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Corrosion Inhibition of Copper with Potassium Octylhydroxamate

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Abstract

The inhibitive effect of potassium octylhydroxamate (P-OHO) on the corrosion of copper in both acidic and neutral NaCl solutions was investigated by means of corrosion tests, electrochemical polarization and infrared spectroscopy. P-OHO was found to be a good inhibitor in chloride environments. The inhibition efficiency was determined from weight loss measurements by using a "spinner" test assembly. The corrosion rate of copper decreased with increasing P-OHO concentration at concentrations over 0.1 m mol/1 in the neutral solutions. Corrosion tests revealed that the maximum inhibition efficiency was 98% at a concentration of 1 m mol/1 in the solutions of pH 6.0~8.6. The polarization curves indicated that P-OHO was a cathodic inhibitor rather than an anodic one. Reflection-absorption infrared spectra of surface films formed on copper in the NaCl solutions in the presence of P-OHO were identified as Cu^{II}-octylhydroxamate. It was concluded that the inhibition action is mainly due to the formation of adherent films of the Cu-octylhydroxamate complex on the surface of copper and/or copper oxide.

1. Introduction

Surfaces of copper and copper alloys are usually covered with their corrosion products, such as copper oxides, hydroxide, chloride, sulfide, sulfate and carbonate. The surfaces are therefore similar to those of copper minerals. Reactions of collector reagents with the surface of copper oxide minerals in the mineral processing are similar to those of corrosion inhibitors applied on the surfaces of copper and its alloys. The inhibitor reactions include adsorption followed by film formation on copper and/or copper oxide surfaces. By this analogy potassium octylhydroxamate (P–OHO), one of the effective flotation collectors for copper oxide minerals[1], has been applied as a corrosion inhibitor for copper in chloride solutions. There have been little publications on corrosion inhibition of copper from this point of view.

In the present paper, corrosion rates of copper in chloride solutions in the presence and the absence of P–OHO are presented together with data indicating the mode of P–OHO retardation of copper corrosion. Results of electrochemical polarizations and reflection-infrared spectroscopic studies are provided.

Department of Metallurgy

2. Experimental

The chemical formula of potassium octylhydroxamate is shown in Figure 1. Potassium octylhydroxamate was prepared by the procedure reported elsewhere[1]. The copper specimens were milled from 99.8% OFHC copper sheets to the size of $50 \times 20 \times 1$ mm for use as corrosion test specimens.   The surface preparation included mechanical polishing with No 500 SiC paper and rinsing with acetone followed by etching with 6 N HNO_3 for 30 seconds.   Then they were rinsed in distilled water, dried, weighed and fixed to a corrosion test spinner. Corrosion tests were carried out in aerated 3% NaCl solutions in the presence and the absence of the inhibitor at 40°C using the corrosion test spinner at the rotation speed of 125 r. p. m.   The linear velocity at 125 r. p. m. is 0.7265 m/sec.   The spinner accommodates eight pieces of the specimens (Figure 2).   The air was made to bubble through the solutions during the tests.   The specimens were exposed to the NaCl solutions of 4 litre at pH from 2 to 8 for periods up to 1 day or more.   The pH of test solution was adjusted with dilute HCl and NaOH. During exposure the anodic and cathodic polarization curves of copper electrodes were recorded to study the inhibition mechanisms using NICHIA model HP V 100 potentiostat.

These polarization curves were measured by polarizing the specimen stepwisely by 20 mV each for 10 seconds from a corrosion potential at a constant rotating speed of 1000 r. p. m.   Potentials of the copper specimens were measured against a saturated calomel reference electrode.   Infrared multiple reflection-absorption spectra of the films formed on copper specimens were recorded in an attempt to identify the inhibitor film.   A HITACHI model 260-30 infrared spectrophotometer equipped with a multiple reflection accessory IRR-7 was used for this purpose. The inhibition concentration was in a range from 0.1 to 1 m mol/l in NaCl solutions.   Reference Cu^{II}-octylhydroxamate was prepared using analytical reagent grade cupric chloride and potassium octylhydroxamate.

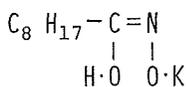$$C_8 H_{17} - C = N$$
$$H \cdot O \quad O \cdot K$$
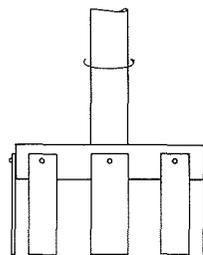
Fig. 1 Potassium octylhydroxamate

Fig. 2 Corrosion Test Spinner

3. Results and Discussion

3.1 Weigt loss corrosion tests

Figure 3 shows that the copper corrosion rate, estimated from the weight loss measurements in the 3% NaCl solution in the absence and the presence of P-OHO, sharply decreased with increasing pH of the solution in the weakly acidic region

and were almost constant in the neutral region.   In the acidic solutions copper dissolution was observed to be accelerated at P–OHO concentration of 0.1 m mol/1 and to produce green precipitates in the solution.   During the corrosion tests the surface oxide on copper dissolved in the solution; it is not stable in acidic solutions at pH below 4.

