

Effect of Antioxidants and Corrosion Inhibitor Additives on the Quenching Performance of Soybean Oil

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Cooling curve analysis was used to evaluate the effect of corrosion inhibitor additives and antioxidants on the quenching properties of soybean oil. The results showed that addition of corrosion inhibitors provided significant changes in the cooling curve behavior and of the yellow metal corrosion inhibitors evaluated tolyltriazole exhibits the greatest rate acceleration of heat transfer. However, the presence of antioxidants did not exhibit a significant effect on quenching properties of soybean oil.

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0 INTRODUCTION

There is an increasing interest in the use of vegetable oils as renewable, biodegradable and non-toxic alternatives to petroleum oil-based quenchants for the heat treating industry. One of the first commercial references to the use of vegetable oil as a metal quenchant was a patent issued to Bardt in 1932 [1]. This was followed by extensive cooling curve analysis studies of rapeseed oil, a common vegetable oil used in Europe for industrial oil formulation, and many other quenching media by Rose in 1940 using a 20 mm silver probe with the thermocouple at the geometric center [2]. Cooling curve results showed that rapeseed oil exhibited heat transfer coefficients for rapeseed oil were 1744 to 2093 W/(m²°C) in the film boiling region, 2907 to 3489 W/(m²°C) in the nucleate boiling region and 465 to 698 W/(m²°C) in the convective cooling region versus 698 to 1395 W/(m²°C) for film boiling, 2326 to 3489 W/(m²°C) nucleate boiling and 232 to 581 W/(m²°C) for convective cooling for a so-called petroleum "heavy oil" quenchant. The higher cooling rates for the rapeseed oil were attributed to the relatively poor stability of the vapor blanket formed by the rapeseed oil [2].

Tagaya and Tamura compared the quench severity of different vegetable oils including soybean, rapeseed and castor oils with mineral oils and other fish and animal oils with respect to viscosity and oxidative stability for various naturally derived fluids [3]. These data showed

that although the Grossman quench severity factors were comparable for both castor oil ($H = 0.199$) and soybean oil ($H = 0.2$), the cooling times from 700 to 300°C were significantly faster for castor oil (1.8 seconds) than for soybean oil (1.42 seconds) using a JIS K 2242 silver probe test which utilizes a 10 mm dia x 30 mm cylindrical silver probe with a surface thermocouple.

Fujimura and Sato [4], also using the JIS K 2242 experimental cooling curve analysis procedure, examined the quenching performance of the vegetable oils reported by Tagaya and Tamura [3], castor oil, and ethyl esters of oleic, palmitic and stearic acid. The quenching properties were compared to different petroleum oil quenchants and it was concluded that the performance of soybean oil and rapeseed oil were essentially equivalent [4]. Quenching performance of the ethyl esters were also equivalent to each other and exhibited greater quench severity than the vegetable oils. Castor oil, however, was found to be thermally unstable and unsuitable for use as a quenchant. This finding was verified by Farah, et. al. [5].

Currently, the most commonly cited vegetable oil basestocks used for quenchant formulation in the USA are based on canola oil [6] and [7], and soybean oil [8]. Totten et. al. reported the results of cooling curve analysis, hardenability measurements, heat transfer, and wettability characterization studies conducted with crude and partially hydrogenated and

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winterized soybean oils [10] provided by Honary [9]. Because of the strong influence of the test specimen surface on the wetting behavior (and therefore on the quenching behavior), unalloyed hardenable (Ck 45) steel probes were used. This work provided a simultaneous examination of the martensitic transformation with local differences, and dependencies on the rewetting time (and dependencies on the metallurgical condition of the steel). Cooling curve analyses showed that heat transfer on the specimen surface was primarily determined by the rewetting conditions and depended on the quenching medium, bath temperatures, and agitation rates. The soybean oils showed no significant differences in cooling behavior and the rewetting conditions on the test specimen surface and the cooling rates were similar. Comparison of the cooling time-temperature and cooling rate curves showed that the vegetable oils exhibited faster cooling rates than the mineral oil used as a reference.

