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Effect of Corrosion Ingibitors on Cooling Curve Behavior of Soybean Oil-Based Quenchants

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The relative inhibitory effect of a series of common yellow-metal (brass) corrosion inhibitors was studied potentiodynamically in a saline solution. The results of this study showed that all of the corrosion inhibitors examined could potentially exhibit substantial cooling time and rate reduction. The magnitude of this effect was corrosion inhibitor specific. Corrosion and cooling curve supporting data are provided.

Utjecaj korozijskih inhibitora na krivulje ohlađivanja sredstva za kaljenje na bazi sojinog ulja

Izvornoznanstveni članak

Relativni inhibitorski efekt niza korozijskih inhibitora obojenih metala (bronca) istraživani su potencijo-dinamički u solnim kupkama. Rezultati istraživanja pokazali su da svi ispitani korozijski inhibitori mogu utjecati na vrijeme ohlađivanja i smanjenje brzine ohlađivanja. Veličina tih efekata ovisila je o pojedinom korozijskom inhibitoru. Prikazani su podaci za koroziju kao i utjecaji na krivulje ohlađivanja.

1. Introduction

The first commercial reference to the use of vegetable oil as a metal quenchant was the use of linseed oil by Bardt in 1932 [1]. This work was followed by cooling curve analysis of rapeseed oil by Rose in 1940 [2], Tagaya and Tamura [3] and Fujimora and Sato [4]. Farah, et. al. compared the quenching performance of soybean oil with castor oil, another common vegetable oil [5]. Currently, the most commonly cited vegetable oil basestocks used for quenchant formulation in the USA are based on canola oil [6,7], and soybean oil [8]. Totten, et. al. reported quenching performance, including hardenability, heat transfer, and rewettability characterization studies, of crude and partially hydrogenated and winterized soybean oils [9] provided by Honary [10]. Typically, owing to the very high boiling points of vegetable oils, they do not exhibit film boiling or nucleate boiling heat transfer. Instead, heat transfer is dominated by convective cooling.

Although the overall quenching performance of various vegetable oils have been reported, there are no reports describing the effect of the addition of additives such as the necessary addition of corrosion inhibitors on cooling performance. The higher acid number and molecular unsaturation of vegetable oils greater oxidative instability leading by-products cause corrosion and the formation of resinous sludges [11].

Corrosion inhibitors used in vegetable oil-based quenchant formulation would typically involve a surface chemisorption process. Surface film protection by smaller aromatic molecules such as benzotriazole and tolyltriazole occurs by chemisorption through an azole nitrogen resulting in a protective film formed from a precipitated insoluble metal complex [12,13]. Poling reported that benzotriazole, for example, produced protective films on copper surfaces from hydrocarbon solutions with film thicknesses of 90Å - 250Å [13]. Furthermore, these chemisorbed films would be expected to affect heat transfer at the boundary between the hot metal and the vegetable oil.

Symbols/Oznake

E_{pitt}	- pitting potential - potencijal
E	- potential - potencijal
I	- current density - gustoća toka struje
E_{corr}	- corrosion potential - korozivni potencijal
E_{pass}	- passive region - pasivno područje
I_{corr}	- corrosion current density - gustoća toka struje korozije
C_{Rmax}	- maximal cooling rate - maksimalna brzina ohlađivanja
TC_{Rmax}	- temperature of maximal cooling rate - temperatura maksimalne brzina ohlađivanja
C_{R300}	- cooling rate at 300 °C - brzina ohlađivanja na 300 °C
$t_{300°C}$	- the time to cool to 300 °C - vrijeme ohlađivanja na 300 °C

Exploratory work was performed on soybean oil containing corrosion inhibitors commonly used for yellow metal corrosion inhibition and their effect on quenching performance as indicated by the cooling curve analysis. The results of this work are reported here

2. Experimental

Soybean oil was purchased at a local market in São Carlos, SP, Brazil. This oil was used without further processing or purification. The corrosion inhibitors included: 2-aminothiazole, 2-mercaptobenzothiazole, 2-mercaptobenzimidazole, 5,6-dimethylbenzimidazole and tolyltriazole were purchased from Aldrich-Sigma. Solution of 0.1 % by weight of each corrosion inhibitor with the soybean oil were prepared for both corrosion inhibitor studies and cooling curve analysis.

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 a solution of 0.3 % by weight of each corrosion inhibitor and 3.5 % (wt. %) sodium chloride in water at room temperature, 25 ± 1 ºC. The electrochemical cell consists of brass metal as the working electrode, saturated calomel electrode (SCE - Hg/Hg_2Cl_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^{-1} was used. The range of potential utilized in the corrosion tests was -250 mV *vs*. SCE up to the pitting potential (E_{pitt}).

