Electrochemical methods for the study of corrosion in lubricant additive systems

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Potentiodynamic polarization has been used to study the corrosion behaviours of mild steel and copper in solutions containing some examples of common types of lubricant additives. A variety of conditions for performing of experiments were investigated. The best results were obtained in a background solution of 0.01 M tetra-*n*-butylammonium perchlorate in 1:1 toluene/ethanol. The behaviour of the aforementioned metals was characterized and compared in solutions containing allyl amine, alkyl phosphite, and organic sulfides. For most solutions, corrosion and pitting potentials and corrosion rates of each metal were found to vary with the compound's concentration. Changes in the corrosivity of chemicals towards metals were monitored as a corrosion inhibitor was added to their solutions. The relative corrosion behaviour observed were consistent with the known performance of these metals in contact with lubricants containing these additives.

Keywords: *corrosion, potentiodynamic polarization, lubricants, steel, copper*

1. Introduction

Corrosion is most often associated with aqueous environments. In fact, however, lubricated systems, which usually contain nonpolar, hydrocarbon-based fluids, can also be subject to corrosion under certain circumstances. For example, corrosion occurs in gears and bearings where only a thin film of lubricant separates the metal pieces. The locally high temperatures and pressures of these systems produce chemical species that attack the metal surfaces [1]. Water, which often occurs as a contaminant in used lubricants, can also contribute to corrosive attack on metals [2]. For these reasons, corrosion inhibitors of various sorts are added to many lubricants.

The relative efficacy of corrosion inhibitors can be evaluated by a variety of methods. The American Society of Testing and Materials (ASTM) has a number of standard test methods specifically designed to examine the corrosivity of lubricants and other hydrocarbon materials [3]. For example, ASTM D-130 detects the corrosiveness to copper of products ranging from gasolines to lubricating oils and ASTM D-1743 determines greases' corrosion prevention properties. Many of these methods have been in use for years and can reliably provide qualitative and/or quantitative information on the corrosiveness of materials or the effectiveness of corrosion inhibitors. However, they often require several hours and specialized apparatus to perform and often rely on somewhat subjective rating techniques based on the discoloration of metal coupons. In addition, they usually do not provide any information about the mechanism of corrosion.

The science of lubricant formulation often involves balancing the surface activities and corrosivities of additive chemicals. It is not unusual to encounter situations in which a particular compound provides protection to one type of metal while, simultaneously, corrosively attacking another. Therefore, means of examining and studying surface activity and corrosion processes in lubricants, and evaluating the relative corrosivity or inhibition ability of lubricant additives, could provide lubricant formulators with knowledge that would help them more effectively design lubricants to prevent or minimize corrosion in mechanical systems while still providing adequate protection.

Electrochemical techniques [4] are ideally suited for studying corrosion in solutions. In recent years, these techniques have been extended to the study of corrosion in nonaqueous systems. Moran *et al.* [5–10] have investigated the behaviour of iron and various types of steels in organic solvent systems containing dimethoxyethane and propylene carbonate. The behaviour of nickel in solutions based on ethanol or acetonitrile [11] and aluminium in methanolic solutions [12] have also been investigated with electrochemical techniques. These techniques have also been used to study the corrosive effects of adding organic compounds to both aqueous and organic solutions [13–16]. As these studies have demonstrated, electrochemistry can be applied quite effectively to the investigation of corrosion behaviours in nonaqueous systems.

The application of electrochemical techniques to the study of corrosion in lubricated systems is complicated not only by low conductivity, but also by the

high temperatures and pressures that can be present in the areas in these systems where corrosion occurs. Although some studies have been performed on the electrochemical reactions of certain lubricant additives at metal surfaces at elevated temperatures [17], the difficulties of duplicating the conditions occurring at surfaces subject to corrosive attack in engines and transmissions, for example, in such a manner that they could be amenable to electrochemical measurements, have presented roadblocks to the use of these techniques for studying corrosion. It is often possible, however, to gain useful knowledge about the behaviour of complicated systems by using simpler systems as models. Therefore, simple solutions of lubricant additives might be substituted for actual lubricants in the study of corrosivity and, on a very simple level, inferences about the corrosion processes in lubricated systems might be made by using electrochemical techniques to study the behaviours of metals in these solutions. In this way, these techniques could allow us to evaluate and compare the behaviours of various additives more quickly and easily than the standard test methods currently used.

As a first step in assessing the feasibility of using electrochemical techniques to study the corrosive behaviour of metals in contact with lubricant additives, a series of experiments were conducted using low-carbon (1018) steel and copper electrodes in contact with solutions of toluene, ethanol, and varying concentrations of electrolytes to identify a suitable background electrolyte system in which to study the corrosion behaviour of these metals. Their behaviours in solutions containing varying concentrations of some common types of lubricant additives were then compared and contrasted.