Although the overall quenching performances of various vegetable oils have been reported, there are no reports describing the effect of the addition of additives on the quenching performance of any vegetable oil. Like petroleum oil quenchants [11], the addition of additives is necessary to provide inhibition of oxidative degradation [12], corrosion protection, etc. to assure commercially feasible use. The use of additives in vegetable oils is even more necessary than with petroleum oils because of their molecular double bond unsaturation which renders them much more oxidatively unstable leading to oxidation by-products that accelerate corrosion and the formation of resinous sludge [13].

Petroleum oils also contain cooling rate accelerator additives that destabilize the vapor film that is typically formed around a metal surface upon initial immersion [14]. There have been various reports regarding the effect of such quench oil additives (quenching process accelerators) on the cooling properties of petroleum oil [15] and [16]. Although vegetable oils do not exhibit film boiling or nucleate boiling as shown in Fig. 1 (vegetable oils do not "boil" under atmospheric pressure conditions), additives may still adsorb to the surface of metals thus potentially affecting their cooling performance by cooling rate acceleration or reduction because of the thermal conductance properties of these

residual films. This would be especially important if additives used for vegetable oil oxidative stabilization (antioxidants) or corrosion protection (corrosion inhibitors) were to degrade or be removed due to additive deposition on the quenched material by a drag-out process which may potentially result in deleterious cooling rate effects over the lifetime of use.

Fig. 2 is a schematic illustration of surface film protection by smaller aromatic molecules such as benzotriazole and tolyltriazole where chemisorption occurs through an azole nitrogen resulting in a protective film formed from a precipitated insoluble metal complex [17] and [18]. This was shown by Poling using reflection infra-red spectroscopic characterization of benzotriazole (BTA) films on copper metal surfaces formed from hydrocarbon solutions. Chadwick and Hashemi showed that Cu_2O is formed first on the copper surface followed by Cu(I) surface complexation with BTA to form Cu-BTA and that the presence of Cu_2O films and its disproportionation are a necessary condition for the formation of thick protective films [25]. Protective film thicknesses on the order of 90 to 250 Å were reported to be formed by chemisorption [18].

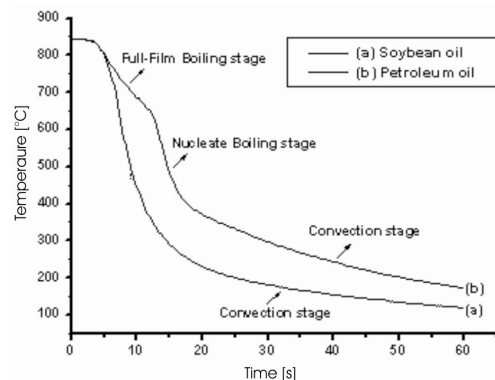


Fig. 1. Comparative illustration of the different cooling mechanisms exhibited by petroleum oil and a vegetable oil

The mechanism of film growth involved precipitation of copper ions as highly insoluble Cu-BTA complexes at the copper (solid)/hydrocarbon solution (liquid) interface.

Some corrosion inhibitors possess a long chain hydrocarbon "tail" and a more polar "head" such as N-oleylsarcosine illustrated in Fig. 3a. Salensky, et. al. examined the adsorption

conformation of protective films formed by such inhibitors using a combination of reflectance

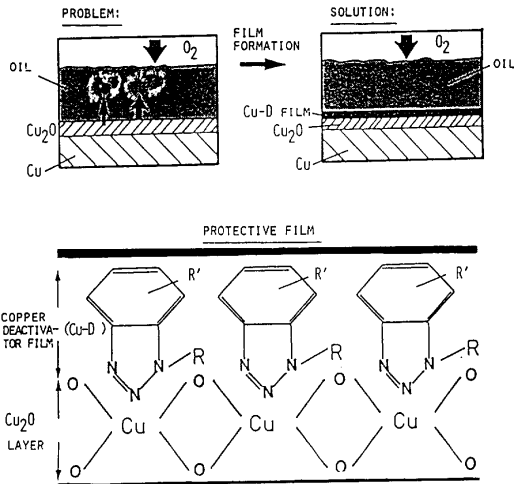


Fig. 2. Schematic illustration of an adsorption mechanism for a copper corrosion inhibitor on a metal surface

