Effect of Some Organic Compounds as Corrosion Inhibitors for Brass in Cooling Water Systems

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Abstract: The inhibition effect of polyvinylpyrrolidone (PVP) of average molecular weights 10,000 (PVP-10) and 40,000 (PVP-40), Benzimidazole (BIA) and 2-Amino-2-Methyl-1-Propanol (AMP) on the corrosion of brass in cooling water systems has been investigated. The investigation was carried out using the weight loss method and open circuit potential measurements. The chemical composition of the make-up water used in the cooling system has been determined. The data showed that the the corrosivity of the water is due to the presence of the aggressive Cl^- and SO_4^{2-} ions. The inhibition efficiency and surface coverage were calculated at various inhibitor concentrations. The obtained results showed that the inhibition efficiencies of these inhibitors enhance with increasing inhibitor concentrations and it was found that the inhibition efficiency of these inhibitors decrease in the order: BIA > PVP 10,000 > PVP 40,000 > AMP. Moreover the inhibition effect of various concentrations of the four inhibitors on the corrosion of brass in the make-up water containing 2% N_2H_4 and 0.005 M Na_2SO_3 was studied. The open circuit potential measurements showed that the presence of these organic inhibitors shifts the steady state potentials (Es) to more noble direction. In water containing hydrazine, the presence of inhibitors shifts Es to more noble values than in hydrazine – free water which leads to improves the corrosion inhibition of the brass .The mechanism of inhibition was proposed on the basis of the adsorption of the inhibitor molecules on the brass surface.

1. Introduction

Copper and its alloys are widely used in industry because of their excellent electrical and thermal conductivity and their good resistance to corrosion [1–3]. Brass has been widely used as tubing material for condensers and heat exchangers in various cooling water systems [4–9]. Brass is susceptible to a corrosion process known as dezincification and this tendency increases with increasing zinc content of the brass [10,11]. Many inhibitors have been used to minimize the corrosion of brass in different media. Particularly, heterocyclic organic compounds containing nitrogen, sulphur and/or oxygen atoms are often used to protect metals from corrosion, [12-14]. The inhibiting action of 2-mercaptobenzothiazole (MBT) and cetyltrimethylammonium bromide (CTAB) on the corrosion of brass in groundwater have been studied [15]. The results revealed that the inhibition occurred by blocking the reaction sites on the surface of brass via chemisorption of the inhibitors. Benzimidazole and its derivatives have been shown to inhibit dissolution of brass [16,17]. Recently, the inhibition effect of some phenylhydrazone derivatives, on the corrosion of brass in 2M HCl solution has been investigated, [18]. The efficiency of 1,3-bis-diethylamino-propan-2-ol (DEAP) as volatile corrosion inhibitor (VCI) for brass in simulated atmospheric water was studied [19]. Polymeric compounds consist of large molecules, which can be adsorbed on the surface of a certain metal, can be considered as a good   corrosion

inhibitors. For instance, the potentiality of polyvinylpyrrolidone as corrosion inhibitors has been investigated [20, 21]. The effect of polyvinylpyrrolidone as an inhibitor was attributed to the adsorption of this polymer through several points of each of its molecules. Recently, 2-Phosphonobutane-1,2,4 tricarboxylic acid (PBTCA) and polyvinylpyrrolidone (PVP) was used as a corrosion inhibitor for carbon steel in cooling water system. The results indicate that the mixture of PBTCA and PVP acts as a synergic inhibitor and found to increase the inhibition efficiency to 96.7%.[22].

The objective of the present work was to investigate the effect of Polyvinylpyrrolidone (PVP) of average molecular weights 10,000 and 40,000, Benzimidazole (BIA) and 2-Amino-2-Methyl-1-Propanol (AMP), as corrosion inhibitors for brass in the cooling water system. Investigation of these inhibitors was performed using weight loss methods and open circuit potential measurements.

