Inhibitive Efficiency of Zinc Organo Amino Phosphate for the Corrosion of α-Brass in 0.5 M Sulphuric Acid Solution.

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INHIBITIVE EFFICIENCY OF ZINC ORGANO AMINO PHOSPHATE FOR THE CORROSION OF α - BRASS IN 0.5 M SULPHURIC ACID SOLUTION.

الكفائة المهبطية للمركب العضوى ZOAP على عملية تآكل سبيكة النحاس الأصفر فى محلول حامض الكبريتك

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خلاصـــة :

أجريت التجارب لدراسة ميكانيكية عملية التآكل لسبيكة النحاس الأصفـر (70/30) فى محلول حامض الكبريتيك (0.5 M) فى غيـاب ووجـود المهبـط العضـوى الـذى يحتـوى علـى الزنك ومركبـات الفوسفات (ZOAP) وتمت الدراسة باستخدام طريقـة النقص فى الـوزن، التحليل الكيميائى للمحاليل والطرق الكهروكيميائية كما تمت دراسة الأسطح بعـد عمليـة التـآكل باستخدام الميكروسكوب الضوئى والتحليل الطيفى باستخدام الأشـعة الـسينية.

أكدت النتائج أن استخدام المهبط العضوى الذى يحتوى على الزنك ومركبات الفوسفات يقلل من معدل التآكل الكيميائى للسبيكة وذلك نتيجـة تكـون المركـب الكيميائـى المعقـد C_4H_6 $(NH_2)_4$ Zn_3 $(P_3O_{10})_2$ $9H_2O$ ، على سطح السبيكة مما يقلل من فرصـة خـروج الزنك.

Abstract :

A study has been made to investigate the mechanism of dezincification and elelctrochemical behaviour 70/30 brass in sulphuric acid in absence and presence of Zinc Organo Amino Phosphate (ZOAP) inhibitor using the weight loss method, solution analysis and electrochemical technique. Attacked surfaces were analyzed by optical metallography and X -ray analysis.

Results showed that ZOAP inhibitor is able to minimize the rate of dezincification due to the formation of a C_4H_6 $(NH_2)_4$ Zn_3 $(P_3O_{10})_2$ $9H_2O$ complex compound on the metal surface.

Introduction :

In the field of non-ferrous alloys, the subject of dealloying is of current interest because its scientific as well as industrial applications. Dezincification is one of the well - known de-alloying process by means of which brass loses the valuable physical and mechanical properties leding of the total failure of structure (1). Dezincification may take place either in localized regions (plug type) or uniformally over the whole surface (layer type) (2, 3). Three mechanisms of dezincification (4) have been proposed :
(i) preferential dissolution of zinc from the alloy.
(ii) simltaneous dissolution of copper and zinc followed by the redeposition of spongy copper, by cathodic reduction of cupric ions in solution, on the surface of the alloy.
(iii) dezincification by both the above mechanisms operating simultaneously.

Sugawar and Ebiko (5) have studied the dezincification of brasses by means of a potentiostat and an electron probe microanalyser and observed that the electrochemical behaviour of the α and $\alpha + \beta$ phases of brasses are essentially similar to those of copper in 3.5% NaCl solution. They have reported that the dezincification is mainly due to the redeposition of copper. Langenegger and Robinson (6) observed a linear relationship between the rates of dezincification and specimen potential, and they have supported the preferential dissolution of zinc theory. Abbas (7) investigated the effect of temperature on the dezincification and corrosion of 70/30 brass in 0.5 M H_2SO_4 and reported that dezincification of 70/30 brass takes place by different mechanisms depending on temperature. In general, NaCl, HNO_3, HCl and H_2SO_4 sblutions have been used to study the dezincification of brasses.

Many organic compounds have been used as corrosion inhibitors for brasses in different media, of theses zinc organo amino phosphate. (ZOAP), has shown a greater inhibitive efficiency when used in water treatment for heat exchangers.