2. Experimental details

Low-carbon (1018) steel electrodes were cut from a piece of a laboratory testing apparatus supplied by the corporate mechanical engineering section. The electrodes were approximately 10 mm long, 1 mm thick and of varying widths. The section of each electrode that would be immersed in the test solutions was delineated by a horizontal mark across one of the electrode's faces about 1.5–2.0 cm from the lower edge of the electrode. The immersed areas of the steel electrodes ranged from 2.5 to 4.5 cm^2. This range of areas was a result of the irregular shapes of electrodes cut from a piece of formed steel. Prior to each experiment, the electrodes were cleaned by polishing with 100 grit silicon carbide paper until their surfaces were bright and free from any visible blemishes. They were rinsed with deionized water, wiped with a lint-free tissue, and then rinsed with acetone and allowed to air dry. Copper electrodes were cut from a piece of high-purity (99.9%) copper foil (Goodfellow Corp., Berwyn, PA) using a metal shearer and were 150 mm long, approximately 10 mm wide and 0.5 mm thick. Although the copper electrodes were more uniform and rectangular than the steel ones, the areas that were immersed in the test solutions varied between 3.5 and 4.7 cm^2 because the shearer did not allow for tight control of their relative widths. These electrodes were polished with 400 grit silicon carbide paper and rinsed with water and acetone prior to all experiments.

All chemicals were used as received. Background electrolyte solutions were prepared from toluene (reagent grade, J.T. Baker, Phillipsburg, NJ) and ethanol (anhydrous, denatured, EM Science, Gibbstown, NJ). The electrolytes used included tetra-n-butylammonium perchlorate (TBAP, ACROS Organics, Fair Lawn NJ), tetra-n-butylammonium iodide (TBAI), and tetra-n-butylammonium fluoroborate (TBAFB; both from Eastman Kodak, Rochester, NY). Di-t-butyl sulfide (t-BS) was obtained from Aldrich Chemical Co. (Milwaukee, WI). The additive compounds, dialkyl phosphite (DAP), allyl amine (AA), and alkyl polysulfides (PS), were production-grade materials. Although the actual compositions of these materials are proprietary, the samples used were typical of the additives commonly found in commercial lubricants. Additive solutions were prepared on a weight/weight basis in approximately 100 ml of background electrolyte solution.

All experiments were performed with a potentiostat (Model 273A, EG&G Princeton Applied Research Corp., Princeton, NJ) controlled by special corrosion analysis software (model 352 'SoftCorr II', also EG&G Princeton Applied Research Corp.). This software also calculated corrosion rates from the experimental data. A standard, three-electrode arrangement was used. The working electrodes, steel and copper, are described above. An aqueous Ag/AgCl reference electrode and a platinum-mesh auxilliary electrode were used throughout. Potentiodynamic polarization (PDP) was employed to study the metal anodic corrosion behaviour. For steel, a potential range of −0.5 to 1.0 V vs Ag/AgCl was used, while, for copper, the range was −0.25 to 0.55 V vs Ag/AgCl; the scan rate for all experiments was 1 mV s^{-1}. These ranges were chosen based on the typical responses of these metals in the background electrolyte solutions and encompassed potentials from about 200 mV less than the corrosion potential to about 200 mV more than the pitting potential. All potentials are reported as V vs SCE (saturated calomel electrode). The potentiostat was operated in iR compensation mode with an interrupt interval of 48 s. Microscopic inspection and elemental analyses were performed on some electrodes using an Amray (model 1830I) integrated scanning electron microscope/X-ray analysis system (Bedford, MA).

About 100 ml of test solution were poured into a 100 ml, three-neck, round-bottom flask which contained the reference and counter electrodes. No special precautions were taken to isolate the flask and its contents from the atmosphere. A freshly prepared working electrode was inserted into the flask. The solutions were magnetically stirred during all experiments, which were performed inside a Faraday cage

to reduce noise in the signals. All experiments were performed at ambient temperatures (20–25 °C) and pressures. Experiments in each metal/solution system were performed in duplicate.

3. Results and discussion

The background electrolyte solution must solubilize the compounds of interest and provide conductivity without influencing the observed corrosion behaviour of the metal so much that no effect due to the presence of the added compounds can be identified. Since lubricant additives tend to be oil-soluble, a lipophilic solvent is required to dissolve them. However, these types of solvents are often not amenable to dissolving the salts necessary for conductivity. A few of the solvents which fulfilled these requirements, such as acetonitrile, tetrahydrofuran, and 1-methyl-2-pyrrolidinone, were investigated, but were found to either oxidize at potentials too low to be useful for investigations of corrosion behaviours or provided insufficient solvency for a wide range of sample types. Prior electroanalytical experience in these laboratories has shown that mixtures of toluene and ethanol dissolve both typical sample materials and relatively high (>0.5 M) concentrations of the ammonium salts commonly used as supporting electrolytes in non-aqueous systems.

An appropriate combination of toluene, ethanol, and ammonium salt in which to perform electrochemical corrosion experiments was sought.

A large variety of tetra-alkylammonium salts are commercially available. The efficacy of three, the tetra-n-butylammonium salts of perchlorate (TBAP), iodide (TBAI), and fluoroborate (TBAFB), were investigated in this work. The potentiodynamic polarization (PDP) behaviour of steel electrodes in 0.1 M solutions of each salt in a 1:1 mixture of toluene and ethanol were examined. Figure 1 shows a representative PDP scan for steel in each electrolyte solution.