Fourier transform infra-red (FTIR) spectroscopy, ellipsometry and ESCA (electron spectroscopy for chemical analysis – also referred to as x-ray photoelectron spectroscopy or XPS) [20]. N-oleylsarcosine was shown to form surface protective films by an adsorbed orientation such as that illustrated in Fig. 3a [20]. Typically, when the concentration is very low, adsorption of the corrosion inhibitor would be insufficient to form a monolayer and corrosion would still occur. As the concentration increases, packing of the molecules will occur at the metal-oil interface until a monolayer is formed.

Luo, et. al. used a contact angle goniometer, FTIR spectroscopy and uv/visible spectroscopy to show that as the concentration of the inhibitor increases, the hydrocarbon chain will become increasingly vertical relative to the metal surface which will promote greater packing of the inhibitor at the interface making it more impenetrable to the corrosion promoting species [21]. For C-18 carbon chains, the monolayer film thickness was found to be approximately 18 Å [20]. As the concentration of the corrosion inhibitor increases, multiple monolayers (a self-assembled monolayer) mechanism will produce greater film thicknesses and further improvement of protective films that are formed as illustrated in Fig. 3b [22]. The self-assembled monolayers (protective film) prevent rust and corrosion by

inhibiting water and oxygen permeation thus inhibiting exposure of metal surface to the corrosive environment. Examples of corrosion inhibitors that such adsorbed films formations are lanolin and sorbitan monostearate. However, non-hydrocarbon chain-type corrosion inhibitors such as 2-mercaptobenzothiazole, a corrosion inhibitor used in this work, have also been reported to form protective films by similar self-assembled monolayers [27].

The other common additive in quench oils, whether a vegetable oil or a petroleum oil is the antioxidant. Antioxidants typically contain aromatic functionality and, in some cases, hydrocarbon chain modification. The functional group that produces antioxidant behavior, is commonly an -OH or -NH- group although other groups may be used such as sulfide -S- or phosphonate. Surface adsorption to metals is not particularly effective since the polar functional group that produces antioxidant behavior is typically sterically hindered.

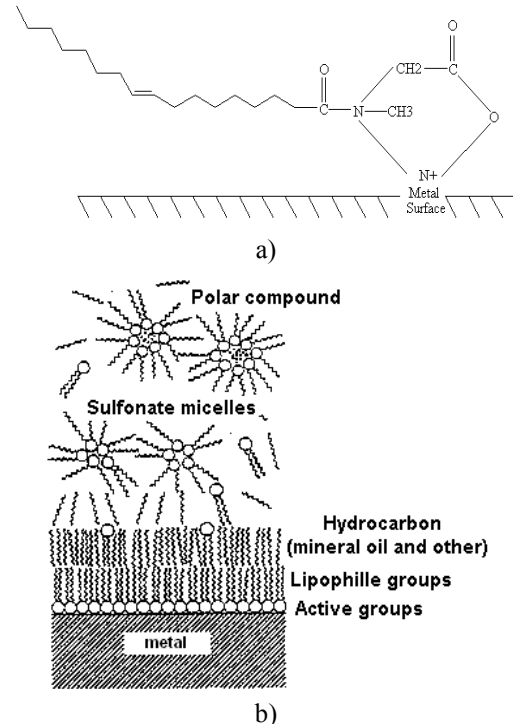


Fig. 3. a) Schematic illustration of the surface adsorption of N-oleylsarcosine on a ferrous surface [20], b) Schematic illustration of self-assembled monolayers formed at higher corrosion inhibitor concentrations than those illustrated in Figure 3a [22]

Therefore, since surface chemisorption is common, at least for corrosion inhibitors that would be typically encountered in industrial oil formulations such as metal quenchants, and since the presence of the chemisorbed films would be expected to affect heat transfer from the metal to the oil at the metal interface, cooling curve analysis was performed to investigate this effect. Also, cooling curve analysis was also performed to verify that the presence of antioxidants in vegetable oil would not be expected to impart a significant, if any, effect on quenching performance. The results of this work are reported here.