Thus, the typical protective multifilm structure of $Cu/Cu_2O/Cu$-inhibitor film[2] cannot be established in acidic solutions.   The inhibition efficiency is expressed as $\{(W_0-W_i)/W_0\} \times 100$, where W_i and W_0 are the weight losses in the solution in the presence and the absence of inhibitor, respectively.   It is found that the inhibition efficiency increased with pH of the solution and the concentration of P–OHO, as shown in Figure 4.   At the concentration of 1 m mol/1 P–OHO the inhibition efficiency reached 98% at pH higher than 6, while the maximum inhibition was 40–45% at the concentration of 0.1 m mol/1 at the same level of pH.

Table 1 represents the influence of spinner rotation speed on the inhibition efficiency.   The inhibition efficiency decreased considerably with increasing the rotation speed.   In general copper corrosion is controlled by diffusion of oxygen dissolved in the solution.   The decrease in inhibition efficiency, however, is attributed to a decrease of the oxygen diffusion layer thickness and also to a
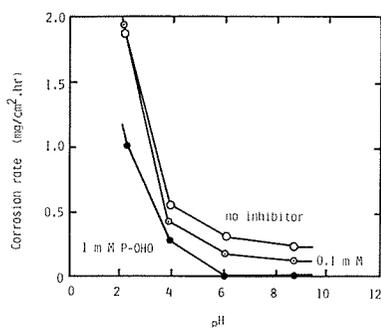
Fig. 3   Effect of the pH of corrosion test solution on copper corrosion rate in aerated 3% NaCl in the presence and absence of P–OHO at 40°C,   Corrosion   test   period: 7 hours
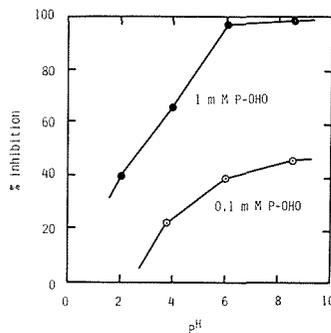
% inhibition $=\{(w_0 - w_i)/w_0\} \times 100$

w_0 : weight loss in aerated 3 % NaCl without inhibitor.

w_i : weight loss in aerated 3 % NaCl with inhibitor.

Fig. 4   Variation of inhibition efficiency with the solution pH at P–OHO concentration of both 0.1 mM and 1 mM

Table 1.   Influence of spinner rotation speed on the inhibition efficiency
Copper Corrosion Test Results

Aerated 3 % NaCl, pH 6.0, at 40°C for 1 day.

Rotating Speed		Weight Loss (mg/cm^2)		% inhibition
(R.P.M.)	(m/sec)	no inhibitor	1 m M P-OHO	
125	0.7265	0.6392	0.0173	97.3
200	1.1624	0.6588	0.1978	70.0
340	1.9761	0.7270	0.3053	58.0

decrease of the protective layer thickness formed on copper.　On the basis of previous work[3] the copper surface was rapidly covered by a thin film of Cu_2O when copper was exposed to air.　The octylhydroxamate ions produce insoluble chelate complex with cuprous and cupric ions in a bulk solution[1].　This insoluble copper complexes may accumulate on the copper surface and inhibit the corrosion process by forming a physical barrier which separates the metal from the corrosive environments.　The rotation speed affects the conditions of copper ion removal from the surface; the greater the rotation speed the thinner the dissolution product film formed on the metal surface, resulting in an acceleration of dissolution process at higher rotation speeds.　The results suggest that the protective layer formed on copper proceeds through "the dissolution-precipitation" mechanism. This mechanism is similar to that of inhibition action of phosphate on iron[4].

　　Table 2 demonstrates the variation of inhibition efficiency with exposure time in the corrosion test.　Surface accumulation of copper complexes is also confirmed by the fact that the inhibition efficiency increases with increasing exposure period of time within several hours in the corrosion test and reached a maximum value of aroud 98%.　This effect would be mainly due to a change in the protective configuration of copper complex films as well as in its thickness by precipitation. During several hours exposure the copper surface became hydrophobic.