The electrochemical tests were performed in a potentiostat/galvanostat (VoltaLab) model 402. 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 voltamaster 4. The brass test specimens were polished from 80 mesh 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.

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 day x 60 mm INCONEL 600 cylindrical probe with a type K thermocouple inserted in 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 unagitated soybean oil formulation 40 °C which was contained in a tall-form stainless steel beaker. The data acquisition rate was at 5Hz. The probe temperature and cooling times are recorded at selected time intervals to establish a cooling temperature versus time curve.

3. Results and Discussion

3.1. Electrochemical corrosion test results

Figure 1 shows the 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 will 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 Figure 1 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 the absence of a protective layer. Curves b, c, d, e in Figure 1 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 an additive which increases electrolyte resistance thus decreaseing the corrosion process until the protective film is destroyed.

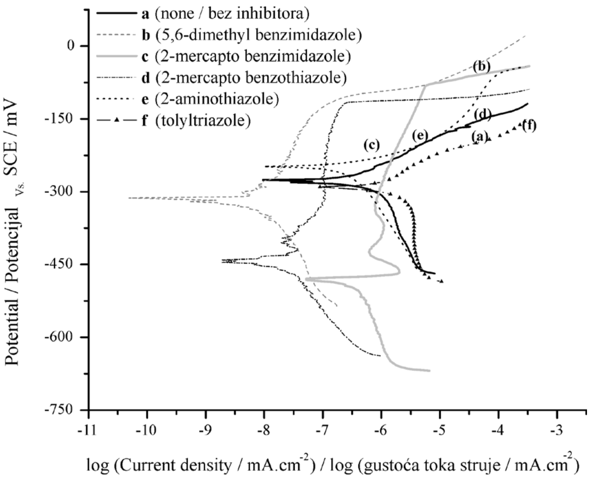

Figure 1. Anodic and cathodic polarization curves for brass in 3.5 % NaCl solution at different corrosion inhibitors

Slika 1. Krivulja anodne i katodne polarizacije za broncu u 3.5 % otopini NaCl za različite korozijske inhibitore

The parameters calculated by Tafel extrapolation and pitting corrosion for brass are shown in Table 1. 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-dimethyl benzimidazole (b) > 2-aminothiazole (e) > 2-mercaptobenzimidazole (c) > tolyltriazole (f) > none (a) > (worst) 2- mercaptobenzothiazole (d)

Table 1. Corrosion parameters from analysis of Tafel plots: E_{corr}, I_{corr} and corrosion rate values.

Tablica 1. Parametri korozije dobiveni analizom Tafelove krivulje: E_{corr}, I_{corr} i veličine brzine korozije

Reference in Figure 1 / Krivulja na slici 1	E_{corr}, mV	I_{corr}, $\mu A/cm^2$	corrosion rate / brzina korozije, μm/year
(a)	- 284	0.674	8.32
(b)	- 326	0.081	0.10
(c)	- 501	0.446	5.51
(d)	- 457	18.260	225.0
(e)	- 261	0.394	4.87
(f)	-298	0.803	6.06

3.2. Cooling curve results

The effect of various additives commonly classified as yellow-metal inhibitors on ASTM D6200 cooling properties is illustrated by the data shown in Table 2. These data show that upon initial immersion, cooling rates for the soybean oil containing these additives are generally slower than soybean oil containing no additives. Of those additives evaluated, 5, 6-dimethylbenzimidazole exhibits the greatest rate acceleration effect in this region. The order of maximum cooling rate reduction from the slowest to the fastest was: 2- mercaptobenzothiazole (d) < 2-aminothiazole (e) < 2-mercaptobenzimidazole (c) < tolyltriazole (f) ≈ 5,6-dimethylbenzimidazole (b) < none (a).

The temperature where maximum cooling rate occurred was not substantially affected by the addition of the corrosion inhibitors.