The corrosion potentials (E_{corr}) for these solutions were essentially the same and in each the metal exhibited behavior indicative of the presence of a passive surface layer. These layers were considered to be made up of native oxides and hydroxides, adsorbed or electropolymerized solvent molecules, and/or salt films [18]. The electrodes exposed to TBAP and TBAFB solutions maintained their bright, polished appearances after the PDP scans. The electrode in the TBAI solution, on the other hand, was covered with a dark grey film that was attributed to the formation of FeI_2 as the iron in the steel, exposed to the solution upon the breakdown of the passive film, was oxidized.

The breakdown or pitting potential (E_{pit}) of the passive layer on the electrode increased as the salt was changed from TBAI (274 mV vs SCE) to TBAFB (503 mV vs SCE) and, finally, to TBAP (754 mV vs SCE). The larger range between E_{corr} and E_{pit} in the TBAP solution indicated that stable pits were less likely to form in the presence of this electrolyte than when TBAI or TBAFB were used. Since corrosion by pitting was one of the behaviours of particular interest to us, a background solution which did not promote pitting was preferred. Also, the effects of uncompensated solution resistance, the so-called IR effect, was greater in the solutions containing TBAI and TBAFB, as seen in the sharply rising signals above about 0.5 to 0.6 V vs SCE in their PDP scans. Therefore, TBAP was chosen as the supporting electrolyte for all corrosion experiments.

The effect of varying the electrolyte concentration was also studied. Figure 2 shows typical PDP curves of steel in three different concentrations of TBAP in 1:1 toluene/ethanol. It was desired to find the smallest reasonable concentration of TBAP which still produced acceptable PDP responses without distortion. As illustrated by the curves in Fig. 2, there was relatively little difference in the behaviour observed in either 0.1, 0.05 or 0.01 M TBAP solutions. In fact,
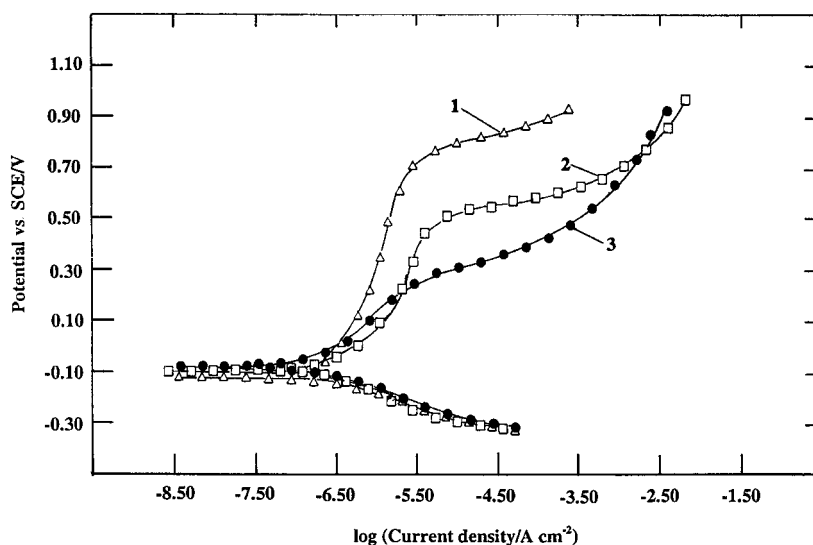

Fig. 1. Potentiodynamic polarization curves for low-C steel in 0.1 M tetra-n-butylammonium (TBA) salt solutions in 1:1 toluene/ethanol: (1) TBA perchlorate; (2) TBA fluoroborate; (3) TBA iodide.
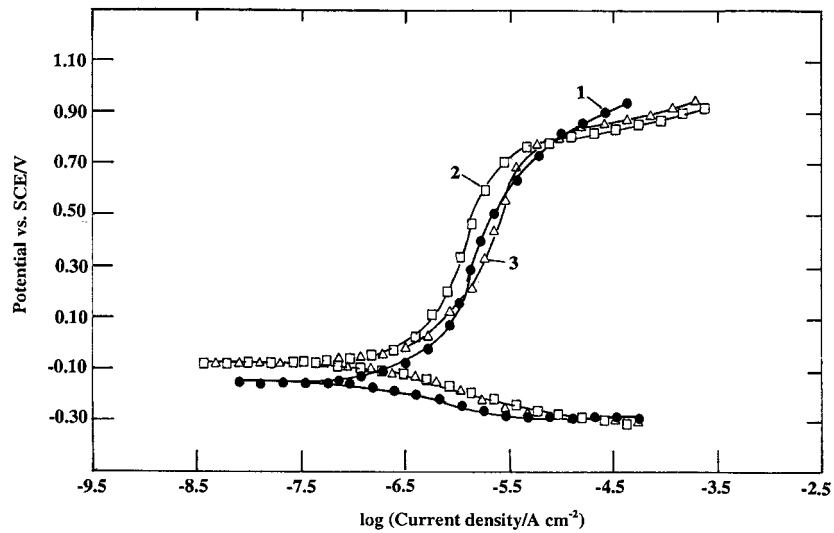
Fig. 2. Potentiodynamic polarization curves for low-C steel in tetra-*n*-butylammonium perchlorate (TBAP) solutions in 1:1 toluene/ethanol; (1) 0.01 M TBAP; (2) 0.05 M TBAP; (3) 0.1 M TBAP.

these curves were quite similar to those reported by Shifler *et al.* [6] for 1018-carbon steel in a solution of 0.5 M TBAP in dimethoxyethane. 0.01 M TBAP was used in the test solutions because it provided adequate conductivity, but did not adversely affect the dissolution of highly non-polar samples, which higher salt concentrations can.

