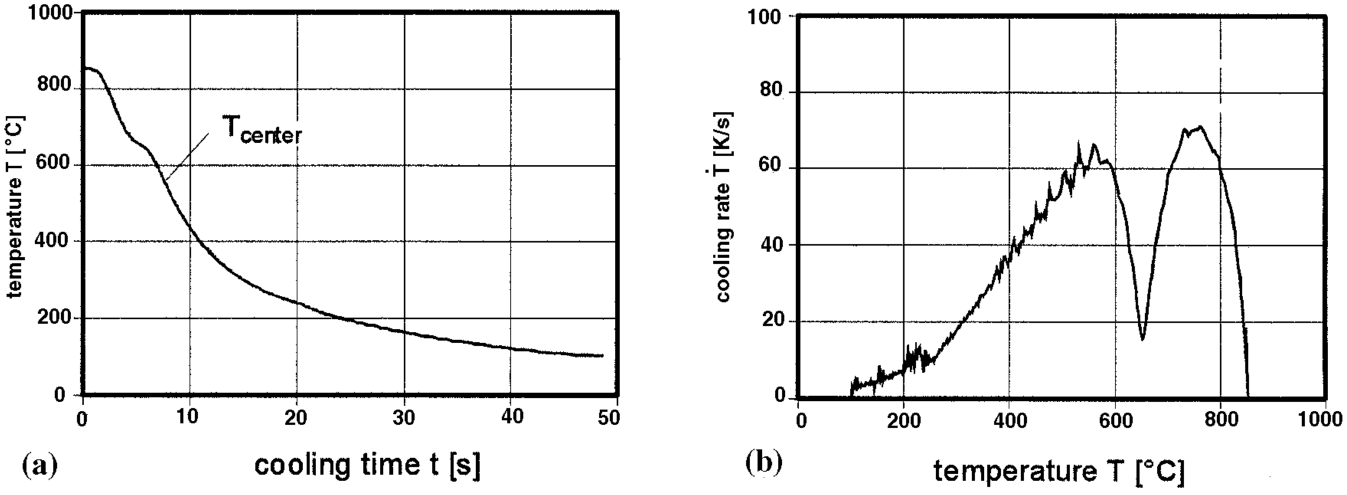

Fig. 7 Measured (a) temperature-time curve and (b)calculated cooling rate at the sample center during immersion cooling of a Ck 45 probe in partially hydrogenated soybean oil at 40 °C and an agitation rate of 0.3 m/s