Table 2. Variation of inhibition efficiency with exposure period of time

Copper Corrosion Test Results

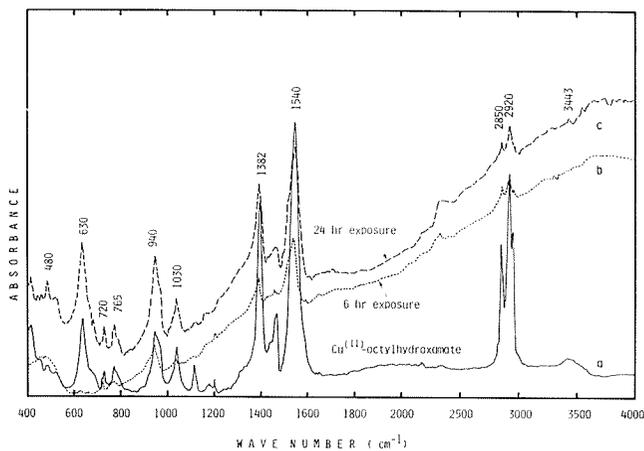Aerated 3 % NaCl, pH 6.0, at 40°C. 125 R.P.M.

	Weight Loss (mg/cm^2)				
Exposure time	3 hrs.	7 hrs.	24 hrs.	48 hrs.	96 hrs.
no inhibitor	0.1246	0.3118	0.6392	0.9900	1.9300
1 m M P-OHO	0.005	0.006	0.017	0.018	0.035
% inhibition	95.9	98.0	97.3	98.2	98.2

3.2　Electrochemical polarization

　　Figure 5 shows the anodic and cathodic polarization curves of copper rotating electrodes at a rotation speed of 1000 r. p. m. for different exposure times in a range from 1 minute to 95 hours in aerated 3% NaCl in the presence of 1 m mol/1 P-OHO at 20°C.　The polarization of the copper electrode was accomplished by applying successively 20 mV potential steps each for 10 sec. to the electrode in the cathodic direction or anodic direction from its corrosion potential E_{corr}.　The E_{corr} of copper was shifted in the cathodic direction in P–OHO inhibited solutions. In the absence of the inhibitor the cathodic current increased sharply with potential and attained a characteristic diffusion current i_d for oxygen reduction reaction in the potential range more cathodic than -0.60 V.　In the preliminary experiments the i_d was found to increase linearly with the root of the rotation speed.　Thus, the process is controlled by diffusion in this potential range.　The cathodic current was found to decrease considerably with an increase of pre-
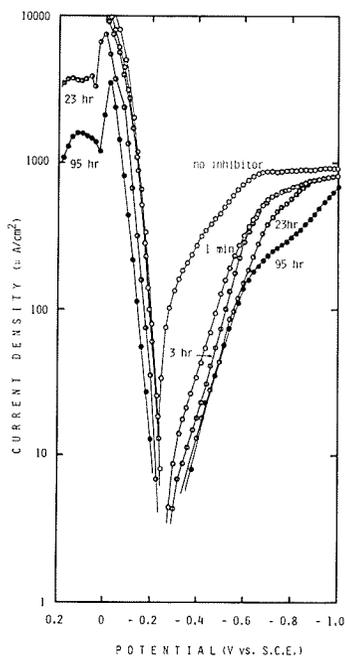
Fig. 5 Anodic and cathodic polarization curves of copper rotating electrode in aerated 3% NaCl in the presence of 1 mM P–OHO, pH 6.0, at 20°C, Rotating speed: 1000 R. P. M. Electrode had been exposed to the same solution for different periods of time prior to polarization

a. Copper octylhydroxamate in KBr pellet.
b. and c. Reflectance spectrum of film formed on copper by P–OHO.
Copper specimens had been exposed to aerated 3% NaCl in the presence of 1 mM P–OHO at 40°C for 6 hours (b) and 24 hours (c), 3 reflections

Fig. 6 Infrared spectra of compounds and film on copper

exposure time in the solution in the presence of P–OHO.   The tendency is pronounced at potentials close to E_{corr}.   It is postulated that octylhydroxamate is initially chemisorbed on the air-formed oxide film on copper to form a chemisorption monolayer on which a copper complex film is formed.   The cathodic Tafel slopes in the presence of P–OHO were in the range of 170–190 mV, while those in the absence of P–OHO were 45 mV.   The anodic branch of the curves is seen to depend slightly on the pre-exposure time for several hours. The anodic current increased with anodic potential giving the Tafel slopes of 55 mV regardless of the presence of an inhibitor and the extent of pre-exposure time.   Current maxima were observed at around 0 V for the copper electrodes which had been exposed to the inhibited solution for 23 to 95 hours.   Figure 5 indicates that the inhibitor exerted only minor influences on the anodic copper dissolution reactions, particularly for the shorter exposure times.   Thus, it appears that the P–OHO acts as a cathodic inhibitor interfering with the occurrence of reduction reaction on copper surface.