1 EXPERIMENTAL

The vegetable oil that was used as a basestock for the quenching studies was commercially available soybean oil which was purchased at a local market. This oil was used for the experimental work described herein without further processing or purification.

The general effectiveness of the corrosion inhibitors was determined by potentiodynamic polarization measurements with data interpretation by the Tafel extrapolation method. Corrosion measurements were conducted using solution of 0.3% by weight of each corrosion inhibitor and 3.5% (wt.%) sodium chloride in water at room temperature, $25 \pm 1^\circ\text{C}$. The electrochemical cell consists of brass metal as the working electrode, saturated calomel electrode (SCE - $\text{Hg}/\text{Hg}_2\text{Cl}_2$) as reference electrode and a platinum foil counter electrode. Before the scan was initiated, the metallic samples were allowed to remain in the solution containing different additives for open circuit potential (OCP) during 1 h. A potential scan rate of 1 mV/s was used. The range of potential utilized in the corrosion tests – 250 mV vs. Saturated calomel Electrode (SCE) up to the pitting potential (E_{pitt}). The electrochemical tests were performed in a potentiostat/galvanostat (VoltaLab) model 402 instrument. The polarization curves were plotted as a logarithmic function of current density ($\log I$, mA/cm^2) versus potential (E , mV). Anodic and cathodic Tafel slopes were used to calculate the corrosion rate using the linear polarization method software Voltmaster 4. The brass test specimens were polished from 80 to 1200 mesh in sequence using sandpaper, chromium oxide and portfolio diamond. Surfaces become bright and

free from any visible blemishes. After polishing, the test specimens were rinsed with ethanol and dried in warm air. Exposed area to corrosion tests was 1.65 cm^2 .

The antioxidants used for this work were Irganox L57 (butylated/octylated diphenylamine) and L109 (an aromatic hydroxy ester-Hexamethylene bis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate] which were used as supplied by Ciba Geigy Corporation at 1.0% by weight in the soybean oil.

A corrosion inhibitor is a chemical compound that, when added to a fluid, decreases the corrosion rate of a metal or an alloy. The corrosion inhibitors used for this work were obtained from Aldrich-Sigma and include: aminothiazole (reported to be a corrosion inhibitor for zinc [23]), 2-mercaptobenzothiazole, 2-mercaptobenzimidazole, 5,6-dimethylbenzimidazole, and tolyltriazole as shown in Table 1. These corrosion inhibitors are similar to those reported earlier by Akada and Fujii [22].

Cooling curves were obtained according ASTM D6200 "Standard Test Method for Determination of Cooling Characteristics of Quench Oils by Cooling Curve Analysis". ASTM D6200 utilizes a 12.5 mm dia x 60 mm INCONEL 600 cylindrical probe with a Type K thermocouple inserted to the geometric center. After heating the probe in a furnace to 850°C , it was then manually and rapidly immersed into 2000 mL of the vegetable oil at 40°C which was contained in a tall-form stainless steel beaker. The data acquisition rate was at 5 Hz. The probe temperature and cooling times are recorded at selected time intervals to establish a cooling temperature versus time curve. From the cooling temperature-time and cooling rate curves, the following critical parameters were determined:

- Cooling rate [$^\circ\text{C}/\text{s}$] at 700°C (CR_{700})
- Maximum cooling rate [$^\circ\text{C}/\text{s}$] (CR_{max})
- Temperature of the maximum cooling rate [$^\circ\text{C}$] (TCR_{max})
- Cooling rate [$^\circ\text{C}/\text{s}$] at 300°C (CR_{300})
- Time to cool to 300°C (t_{300})
- Cooling rate [$^\circ\text{C}/\text{s}$] at 200°C (CR_{200})
- Time to cool to 200°C (t_{200}).