The relative proportions of toluene and ethanol in the background electrolyte solution were also varied. The PDP curves for steel in solutions containing 0.01 M TBAP in 0:1, 1:1, and 2:1 toluene/ethanol mixtures had the same general appearance as those shown in Fig. 2. E_{corr} for all three systems was about −60 mV vs SCE, although E_{pit} for the ethanol-only system, 725 mV vs SCE, was about 40 mV lower than those of steel in either of the toluene-containing solutions. The 1:1 mixture of toluene and ethanol was selected as the solvent of choice for these experiments

because it provided a good compromise between conductivity and solubilizing power.

The corrosion behaviour of copper in solutions containing either TBAFB or TBAP was also studied. However, in TBAFB solutions, copper exhibited an active/passive transition which might have complicated the interpretation of additive effects on the corrosion behavior. This behaviour towards copper, and the desire to use the same background electrolyte solution for both steel and copper PDP experiments in order to make comparisons easier, supported the choice of TBAP as the electrolyte for use in additive-solution experiments. The typical behaviour of copper in the 0.01 M TBAP, 1:1 toluene/ethanol solution is illustrated in Fig. 3. The copper had a much smaller potential range between E_{corr} and E_{pit} and was generally more active in this region than was steel under the same conditions. As with steel, copper
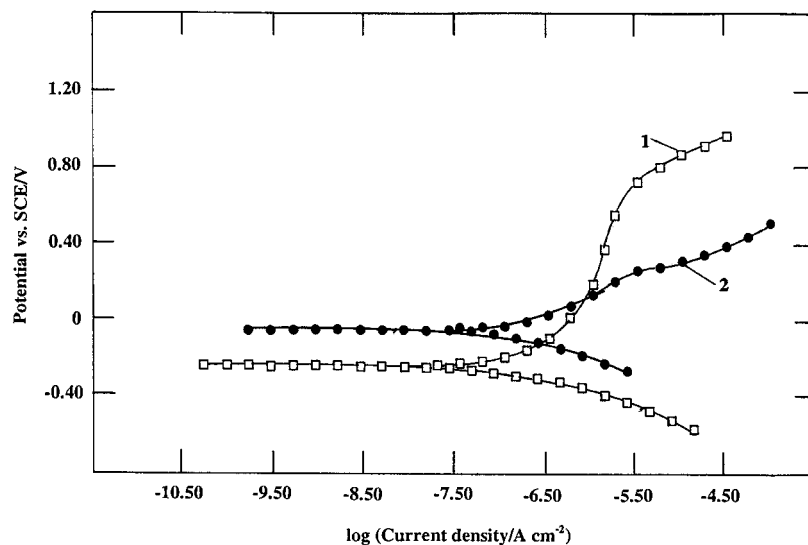

Fig. 3. Potentiodynamic polarization curves of metals in solutions of 0.01 M tetra-*n*-butylammonium perchlorate in 1:1 toluene/ethanol; (1) low-C steel; (2) copper.

potential range was not significantly affected by varying concentrations of TBAP, toluene, or ethanol.

There is a large number of materials added to lubricants to inhibit corrosion in different parts of lubricated mechanisms. For example, allyl amine (AA) is often used to protect so-called 'yellow metals', like brass, which contain relatively large amounts of copper. The changes typically seen in the behaviour of copper in solutions containing as little as 0.5% (w/w) AA are shown in the PDP curves in Figure 4. E_{corr} was essentially unchanged by the presence of AA, but a breakdown in the copper surface film was not observed below 550 mV vs SCE, the upper potential limit of the PDP scan in these solutions. Thus, the copper was somewhat less susceptible to anodic corrosion processes like pitting in the presence of AA and, in fact, its corrosion rate was about 36% smaller in the AA solutions.

In contrast, this compound appeared to be somewhat corrosive to steel. E_{pit} for steel was about 200 mV less in the AA solutions and its corrosion rate was about 2.5 times greater in these solutions than in the background solution alone (Fig. 5). For both copper and steel, the system behaviour was not substantially different when the AA concentration was increased from 1 to 10% (w/w); additional corrosion-rate inhibition due to the presence of more AA was not observed.

Another compound sometimes added to certain lubricants is dialkyl phosphite (DAP). DAP protects iron-containing metal surfaces from wear, but it also is known to exhibit corrosivity towards some other metals. The typical behaviour of copper and steel in solutions containing DAP are shown in Figs 6 and 7, respectively. DAP significantly increased the overall activity of the copper surface. As little as 0.05% (w/w) DAP produced a fivefold increase in the copper corrosion rate and effectively eliminated any native passive film and E_{pit}.