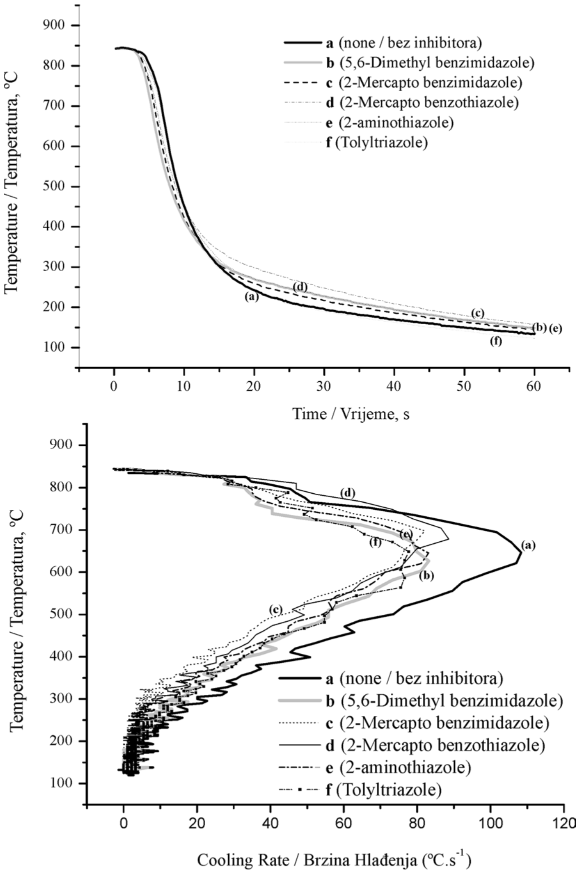

Figure 2. a.) Cooling temperature-time curves and b.) cooling rate curves for soybean oil containing yellow metal inhibitors.

Slika 2. a) Krivulje temperatura ohlađivanja-vrijeme i b) krivulje brzine ohlađivanja za sojino ulje koje sadrži obojene metalne inhibitore

Interestingly, the cooling temperature-time curves shown in Figure 2a illustrate that at approximately 400 °C, there is a general inversion at which point the soybean oil containing no additives is clearly the fastest cooling medium. Below approximately 400 °C, mercaptobenzothiazole exhibits the greatest rate reducing effect. The general order of cooling rate from the slowest to the fastest was: 2- mercaptobenzothiazole (d) < 2-aminothiazole (e) ≈ 5,6-dimethylbenzimidazole (b) < 2-mercaptobenzimidazole (c)< tolyltriazole (f) < none (a).

The time to cool to 300 °C, with the exception of tolyltriazole which was approximately equivalent to soybean oil with no additive, was substantially affected by the presence of the corrosion inhibitor and followed the trend from the longest cooling time to the shortest cooling time of: 2- mercaptobenzothiazole (d) < 2-aminothiazole (e) ≈ 5,6-dimethylbenzimidazole (b) < 2-mercaptobenzimidazole (c) < none (a) ≈ tolyltriazole (f).

These results show that the expected film formation proposed for corrosion inhibitors does significantly affect the overall cooling performance of soybean oil. Presumably this effect is concentration dependent, although this was not examined in this study. Also, more work is required to establish the chemistry of the chemisorbed film and its thickness relative to both the effectiveness of the corrosion inhibition and effects on cooling performance.

Table 2. Cooling curve parameters for soybean oil with various yellow metal inhibitors vs soybean oil with no inhibitors added.

Tablica 2.Parametri krivulje ohlađivanja za sojino ulje s različitim obojenim metalnim inhibitorima u usporedbi sa sojinim uljem bez inhibitora

Cooling Parameter / Parametar hlađenja	(a)	(f)	(b)	(d)	(e)	(c)
C_{Rmax} (ºC/s)	108	78	89	82	83	83
Rel. Change / Rel. promjena	1.0	0.72	0.82	0.76	0.77	0.77
TC_{Rmax} (ºC)	647	649	678	698	645	627
Rel. Change / Rel. promjena	1.0	1.0	1.05	1.08	0.99	0.97
C_{R300} (ºC/s)	20.18	14.67	8.39	5.44	9.76	12.62
Rel. Change / Rel. promjena	1.0	0.73	0.42	0.27	0.48	0.62
$t_{300ºC}$ (s)	15.06	14.75	16.00	19.98	16.08	15.46
Rel. Change / Rel. promjena	1.0	0.98	1.06	1.33	1.07	1.03

4. Conclusions

The relative inhibitory effect of a series of common yellow-metal (brass) corrosion inhibitors was studied potentiodynamically in a saline solution. The effect of this same series of corrosion inhibitors formulated in soybean oil on cooling curve performance was determined under nonagitated conditions using ASTM D6200 test procedure. The results of this study showed that all of the corrosion inhibitors examined could potentially exhibit substantial cooling time and rate reduction. The magnitude of this effect was corrosion inhibitor specific. Further work is required to define the nature (structure and thickness) of the films formed on the metal surface and to relate this data to the cooling rate effects observed.

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