Investigation of dezincification and electrochemical behaviour of brasses in H_2SO_4 has the practical applications of estimating the corrosion properties of heat exchangers which operate in atomospheres contaminated with SO_3 (7). Thus the present investigation is concerned with the study of the mechanism of dezincification of α- brass and the inhibitive action of Zinc organo amino phosphate (ZOAP) on the corrosion rate of α- brass in 0.5M H_2SO_4 solution.

Experimental :

To study the mechanism of dissolution of brass in 0.5 M H_2SO_4 solution and to study the effect of inhibitor, two sets of experiment were done.

a) Study of the corrosion and inhibition behaviour by weight loss method and solution analysis to determine the concentrations of Cu and Zn in solution.

b) Study of electrochemical behaviour of brass in 0.5 M H_2SO_4, with and without inhibitor, with the help of a poteutioscan.

Determination of inhibitive efficiency :

Sample of cylinderical shape, 1.5 and 1 cm in diameter and height respectively, were cut from a commercial grade brass bar (70 Cu - 29.9 Zn - 0.07 Fe - 0.03 Pb). A small hole was drilled at the upper edges of the samples for hanging them with nylon thread in the solutions. The samples were polished, successively with 400, 500 and 600 grades of emery papers and then throughly cleaned with water and acetone. The experiments were conducted in 200 ml conical flask containing 150 ml of 0.5 H_2SO_4 and with 0.0, 0.2, 0.5, 1.2 ml/liter concentration of inhibitor. The weight losses were determined after removing the corrosing products from the specimens by immersing them in 15% HCl for 5 min and then washing them throughly with distilled water and drying. All experiments were carried out at 25 ± 2°C. Inhibitive efficiency was caluculated using the equation

$$E = \frac{a-b}{a} \times 100 \, \% \, [2] \qquad\qquad (1)$$

Where :
E = percentage inhibitive efficiency.
a = weight loss in 0.5 H_2SO_4 solution
b = weight loss in 0.5 H_2SO_4 solution containing the inhibitor.

Solution analysis :

Solutions were analysed with A - 475 atomic absorption spectrometer. The instrument was standarized using solutions of known concentration; a minimum of 10 readings for each analysis was taken and the average value has been reported. The dezincification factor (Z) is defined by [2] .

$$Z = \frac{R_s}{R_a} \qquad\qquad (2)$$

Where :
R_s = Zn/Cu ratio in solution.

R_a = Zn/ Cu ratio in the alloy.

The Zn / Cu ratio (R_s) in the solution was determined by chemical analysis of the solution and the ratio of Zn / Cu in the alloy (R_a) obtained from their percentage weights in the alloy.

Open circuit potential and polarization measurements :

A wenking potentioscan model POS - 73 was used for monitoring the corrosion potential of the brass as well for potentiostatic ploarization measurements. The open circuit potential of brass against a saturated calomel electrode was continuously monitored using the potentioscan. Potentiostatic polarization curves were obtained manually starting from the steady potential. A platinum counter electrode was used.

Surface analyses of attacked metal :

Corroded metal was analysed by two methods : optical metallography and X-ray diffraction analysis.

Results:

Inhibitive efficiency:

From table {I} and Fig. (1) it is clear that ZOAP gives 86% efficiency at its optimum concentration of 1ml/L. In Fig.2 the percentage inhibitive efficiencies of ZOAP inhibitor is plotted as a function of immersion period. The maximum efficiency was reached after 24 hrs immersion, after which the efficiency decreased [Fig.(2) and table {II}]. This may be due to the dissolution of a complex protective film from the metal surface. The lower inhibitive efficiency of the compounds prior to 24 hrs may be due to the presence of an imperfection complex protective film on the surface of the metal not capable of inhibiting the dissolution of zinc and copper ions from brass.