In the case of steel, the addition of DAP not only increased E_{corr} to about 53 mV vs SCE, but also caused the introduction of an active/passive transition into the observed PDP behaviour. At potentials less than 100 mV greater than E_{corr}, the DAP showed considerable corrosivity towards the steel. However, as the potential was raised to above about 200 mV vs SCE, a layer began to form on the electrode which reduced the activity of its surface. This transition became more pronounced as the DAP concentration was increased, although the values of E_{corr} and E_{pit} were not significantly affected. E_{pit}, in fact, was the same as its value in the background solution alone, but the current density at this potential increased with the DAP concentration. Therefore, as the level of DAP increased more corrosive and then passivating reactions occurred at the steel electrode, but the passive film that formed did not alter the electrode surface enough to greatly inhibit the oxidation of the background electrolyte solution.

The contrasting behaviour of copper and steel in AA and DAP solutions illustrate the delicate balance between protecting one type of metal, while possibly exposing another type to attack, that the lubricant designer strives to maintain. An example of this balance is shown in the PDP curves for steel in solutions containing various proportions of these compounds (Fig. 8). When AA and DAP were in equal proportions, the solution was slightly more active towards the steel than the background electrolyte solution alone. However, when the amount of AA was four times more than that of DAP, the steel was more active and its behaviour resembled that shown in Fig. 5 for solutions containing AA alone. Similarly, as the DAP concentration exceeded that of AA, the steel took on the behaviour it had shown in DAP-only solutions, where it was somewhat passivated. The circumstances would be reversed for copper in these solutions: higher AA levels would
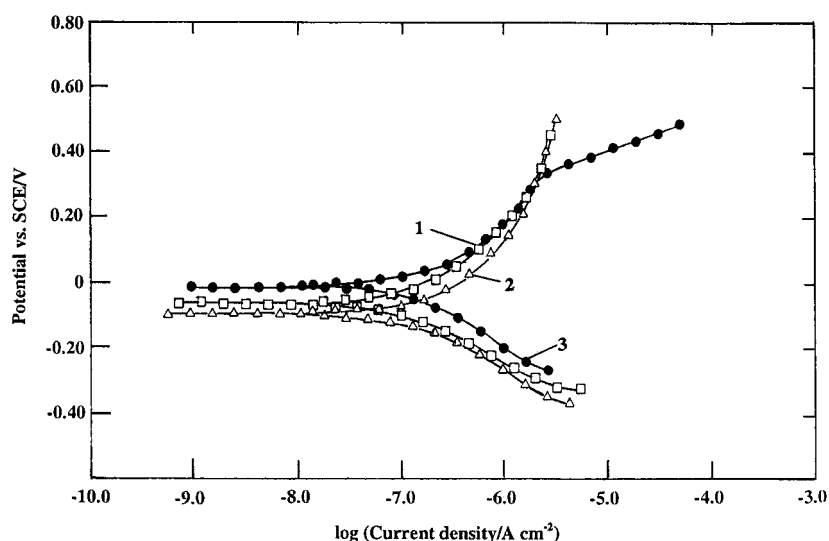

Fig. 4. Potentiodynamic polarization curves of copper in solutions containing allyl amine (AA): (1) 10% (w/w) AA; (2) 5% (w/w) AA; (3) background electrolyte solution only (0.01 M TBAP in 1:1 toluene/ethanol).
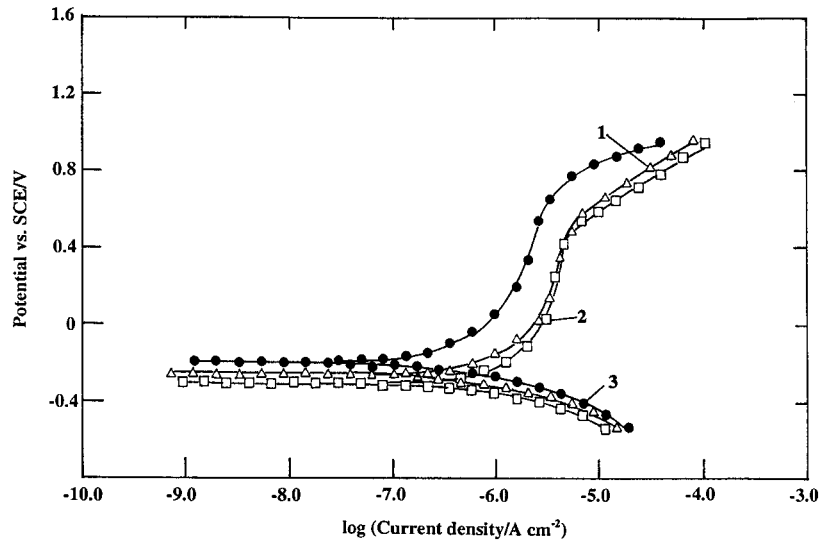
Fig. 5. Potentiodynamic polarization curves of low-C steel in solutions containing allyl amine (AA): (1) 10% (w/w) AA; (2) 5% (w/w) AA; (3) background electrolyte solution only (0.01 M TBAP in 1:1 toluene/ethanol).
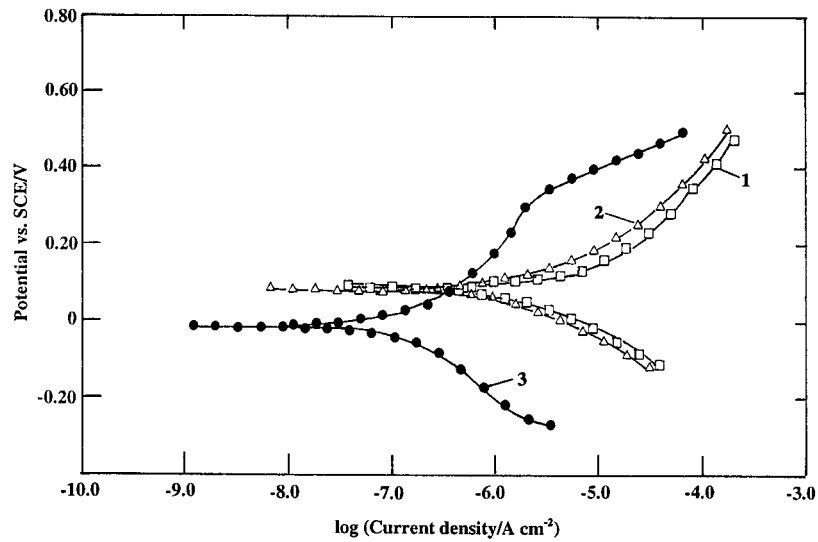