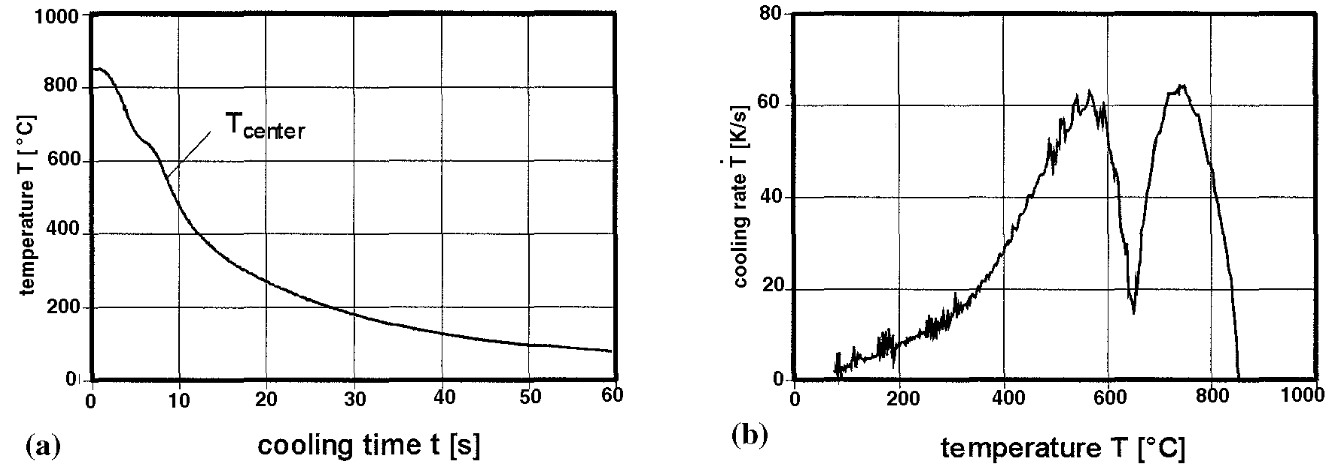

Fig. 8 Measured (a) temperature-time curve and (b)calculated cooling rate at the sample center during immersion cooling of a Ck 45 probe in crude expelled soybean oil at 40 °C and an agitation rate of 0.3 m/s

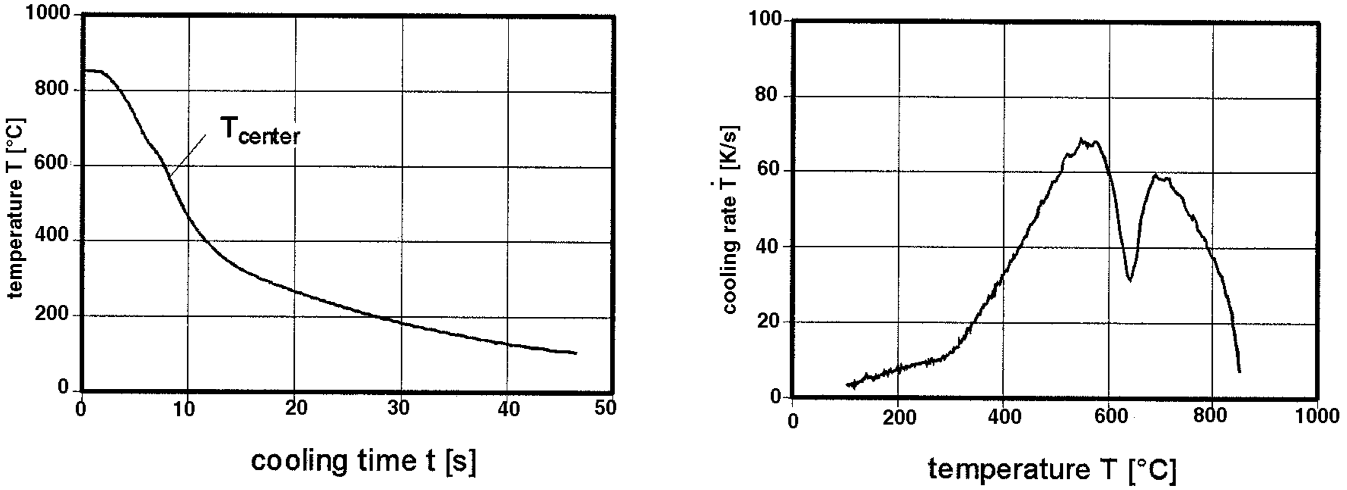

Fig. 9 Measured (a) temperature-time curve and (b)calculated cooling rate at the sample center during immersion cooling of a Ck 45 probe in mineral oil at 40 °C and an agitation rate of 0.3 m/s

During immersion cooling in vegetable oils, the three periods of heat transfer, with strongly varying heat transfer coefficients, are simultaneously present on the sample surface for a significant period of time (see Fig. 5). The wetting process is described by the time when wetting starts, t_s, and the time when wetting is finished, t_f, as shown in Fig. 6. In this case, the cooling of the sample is primarily affected by the time interval of wetting, t_w (time interval of simultaneous presence of film boiling and nucleate boiling, $t_w = (t_f - t_s)$). As a result, the cooling and therefore, the microstructure and surface hardness exhibit large local variations.