The effect of inhibitor at different concentrations on copper and zinc dissolution is shown in Fig.(2). ZOAP mainly inhibits zinc dissolution, it is not very effective in the case of copper which shows that ZOAP is able to minimize the rate of dezincification.

Dezincification:

Equation (2) was used to calculate the dezincification factor (Z) from the solution analysis data obtained for solution containing 1ml/L ZOAP. Fig. (3) shows the dezincification factors obtained for without and with ZOAP containing 1ml/L solutions. For free ZOAP solutions the dezincification factor is high in the initial period due to the preferential dissolution of zinc, which gradually decrease with time until Z becomes

unity, suggesting that both copper and zinc ions are going into solution at the same rate (7). On the other hand solutions containing 1ml/L ZOAP shows a lower dezincification indicating a much low dissolution of zinc.

Open circuit potential:

The corrosion potential of brass 70/30 in 0.5 M H_2SO_4 solution without and with 0.2, 0.5, 1 and 1.2 ml/L ZOAP at 25±C was recorded as a function of time and results are given in Fig. (4). This shows that the potential, irrespective of inhibitor concentration, shifts with time to the nobbler direction before attaining a stable, steady maximum value. Generally initial as well as steady potentials became more positive as the content of ZOAP increased up to 1%. However 1.2 ml/L more or less shows the same effect as 1 ml/L ZOAP.

The general shift of steady state potential in the nobbler direction indicates greater polarization of the anodic than cathodic processes at the brass surface with increasing ZOAP concentrations.

Potentiostatic polarization :

The anodic polarization and the cathodic polarization curves in the absence and with presence of ZOAP inhibitor at different concentrations are shown in Fig. (5) and Fig. (6). The polarization curve of α- brass in 0.5 M H_2SO_4 solution without inhibitor shows two passive regions, primary and secondary, which are suggested to be due to the formation of cuprous oxide and cupric oxide films respectively [7]. Moreover Fig.(5) shows that as the inhibitor concentration is increased up to 1% ml/L anodic polarization curves shift towards lower current densities. ZOAP shows maximum passivation in the primary passivation region and above this region it does not inhibit the corrosion of brasses. It is supposed that ZOAP forms a stable complex with zinc and thus gives protection in the primary passivation region hence ZOAP is not effective inhibitor in the higher potential region. The small indication of a secondary passivation region obtained in the presence of ZOAP may be due to the formation of CuO film. The corrosion current density computed by a rough extrapolation of cathodic and anodic curves indicates that the corrosion current decreases with increasing the ZOAP in 0.5 M H_2SO_4 solution table {III}. Generally the results obtained by potentiostatic polarization technique are in good agreement with those obtained by weight loss method.

X-ray analysis:

Fig. (7) shows the result of X-ray diffraction analysis of brass surface exposed to solution without and with ZOAP inhibitor (1ml/L) for 24 hrs. It is clear that a complex compound of C_4H_6 $(NH_2)_4$ Zn_3 $(P_3 O_{10})_2$. $9H_2O$ is formed on the metal surface.

Microscopy:

In the presence of ZOAP inhibitor a thin black film has been observed on the surface of the specimens. This confirms that the inhibition is due to the formation of some complex film with metal ions.

Discussion:

Gupta and others [2] showed that the organic inhibitors act as proton acceptors, releasing H^+ ions into the sulphuric acid solution and forming an organo metallic complex layer with the metal ions on the surface of the metal, thus inhibiting the corrosion.

In ZOAP, the Amino group acts as the reaction center, on which is formed a complex with the metal ions. The primary passivation in the presence of inhibitor is supposed to be due to the formation of cuprous oxide film along with a stable zinc complex and, on further increasing the anodic potential the inhibitive effect of ZOAP becames insignificance. Generally, the dezincification factor decreases in presence of ZOAP.

The dissolution of α- brass in 0.5 M H_2SO_4 solution without or with 1ml/L ZOAP is schematically represented in Fig. (8) which has been compiled with the help of publicated data [2,7].