Cooling rate at 700°C is measured since it is usually desirable to maximize this cooling rate to avoid the steel pearlite transformation region. Generally, it would be desirable to maximize TCR_{max} and minimize TCR_{max} . The rates of

cooling at temperatures such as 200 and 300°C ($t_{200^\circ\text{C}}$ and $t_{300^\circ\text{C}}$ is the necessary cooling time to the metal probe to reach 200 and 300°C, respectively) are also determined since they are related to the potential for steel cracking and distortion. To minimize these problems, it is desirable to minimize cooling rates in this region.

Table 1. Corrosion inhibitors used for soybean oil addition at 0.3% by weight

Inhibitor	Used Primarily for Corrosion Protection of:
2-Aminothiazole	Zinc alloys
2-Mercaptobenzothiazole	Yellow metals*
2-Mercaptobenzimidazole	Yellow metals*
5,6-dimethylbenzimidazole	Yellow metals*
Tolyltriazole	Yellow metals*

* Yellow metals typically include copper and alloys of copper including brass and bronze.

2 RESULTS AND DISCUSSION

2.1 Corrosion Results

Corrosion inhibition properties were determined from potentiodynamic polarization curves of brass in the presence of sodium chloride solution with different corrosion inhibitors. When the electrochemical potential increases to values in excess of the corrosion potential (E_{corr}), the current density increases up to the passive region (E_{pass}) where there is little change with further potential increase. This is the point where pitting is observed. This is indicated by the large increase in current density.

Curve (a) in Fig. 4 shows the behavior of brass when exposed to a highly corrosive solution of sodium chloride without any corrosion inhibitor. When the anodic process starts, corrosion begins and spreads easily due to absence of a protective layer. Curves b, c, d, e in Fig. 4 illustrate the inhibitory effect toward brass of the various corrosion inhibitors evaluated in the saline solution. In all cases, there is a small range of potential, designated as the passivation potential, where the metal is protected by the additive which increases the electrolyte resistance, which decreases the corrosion process until the protective film is destroyed.

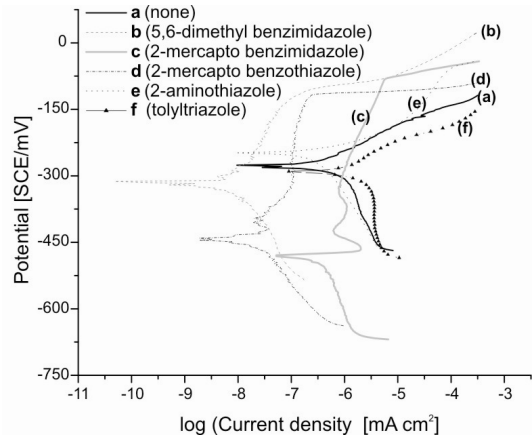


Fig. 4. Anodic and cathodic polarization curves for brass in 3.5% NaCl solution at different corrosion inhibitors

The parameters calculated by Tafel extrapolation and pitting corrosion for brass are shown in Table 2.

The corrosion current (I_{corr}) and corrosion rate are proportionately related. These data indicate that the order of effectiveness of the corrosion inhibitors evaluated toward brass follow the order of:

(best) 5,6-dimethylbenzimidazole (b) > 2-mercaptobenzothiazole (d) > 2-aminothiazole (e) > 2-mercaptobenzimidazole (c) > tolyltriazole (f) > none (worst) (a).