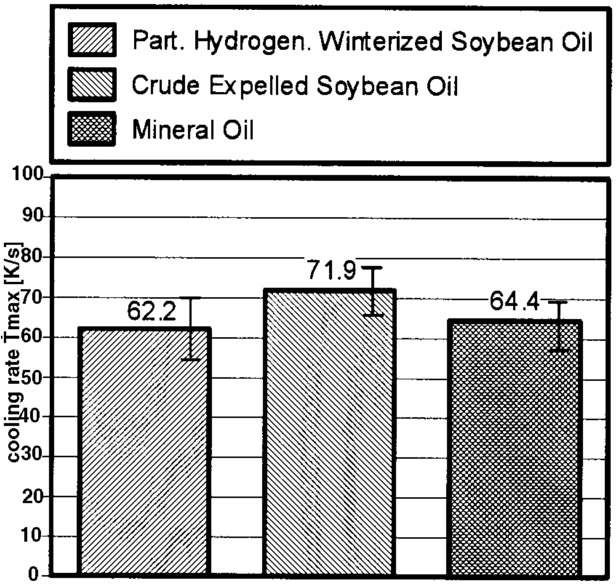

Fig. 10 Maximum cooling rate in the sample center during immersion cooling in different hardening oils at 40 °C and an agitation rate of 0.3 m/s. Tested material: Ck 45

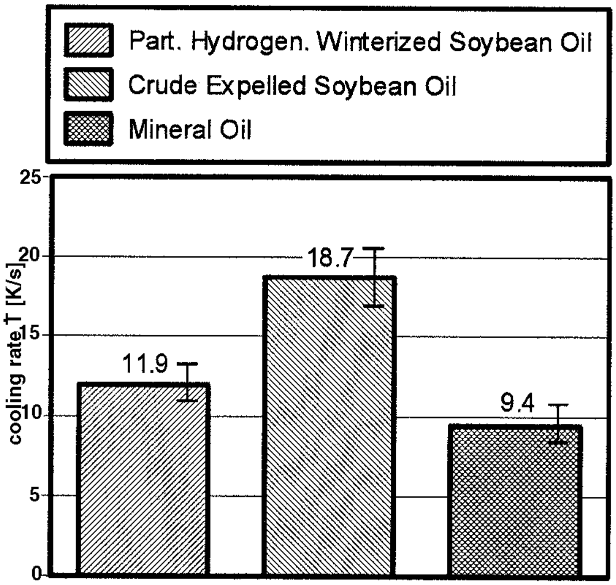

Fig. 11 Cooling rate in the sample center at 300 °C during immersion cooling in different hardening oils at 40 °C and an agitation rate of 0.3 m/s. Tested material: Ck 45

4. Cooling Curve Analysis

The performance of three different hardening oils, partially hydrogenated winterized, crude expelled soybean oil, and a standard mineral oil, are compared by a cooling curve analysis. The resultant cooling curves show different cooling characteristics at the same cooling conditions. The tested material is Ck 45 with an initial temperature of 850 °C. The bath temperature is 40 °C with an agitation rate of 0.3 m/s. The recorded temperature-time curve at the sample center is primarily influenced by the rewetting process on the sample surface (see Fig. 7, 8, and 9). The cooling rates increase after the wetting front passes the thermocouple location and the vapor film phase changes to nucleate boiling phase. Figure 10 shows the maximum cooling rates of the three tested quenchants. The differences between the tested products are within 15%. The values of cooling rates decrease with increasing cooling time. At a center temperature of 300 °C, the cooling rate of the two soybean oils has similar values (9.4 to 11.9 K/s). These values are distinguished from the corresponding value of the mineral oil of ~8.05 to 18.7 K/s values of mineral oil. The significant differences between the tested products are visible (Fig. 11). Figure 12 shows the cooling time to achieve a desired sample temperature of 600, 400, and 200 °C.