Conclusion:

From the present study the following conclusions can be drawn :

1- ZOAP is effective inhibitor for 70/30 brass in 0.5 M H_2SO_4 solution and its inhibitive efficiency reaches maximum value of 86% at its optimum concentration of 1ml/L.

2- The inhibitive action of ZOAP is due to the formation of a protective complex film mainly with zinc metal ions on the surface of the allay.

References:

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Table (I): Effect of inhibitor concentration on inhibitive efficiency towards 70/30 brass in 0.5 M. H_2SO_4 at 25 ± 2°C, after 48hrs.

Inhibitor concentration ml/L	Weight Loss mg	Solution analysis		Efficiency	Dezincification factor (Z)	Efficiency	
		Cu mg/L	Zn mg/L			Cu	Zn
1- Without inhibtor	13	42.7	24.0	--	1.3	--	--
2- With inhibitor							
a- 0.2	8.5	20.4	8.5	35	0.97	52	65
b - 0.5	6.2	16.3	6.3	52	0.90	62	74
c - 1.0	1.8	13.1	3.2	86	0.57	69	87
d - 1.2	4.1	19.0	8.6	68	1.06	56	64

Table (II): Variation with time of Cu and Zn dissolution from 70/30 brass in absence and presence of ZOAP inibitor.

Time hrs	0.5 M H_2SO_4			1 ml ZOAP /L				
	Cu mg/L	Zn mg /L	Z	Cu mg/L	Zn mg/L	Z	Eficiency	
							Cu	Zn
2	2.6	8.29	12.0	1.6	3.69	5.38	39	55
8	4.65	11.6	5.8	2.6	3.8	3.41	44	68
16	14.4	18.6	3.01	6.7	4.3	1.18	53	82
24	28.1	25.0	2.07	10.5	2.0	0.44	63	93
36	51.2	38.7	1.76	20.9	3.2	0.35	59	92
48	63	38.1	1.4	30.2	4.5	0.35	52	88

Table (III): Effect of inhibitor concentrations on some electrochemical parameters towards 70/30 brass.

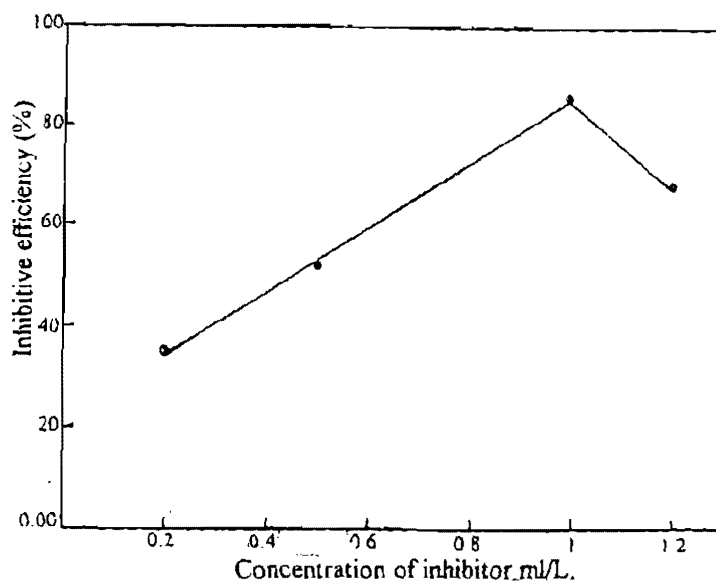| Series	Inhibitor concentration ml/L	I_{corr} mA/Cm^2	E_{corr} mV (SCE)	$i_{crit.}$ mA/Cm^2
1-	without inhibitor	0.038	- 160	2.5
2-	ZOAP			
	(a) 0.2	0.025	- 120	2.2
	(b) 0.5	0.021	- 70	0.52
	(c) 1	0.018	+ 30	0.51
	(d) 1.2	0.020	+ 20	0.60