2- Experimental

The chemical composition of the make-up water used in the cooling system is given in Table 1. All chemical analyses were carried out as standard methods [23]. The experiments were performed with brass sheet having the chemical compositions Cu 70 % and Zn 30 %. Coupons of the dimensions 4.0 × 2.0 × 0.09 cm with exposed surface of 1.7 cm^2 used for the measurement of weight loss. Before immersion, brass sheet were polished using different grades of emery

paper, washed with distilled water and finally degreased with acetone. Weight loss experiments were carried out for a period of seven days as described by Ajmal et al. [24]. The results were mean values of four runs, each with fresh specimen and fresh solution.and the results were quite reproducible.

Open circuit potential(OCP) measurements were performed using a cell assembly consisting of two electrodes. The working electrode was brass sheet of the same composition with an exposed area of 1.7 cm^2 and a saturated calomel electrode as reference electrode. The potential was measured as a function of time until the steady state potential was attained, using a potentiostat type EG & G model 273A

Polyvinylpyrrolidone (PVP) of average molecular weights 10,000 (PVP-10) and 40,000 (PVP-40), Benzimidazole (BIA) and 2-Amino-2-Methyl-1-Propanol (AMP) were used as corrosion inhibitors of the cooling water system. Some experiments were performed to show the influence of addition of scavengers Na_2SO_3 and N_2H_4 on the corrosion behavior of brass in the make-up-water cntaining inhibitor.

| Polyvinylpyrrolidone (PVP) | Benzimidazole (BIA) | 2-Amino-2-Methyl-1- Propanol (AMP) |
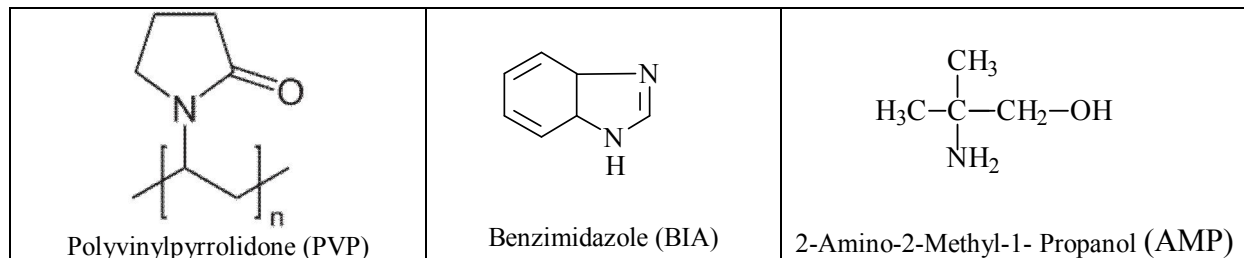
3- Results and Discussion

Physicochemical characteristics of the make-up water used in this study is given in Table 1.The data indicate that the water is slightly alkaline (pH = 8.2), The alkalinity of water is mainly due to the presence of HCO_3^- ions. This water has low hardness since the average total hardness is about 8.7 ppm., Langelier saturation index has negative value (-0.53) and Ryznar stability index is (9.3) greater than 7 [25,26]. The corrosivity of the water is due to the presence of the aggressive Cl^- and SO_4^{2-} ions. The Cl^- ions (143 ppm) can strongly adsorbe on the brass surface and destroy any pre-immersion oxide layer on the surface and making it difficult to be passive. On the other hand, SO_4^{2-} ions (97 ppm) are less aggressive than Cl^- ions.

3.1 Weight loss measurements:

The weight loss of the brass in the aerated make-up water in the absence and presence of different concentrations of PVP (10000), PVP (40000), BIA and AMP was determined after 24 h immersion. The weight loss (in mg cm^{-2} day^{-1}) values are given in Table 2. Inspection of the data reveals that the presence of either of the cited organic compounds inhibits the corrosion of brass in the make-up water. The weight loss decreases with increasing the concentration of each inhibitor.