5. Surface Hardness Distribution

Figures 13 to 15 show the hardness distribution on the sample surface in a lateral direction for a steel specimen made of Ck 45 (AISI 1040) quenched in two different soybean oils and in mineral hardening oil. Between the two soybean oils only small differences in the hardness distribution can be seen. This effect

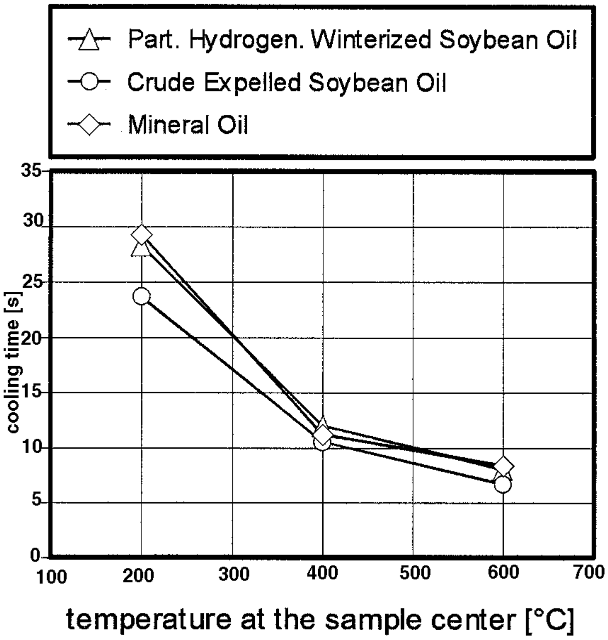

Fig. 12 Times to cooling down from 850 °C to 600, 400, and 200 °C at the sample center during immersion cooling in different hardening oils at 40 °C and an agitation rate of 0.3 m/s.

is caused by the low variations in wetting process on the surfaces of the sample during the immersion cooling process. The rewetting begins at the lower sample end, and the wetting front arises in an upward direction. A short time later a second wetting front starts from the upper end face. This fact results in higher hardness values on both sample ends (see the hardness diagrams for both vegetable oils in Fig. 13 and 14). The maxima of the lateral hardness values are caused by the brevity of the wetting time (depending on the points of the beginning of the rewetting process). Near the middle of the sample length the hardness values decrease to a minimum because of the length of the film boiling phase at this position (compare with Fig. 6). The two tested soybean oils show good reproducibility in their final hardness distribution.

The tested mineral oil shows only small differences in hardness distribution compared to the two vegetable oils because of almost the same rewetting process on the surface of the specimen. The maximum hardness occurs at the lower end of the probe. That means that no stable film boiling phase is present on the surface of the sample for a significant time.

6. Conclusions

In this study, a standard mineral oil, which has been in industrial use for many years, and two new biodegradable vegetable oils were evaluated. The vegetable oils were partially hydrogenated and winterized and crude expelled soybean oils. The tests were performed according to a modified ISO 9950 testing procedure using an agitation of 0.3 m/s and an austenitic steel probe made from X 6 CrNi 18 10 alloy instead of INCONEL 600. The use of an austenitic steel shows a lot of advantages for a multiple useful quenching probe (Ref 19). The operation with agitation corresponded to the industrial use of these quenching media. Because of the strong influence of the surface of the specimen on the wetting behavior (and therefore on the quenching behavior), additional unalloyed hardenable steel probes (Ck 45) were used. This shows simultaneously the metallurgical transformation in martensite, local differences, and dependencies on the rewetting time (and additionally dependencies on the metallurgical steel condition).

Cooling curve analyses showed that immersion quenching was primarily influenced by the sequence of the cooling phases and different heat transfer rates. Heat transfer on the specimen surface was primarily determined by the rewetting conditions and depended on the cooling characteristic of the quenching medium used, bath temperatures, and agitation rates.

The two soybean oils investigated showed no significant differences in cooling behavior. The rewetting conditions on the sample surface and the cooling rates were similar. A comparison of the time-temperature curve and cooling rate of min-