Fig 1 :Effect of inhibitor concentration on inhibitive efficiency towards 70/30 brass in
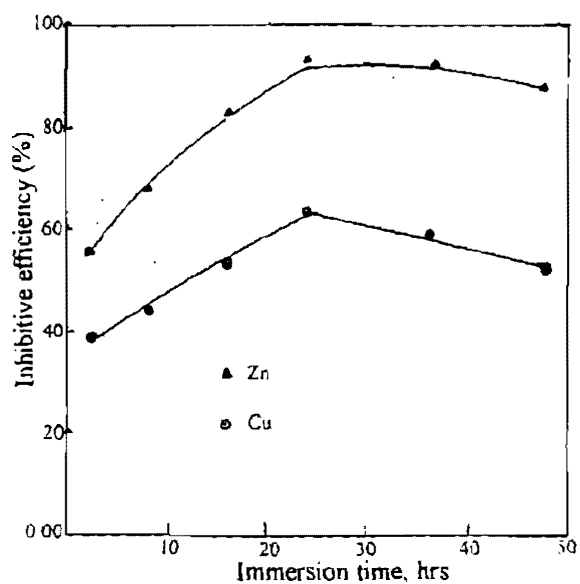0.5 M H$_2$SO$_4$ solution at 25 ± 2°C after 48 hrs

Fig. 2: Variation of inhibitive efficiency with immersion time towards 70/30 brass in
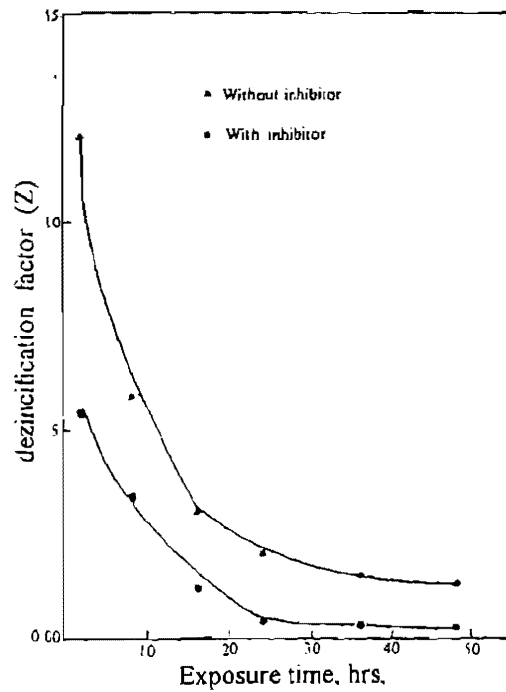0.5 M H$_2$SO$_4$ solution with 1 ml inhibitor concentration at 25 ± 2°C.

Fig. 3: Variation of dezincification factor (Z) with exposure time in 0.5 M H_2SO_4 solution without and with inhibitor (1 ml/L).
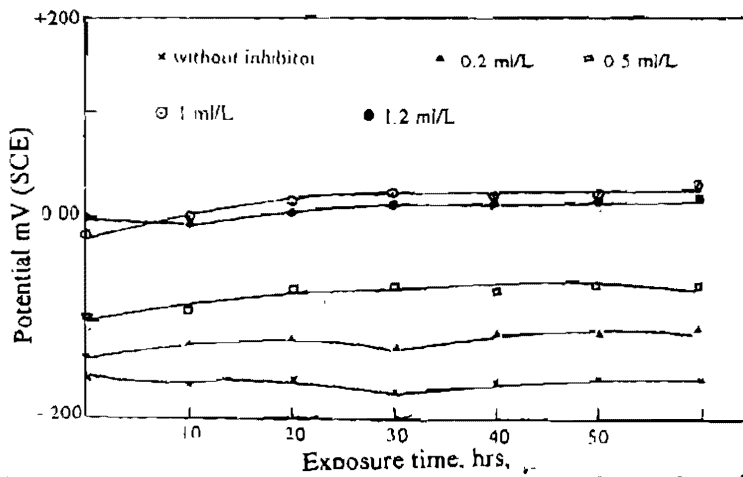