3.3 Infrared spectroscopy

Figure 6 shows infrared spectra of the compound and films formed on copper; Curve a is the transmission spectrum of Cu^{II}-octylhydroxamate in KBr pellet as a reference spectrum, and b and c are infrared reflection absorption spectra recorded using 3 reflections of copper specimens which had been exposed to the

aerated 3% NaCl solution in the presence of 1 m mol/1 P–OHO at 40°C for 6 hours (b) and 24 hours (c) under stagnant conditions.   The reference infrared spectrum was recorded in Cu-octylhydroxamate precipitates prepared in bulk solutions containing cupric ions and P–OHO.   Some of the characteristic absorption bands were observed in the spectrum a.   They are the C–H stretching multi-peaked band in the wave length region of 2850–2930 cm^{-1}, the $=$C–N– stretching band at 1540 cm^{-1}, and the $\equiv$ C–H bending vibration band in the methyl group around 1382 cm^{-1}.   These bands are also observed in the spectra b and c, and the other weak bands appearing in the spectrum a in short wave number are identical to those of b and c.   Thus, the complex film formed on copper in the inhibited solution is identified as Cu^{II}-octylhydroxamate.   Although the complex film thickness on copper was not accurately estimated, it grew up to a visible dimension, i. e., several hundred angstrom or more.   It is noted that the fractional change in reflectivity ΔR at the band maximum 1540 cm^{-1} for 6 hours exposure was 0.04 compared with 0.15 for 24 hours exposure.   Since the ΔR is related to the film thickness, this also suggests that the copper complex film grew with pre-exposure time.

3.4 Inhibition action of other alkylhydroxamate derivatives

Table 3 lists a comparison of the inhibition efficiencies estimated from weight loss data obtained with relatively long-chain (C_6–C_{10}) alkylhydroxamates as corrosion inhibitors in the NaCl solution.   As seen in Table 3, those alkylhydroxamates conferred inhibition varying from a low value of 1.2% inhibition for hexylhydroxamate to a high value of 100% for decylhydroxamate on copper.   The inhibition efficiency is increased with the increasing chain length of the hydroxamate and their concentration.   This fact is in good agreement with the results obtained with benzotriazole relative compounds and copper in which the inhibition

Table 3. Comparison of corrosion inhibition efficiency with five different alkyl hydroxamates

COPPER CORROSION TEST RESULT

Aerated 3 % NaCl, $_p$H 6.0, at 40°C for 1 day
125 R.P.M.

INHIBITORS	CONCENTRATION (m M/l)	WEIGHT LOSS (mg/cm^2)	% INHIBITION
Hexyl-hydroxamate	0.1 1.0	0.6480 0.6313	Acceleration 1.21
Heptyl-hydroxamate	0.1 1.0	0.5739 0.3935	10.2 34.8
Octyl-hydroxamate	0.1 0.5 1.0	0.5095 0.1186 0.0173	20.3 81.5 92.5
Nonyl-hydroxamate	0.1 1.0	0.3030 0.0258	52.6 96.0
Decyl-hydroxamate	0.1 Saturated	0.0529 +0.0286	91.7 100

No inhibitor: 0.6392 mg/cm^2

efficiency was found to increase with the size of inhibitor molecules[5].   Complete protection was attained in the case of saturated solution of dodecylhyroxamate. The protection mechanisms of those inhibitors are believed to be the same as that of P–OHO which forms complex layers precipitated on copper and its oxides from aqueous solutions.

4.   Conclusion

Potassium octylhydroxamate is a good inhibitor for copper in neutral chloride solutions.   Maximum protection accounting 98% inhibition efficiency was attained at the concentration of 1 m mol/1 potassium octylhdroxamate in the solutions. Inhibition action of the inhibitor is mainly due to the film formation of an adherent film of copper complex by potassium octylhydroxamate on the surfaces of copper and/or copper oxide.   These protective films, which were identified as Cu^{II}-octylhydroxamate, act as physical barriers against corrosion processes.

References

1) H. D. Peterson, M. C. Fuerstenau, R. S. Rickard and J. D. Miller Trans. Soc.   Mining Engineers Dec. p. 388 (1965).
2) T. Notoya and G. W. Poling Corrosion 32 No. 6 216 (1976).
3) J. A. Allen Trans. Faraday Soc. 48 273 (1952).
4) G. M. Florianovich, Ya. M. Kolotyrkin and A. N. Katrevich Eur. Symp. Corros. Inhibitors 4th (2) 455 (1975).
5) R. Walker Corrosion 31 No. 3 97 (1975).