Fig. 6. Potentiodynamic polarization curves of copper in solutions containing dialkyl phosphite (DAP): (1) 0.5% (w/w) DAP; (2) 0.05% (w/w) DAP; (3) background electrolyte solution only (0.01 M TBAP in 1:1 toluene/ethanol).
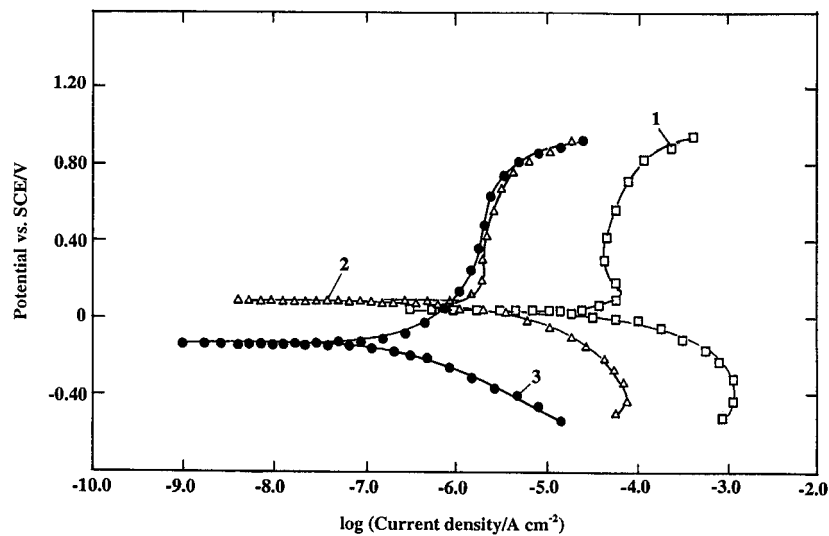

Fig. 7. Potentiodynamic polarization curves of low-C steel in solutions containing dialkyl phosphite (DAP): (1) 0.5% (w/w) DAP; (2) 0.1% (w/w) DAP; (3) background electrolyte solution only (0.01 M TBAP in 1:1 toluene/ethanol).
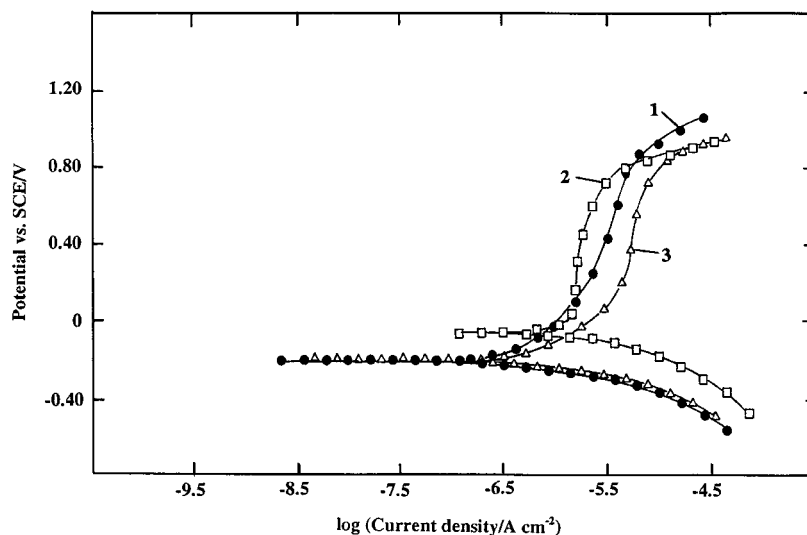
Fig. 8. Potentiodynamic polarization curves of low-C steel in solutions containing dialkyl phosphite (DAP) and oleyl amine (AA): (1) 1:1 DAP:AA; (2) 4.5:1 DAP:AA; (3) 1:4 DAP:AA (All solutions in 0.01 M TBAP in 1:1 toluene/ethanol).

inhibit, while higher DAP levels would promote its corrosion.