Fig. 4: Effect of exposure time on the corrosion potential of 70/30 brass in 0 5M H_2SO_4 solution without and with different concentrations of inhibitor at 25 ± 2 °C.
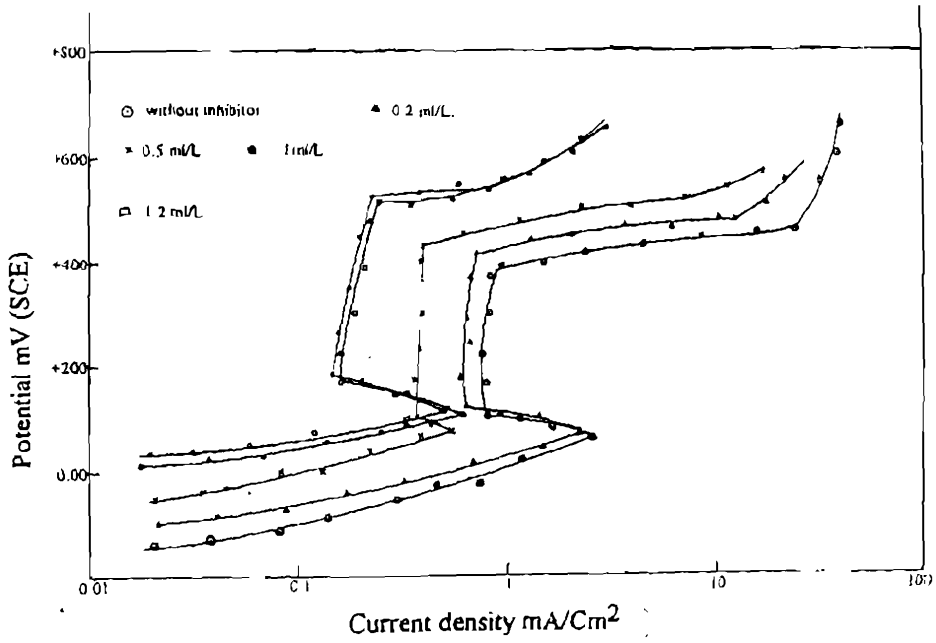
Fig. 5: Potentiostatic anodic polarization curves for 70/30 brass in 0.5 M H_2SO_4 solution without and with different concentrations of inhibitor.
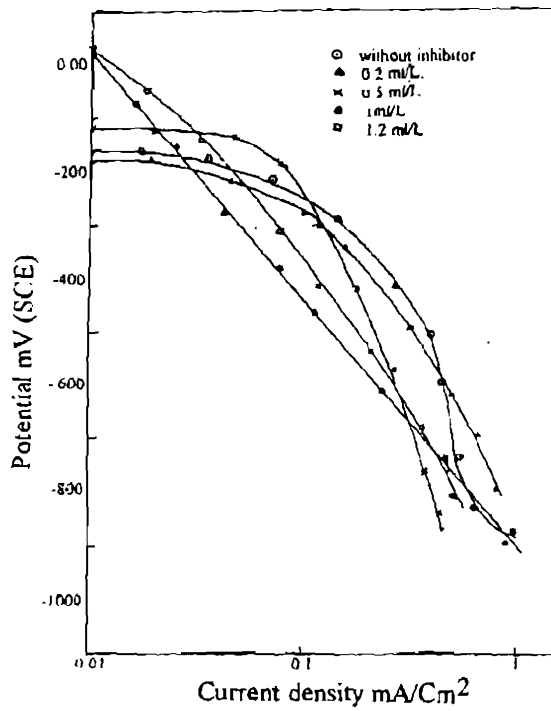