Table 2. Corrosion parameters from analysis of Tafel plots: E_{corr} , I_{corr} and corrosion rate values for corrosion inhibitors on brass

Corrosion Inhibitors	E_{corr} [mV]	I_{corr} [$\mu\text{A}/\text{cm}^2$]	corrosion rate [$\mu\text{m}/\text{year}$]
None	- 284	0.674	8.32
5,6-dimethylbenzimidazole	- 326	0.081	0.10
2-mercaptobenzimidazole	- 501	0.446	5.51
2-mercaptobenzothiazole	- 457	0.316	3.91
2-aminothiazole	- 261	0.394	4.87
tolyltriazole	-298	0.803	6.06

Although this particular comparison of the relative inhibitory properties of these inhibitors has not been performed previously, there have been some relevant comparisons. For example, Chadwick and Hashemi studied the adsorption of benzotriazole (BTA) on copper and its alloys, including a 70:30 brass alloy by electron spectroscopy [25]. Although the mechanism of protective film formation was proposed to be generally the same as illustrated in Fig. 2, the brass alloy exhibited preferential complexation with zinc relative to copper. Therefore, corrosion protection on brass is a more complex process than protection of copper since zinc is incorporated into the films.

The work described here utilizes tolyltriazole (TTZ) whereas many literature references relating to surface film formation are actually based on BTA. Loo, et. al. compared relative surface adsorption of TTZ and BTA using surface enhanced Raman spectroscopy [26]. It was found that fractional coverage on copper surfaces was dependent on the concentration of TTZ and BTA. The adsorption equilibrium constant for TTZ was found to be approximately 3 times that of BTA which means that TTZ is more strongly adsorbed on copper than is BTA which explains why TTZ is often more commonly used for industrial oil formulations.

Surface film formation of 2-mercaptobenzothiazole (MBT) and 2-mercaptobenzimidazole (MBIA) have been compared and both MBT and MBIA on Cu. Surface films of stoichiometric complexes of Cu-MBT or Cu₂-MBIA [28] were identified which are analogous to those reported for BTA [18].

Benzimidazole corrosion inhibition of brass has been examined by Mamaş, et. al. using electrochemical polarization and solution analysis and it was shown that although solution dezincification of brass is inhibited by the formation of ZnO, copper corrosion is increased [29]. This effect is seen even at low concentrations. Given the similarity of TTZ, it is not surprising that it is not an especially good inhibitor for brass and the relative propensity to promote surface dezincification at least partially explains the relative order of the corrosion inhibitors in the series evaluated here.

2.2 Cooling Curve Analysis - Antioxidant Effects

Cooling temperature-time and cooling rate curves for soybean oil with no additives and soybean oil containing 1% of Irganox L57 and Irganox L109 are shown in Fig. 5. Concentrations of antioxidants in vegetable oils depend on the industrial application and may range from parts per million (ppm) to as high as 3 to 5% by weight. Typically, antioxidant concentrations in vegetable oils used in industrial oil applications such as lubricants and quenchants are approximately in the 1 to 5% range [24]. For the work reported here, an unoptimized antioxidant concentration of 1% was selected as being representative of a "typical" concentration.

Table 3 provides the cooling parameters for these experimental quench oils. The data shows that although the presence of either L57 or L109 does provide some cooling rate acceleration relative to soybean oil containing no additive, the