The behaviour of steel and copper in solutions containing di-t-butyl sulfide (t-BS), is illustrated in the PDP curves in Figs 9 and 10, respectively. Organic sulfides are added to lubricants to protect iron-containing metals from wear; a lubricant might contain DAP or sulfides, but probably not both. Unlike its behaviour in DAP solutions, E_{corr} of steel increased from about -172 mV vs SCE in the background solution alone to -62 mV vs SCE and 188 mV vs SCE as the amount of t-BS in the solution was increased from 5% (w/w) to 10% (w/w), respectively. E_{pit} was not affected by the presence of t-BS. The steel's corrosion rate decreased about 12.5% as the t-BS concentration increased from 5 to 10% (w/w).

t-BS was similar to DAP in its aggressiveness towards copper. At 5% (w/w) t-BS, the corrosion rate was only about 4% higher than in the background

solution, but E_{pit} had decreased by around 125 mV. When the t-BS concentration was increased to 10% (w/w), a pitting potential was no longer present in the PDP curve and the corrosion rate had increased to 0.25 mm y^{-1}, almost 140 times greater than in the 5% (w/w) solution.

The copper electrodes exposed to solutions containing t-BS or other organic sulfides developed dark surfaces during the PDP experiments. In fact, these discolorations were the only noteworthy ones that occurred in this work. These dark surfaces were attributed to the formation of CuS on the electrodes. Although many of the surfaces were quite dark, analyses by scanning electron microscopy and X-ray microanalysis did not show any significant differences between the portions of the electrodes that had been immersed in the sulfide solutions and those that had not. However, solutions containing as little as 1% (w/w) alkyl polysulfide (PS), a mixture of compounds with polysulfide linkages of ≥2 sulfur atoms, pro-
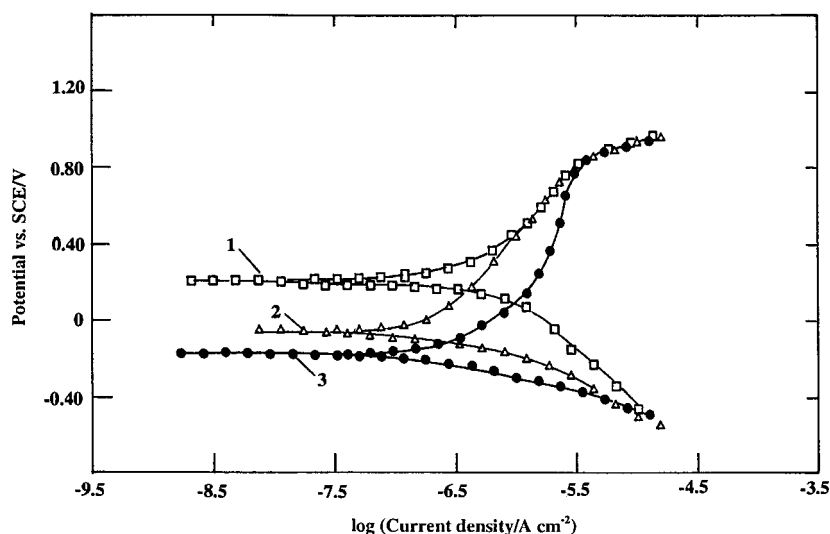

Fig. 9. Potentiodynamic polarization curves of low-C steel in solutions containing di-t-butyl sulfide (t-BS): (1) 10% (w/w) t-BS; (2) 5% (w/w) t-BS; (3) background electrolyte solution only (0.01 M TBAP in 1:1 toluene/ethanol).
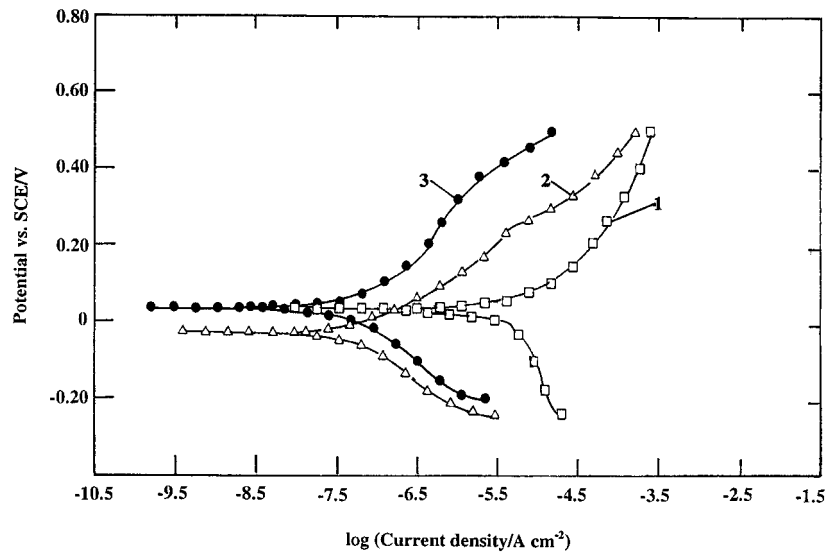
Fig. 10. Potentiodynamic polarization curves of copper in solutions containing di-*t*-butyl sulfide (*t*-BS): (1) 10% (w/w) *t*-BS; (2) 5% (w/w) *t*-BS; (3) background electrolyte solution only (0.01 M TBAP in 1:1 toluene/ethanol).