Fig. 6: Potentiostatic cathodic polarization curves for 70/30 brass in 0.5M H_2SO_4 solution without and with different concentrations of inhibitor.
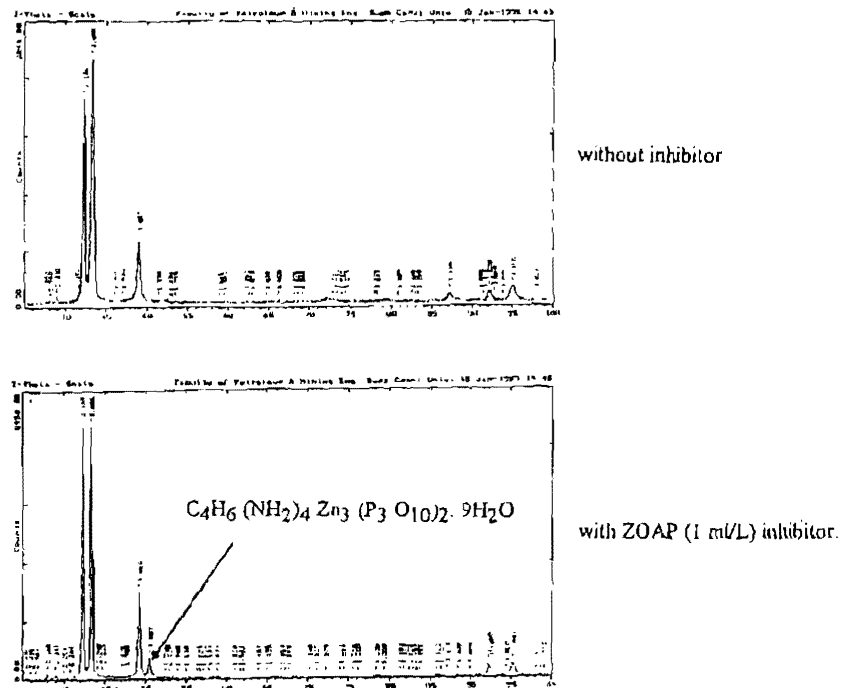
without inhibitor

$C_4H_6 (NH_2)_4 Zn_3 (P_3 O_{10})_2 . 9H_2O$

with ZOAP (1 ml/L) inhibitor.

Fig. 7: X-ray analysis of 70/30 brass surface exposed to 0.5 M H_2SO_4 solution without and with inhibitor 1ml/L for 24 hrs at 25 ± 2°C.
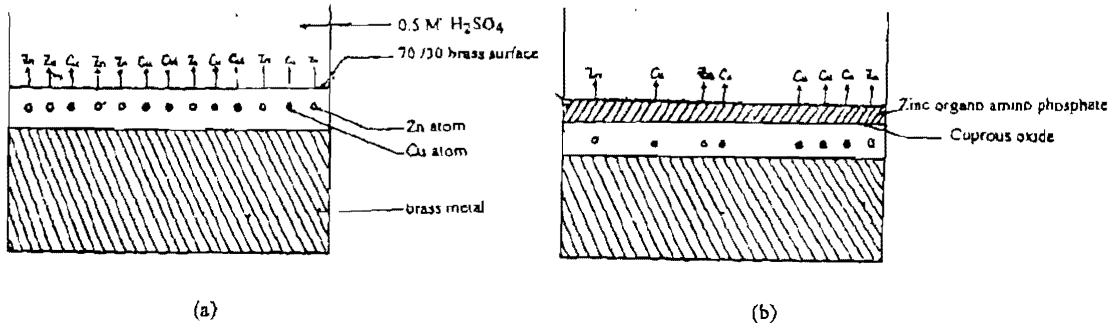

(a)   (b)

Fig. 8: Schematic diagrams showing mechanism of dissolution of α-brass in 0.5 M H_2SO_4.
(a) without inhibitor   (b) with ZOAP (1 ml/L) inhibitor.