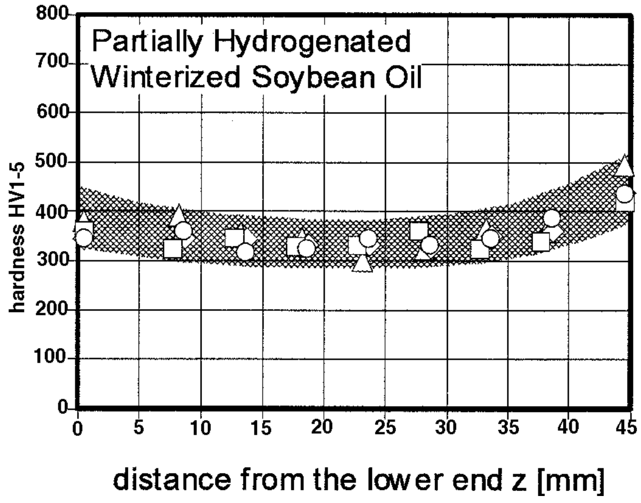

Fig. 13 Hardness distribution on the sample surface in lateral direction as result of an immersion cooling process of Ck 45 (AISI 1045) material in partially hydrogenated winterized soybean oil with 40 °C and 0.3 m/s agitation rate

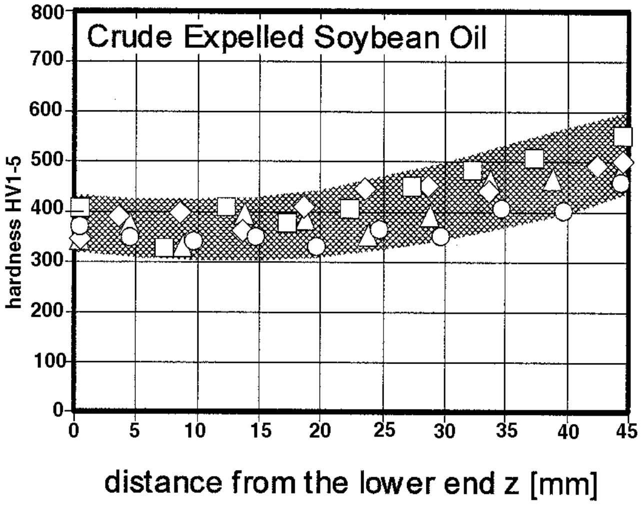

Fig. 14 Hardness distribution on the sample surface in lateral direction as result of an immersion cooling process of Ck 45 (AISI 1045) material in crude expelled soybean oil with 40 °C and 0.3 m/s agitation rate

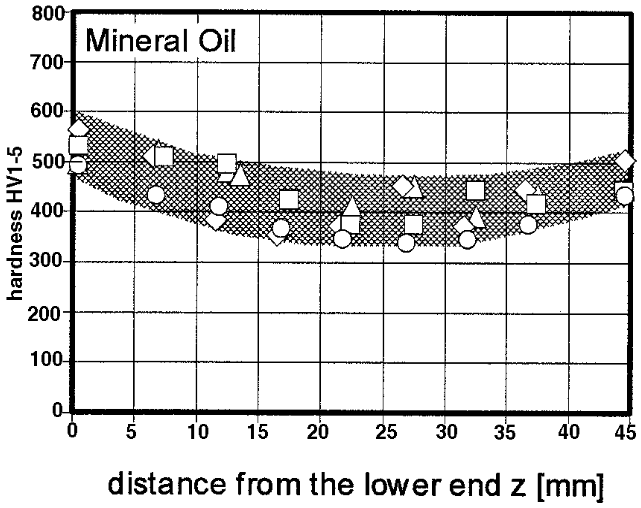

Fig. 15 Hardness distribution on the sample surface in lateral direction as result of an immersion cooling process of Ck 45 (AISI 1045) material in mineral oil with 40 °C and 0.3 m/s agitation rate

eral oil and vegetable oil were within tolerable limits. The cooling characteristics of vegetable oils was faster than that of the mineral oil used. The tests were conducted under laboratory conditions, and therefore no statement can be made about longterm stability.

In this study, the potential of the use of vegetable oils as alternatives to mineral oils was established for industrial heat treating processes. Further research is necessary to characterize a number of different vegetable oils such as canola and rapseed oils under the described modified standard cooling conditions. In addition, further work is necessary to evaluate comparative oxidation stability, sludge and stain forming tendency, and flash point stability.

Acknowledgments

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