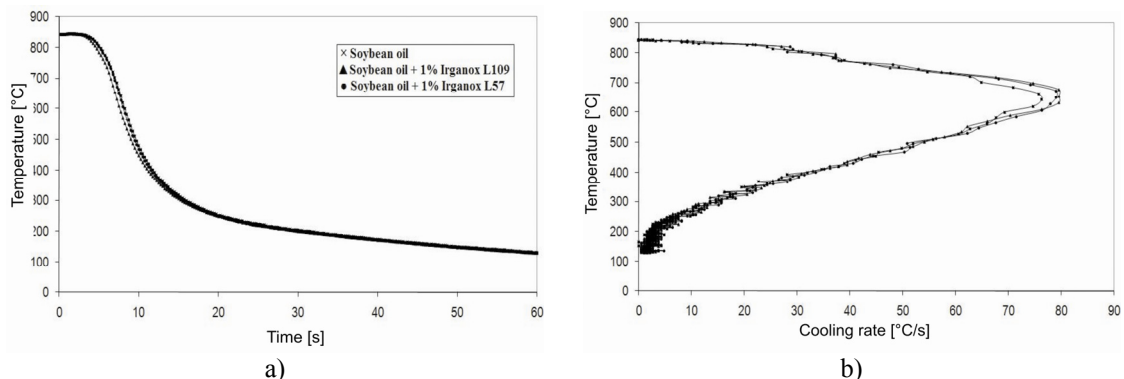


Fig. 5. Cooling temperature-time curves a) and cooling rate curves, b) for Soybean oil containing no antioxidant and 1% of Irganox L57 (butylated/octylated diphenylamine) and 1% Irganox L109 (hexamethylene bis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate])

overall effect is small the variation of these results is within the stated repeatability of ASTM D6200 cooling curve analysis procedure. Therefore, it is concluded that the presence of these antioxidants does not exhibit any significant on quenching properties.

Table 3. Effect of antioxidants on cooling curve performance

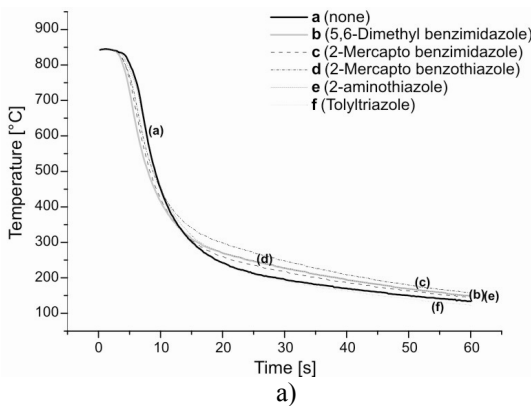
Cooling parameter	Soybean Oil		
	None	Irganox L-57 1.0%	Irganox L-109 1.0%
C_{Rmax} [°C/s]	76.3	79.5	79.0
TCR_{max} [°C]	642	676.3	671.1
C_{R700} [°C/s]	65.0	74.7	74.1
C_{R300} [°C/s]	14.6	15.7	13.5
C_{R200} [°C/s]	2.2	3.2	3.2
$t_{300°C}$ [s]	16.0	15.3	15.8
$t_{200°C}$ [s]	31.5	30.0	30.5

Obtained by ASTM D6200 at a quench bath temperature of 40°C and with no agitation.

2.3. Cooling Curve Analysis – Corrosion Inhibitor Effects

The effect of various additives commonly classified as yellow-metal inhibitors on ASTM D6200 cooling properties is illustrated in Fig. 6 and the cooling parameters are tabulated in Table 4. According to Fig. 6 it is possible to note that the presence of corrosion inhibitors affects the cooling property of pure soybean oil, hence the cooling curves in Fig. 6 are displayed in a different position.

In the Fig. 6a shows that upon immersion (near 850°C) soybean oil containing no corrosion inhibitors and soybean oil with corrosion



inhibitors exhibit the same ability to remove heat from the metal probe, however, as the cooling process progresses the soybean oil containing no corrosion inhibitors is cooled faster than soybean oil with corrosion inhibitors. Its can be seen in Fig. 6b, that with decreasing temperature of the probe the cooling rate of soybean oil containing no corrosion inhibitors increases and remains higher than soybean oil with additives throughout the cooling process.

These results can be explained by the mechanism of the surface chemisorption of the corrosion inhibitors (Fig. 2). At higher temperatures, the presence of this film exhibits a cooling rate accelerating effect relative to soybean oil with no additive, below approximately 400°C the presence of the chemisorbed film exhibits a cooling rate inhibiting effect does significantly affect overall cooling performance of soybean oil (Fig. 6a).