duced visible thicker films than higher concentrations of *t*-BS, for example, although their PDP curves were very similar to that of the 10% (w/w) *t*-BS solution shown in Fig. 10. Microscopic examination of the dark film on an electrode after a PDP experiment in a 1% (w/w) PS solution showed a definite surface film with many large breaks in it (Fig. 11). Elemental analyses of the coated areas showed significant concentrations of sulfur, while the analyses of the uncoated areas showed only copper (Fig. 12). Thus, the aggressive behaviour of sulfide-containing solutions towards copper was evident in these PDP experiments. Although a surface film was formed, it did not protect the surface from corrosion, but, rather, it was a direct result of the anodic corrosion reaction between the copper electrode and the organic sulfides.

4. Conclusions

Electrochemical corrosion techniques, like PDP, can be used to qualitatively compare the corrosive behaviour of a variety of metals in solutions containing compounds commonly added to lubricants. Although
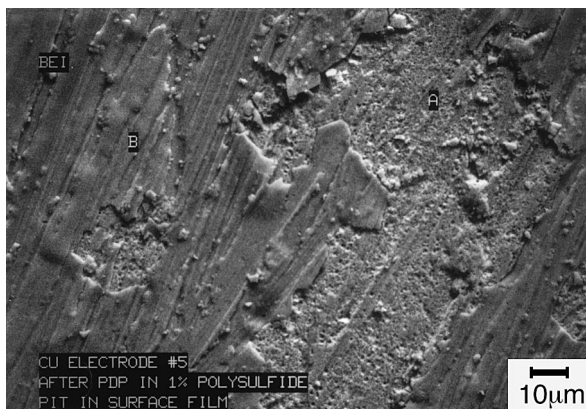
these systems are not representative of the conditions present in operating, lubricated machinery, the results of these types of experiments have been shown to at least qualitatively agree with the known behavior of certain compounds in contact with specific metals. For example, the PDP experiments distinguished compounds which were beneficial and detrimental to both copper and steel and were useful in investigating how these mixtures of these compounds behaved towards both metals. These experiments also showed the effects of different concentrations of additives and might be used to identify concentration ranges wherein they are the most corrosive or provide the

Fig. 11. Micrograph of copper electrode surface after PDP in 1% (w/w) PS in 0.01 M TBAP in 1:1 toluene/ethanol, backscattered electron image.
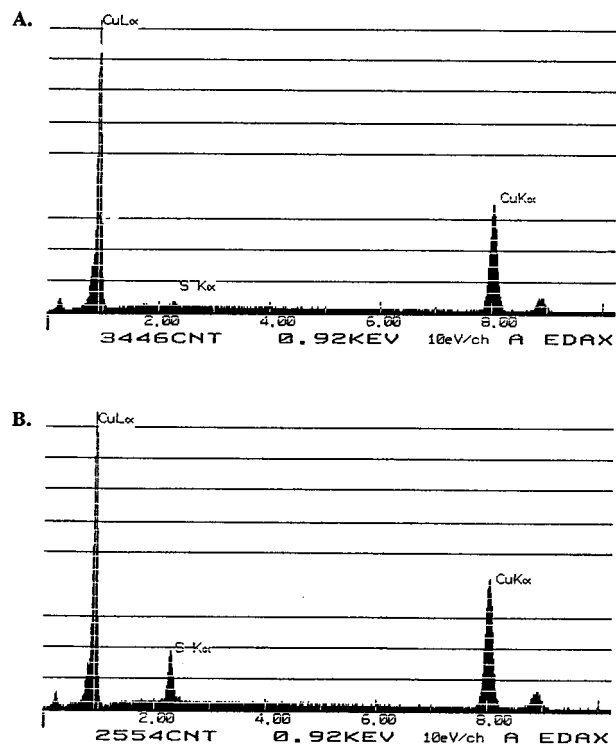

Fig. 12. X-ray microanalysis spectra of copper electrode surface shown in Fig. 11: (A) pit in surface film; (B) surface film.

most corrosion inhibition. It should be noted, how-ever, the lubricants are complicated chemical systems and their performance depends not only on the additives they contain, but also on the conditions to which they are exposed during usage. A reliable correlation between the results of electrochemical corrosion experiments and lubricant performance needs to be established before these techniques can be used as an aid in the development and study of new lubricants.

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