Table 4. The values of cooling parameters for corrosion inhibitors to brass

Cooling parameter	Soybean Oil					
	a*	b*	c*	d*	e*	f*
C_{Rmax} [°C/s]	108.4	83	81.5	88.3	82.8	77.6
TCR_{max} [°C]	649.1	625.5	695.9	679	644.7	649
C_{R700} [°C/s]	98.7	70.05	81.67	86.74	73.53	63.83
C_{R300} [°C/s]	20.2	12.9	6.4	7.9	9.4	15.2
C_{R200} [°C/s]	4.7	2.0	3.4	3.4	2.62	2.2
$t_{300°C}$ [s]	15.06	15.97	15.56	19.84	16.45	14.75
$t_{200°C}$ [s]	28.30	38.45	35.52	42.43	38.2	27.25

Obtained by ASTM D6200 at a quench bath temperature of 40°C and with no agitation.

* (a = none; b = 5,6-dimethyl benzimidazole; c = 2-mercapto benzimidazole; d = 2-mercapto benzothiazole; e = 2-aminothiazole; f = tolyltriazole)

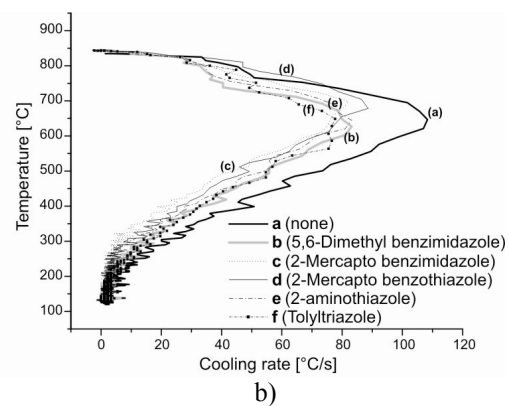


Fig. 6. a) Cooling temperature-time curves and b) cooling rate curves for soybean oil containing yellow metal corrosion inhibitors

The magnitude of the effect of corrosion inhibitors on the quenching properties of soybean oil is expected due to the chemical structure, thickness and the temperature-dependent adsorption of these additives at the cooling metal interface. Studies are underway to delineate these affects.

3 CONCLUSIONS

Potentiodynamic polarization experiments were performed to evaluate the relative corrosion protection of various well-known and commercially available yellow metal corrosion inhibitors toward brass was evaluated. The order of effectiveness of the corrosion inhibitors evaluated was:

(best) 5,6-dimethylbenzimidazole > 2-mercaptobenzothiazole > 2-aminothiazole > 2-mercaptobenzimidazole > tolyltriazole > (worst) none.

It is known that vegetable oils require the use of corrosion inhibitors, such as those reported here, when formulating industrial oils such as quenchants. Cooling curve analysis was performed to examine the impact of the presence of this series of corrosion inhibitors in soybean oil. Not surprisingly, the presence of these corrosion inhibitors does affect the cooling curve performance. The fact that there is an affect is not surprising in view of the chemisorption mechanism that is expected for this class of chemical compositions. From the corrosion inhibitors evaluated in this study, tolyltriazole has the least overall affect on quenching performance, which is consistent with the fact that it exhibited the poorest corrosion inhibitor effect of the additives studied. These data indicate that the concentration of the corrosion inhibitor used in vegetable oil formulations must be monitored with time since quenching performance would be expected to vary due to depletion of the inhibitor on the parts being quenched by an additive drag-out process.

This is the first study that has been reported describing the effect of corrosion inhibitors on vegetable oil quenching performance. Similarly, fundamental corrosion inhibitor performance coupled with quenching performance has not been reported previously for either petroleum oil or vegetable oils. Work is currently in progress to correlate corrosion

inhibitor protective film structure and thickness with quenching performance.

The effect of the presence of two illustrative antioxidants, IRGANOX L-57 and IRGANOX L-109 that are currently promoted commercially for the use in formulating vegetable oil-based industrial oils was also studied by cooling curve analysis. The results of this work indicate that although the presence of either L57 or L109 does provide some cooling rate acceleration relative to soybean oil containing no additive, the overall effect is, as expected, small and not particularly significant.

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