The inhibition efficiency P and the surface coverage θ were calculated from the relation:

$$P = (1 - \frac{W}{W^o}) \times 100 = \theta \times 100 \quad \text{..............} (1)$$

Where W^o and W are the weight of brass sheet afte immersion in the water in a absence and in presence of the inhibitor respectively. The value of P are listed in Table 2. The data Show that the inhibition efficiencies of these inhibitors enhance with increasing inhibitor concentrations. The inhibition effect of these compounds is due to their ability to adsorb on the brass surface. These compounds are characterized by the existence of active function groups. These groups are regarded as the reaction centers for the establishment of adsorption process via electron pairs of nitrogen and oxygen atoms [27,28] .The effectiveness of nitrogen atom with respect to adsorption process is greater than oxygen atom as a result of basic character of the former atom, in which an easier polarization can be formed. Moreover, adsorption of PVP and BIA can occur via donor-acceptor interaction between π electrons of the cyclic ring and the vacant d-orbitals on the surface of brass atoms. These inhibitors may also be adsorbed through electrostatic interaction between the inhibitors and the metal surface . The reaction center can block the active sits accessible for corrosion and leads to an increase in the activation energy.

The data show that the inhibition efficiency of these inhibitors decrease in the order:
BIA > PVP 10,000 > PVP 40,000 > AMP. The difference in the efficiency of PVP 10,000 and PVP 40,000 can be attributed to the high mobility of the shorter polymeric chain PVP 10,000 as compared to PVP 40,000 of large molecular weight. This agrees with the results obtained previously [21-22, 29-30].

The inhibitive effects of various concentrations of the four inhibitors on the corrosion of brass in the make-up water containing either 2% N_2H_4 or 0.005 M Na_2SO_3 at 25 ^{o}C were studied. The

weight loss values and inhibitive efficiency in these cases were determined and the results are given in Table 2. As can be seen, the inhibition efficiency of these inhibitors are higher in water containing 2% N_2H_4 than those without N_2H_4, indicating that the presence of N_2H_4 in the water improves the corrosion inhibition. In the presence of N_2H_4, the inhibition efficiency of the cited inhibitors decreases in same order as in case of water containing inhibitor without N_2H_4. It is seen that a mixture of N_2H_4 and BIA is a very effective corrosion inhibition for the brass in cooling system. On contrary, the presence of 0.005 M Na_2SO_3 in the water decreases the inhibition efficiency of the four inhibitors. This observation can be interpreted on the basis that the reduction of the dissolved oxygen takes place as follows:

$$2 SO_3^{2-} + O_2 = 2 SO_4^2 \quad …………… (2)$$
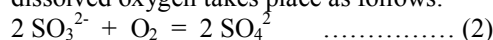
The decrease in the efficiency could be related to the formation of SO_4^{2-} ions which enhances brass dissolution by adsorption at the brass surface with displacement of water molecules. On The other hand, the interaction between N_2H_4 and dissolved oxygen proceeds as follows:

$$N_2H_4 + O_2 = 2 H_2O + N_2 \quad ……………. (3)$$
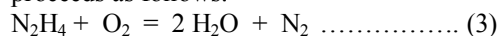
The advantage of N_2H_4 over SO_3^{-2} as scavengers is that the end product is N_2, which can be preferentially adsorbed on the brass surface and block the anodic sites.

The observed changes in θ are shown in Figs 1 and 2 as a function of the logarithm of the concentration of the examined inhibitors in the absence and in the presence of 2% N_2H_4 respectively. The data were tested graphically to find a suitable adsorption isotherm. A plot of log θ vs log C would give a straight line of intercept log K, indicating that the adsorption of these inhibitors on brass surface follows the Freundlich adsorption isotherm. This isotherm is represented by equation 4

$$\log \theta = \log K + n \log C \quad ……………... (4)$$

where K is the equilibrium constant of adsorption, C is the bulk concentration of inhibitor and n is a constant. if the above equation is applicable. The values of K were calculated and they are listed in Table 3. As can be seen the values of K increases in the order: BIA > PVP 10,000 > PVP 40,000 > AMP. The higher the values of K, the better the inhibitive activity of the substance.

3.2 Potential – time measurements

The effect of adding increasing concentrations of the four inhibitors in make-up water in the absence and in the presence of 2% N_2H_4 or 0.005 M Na_2SO_3 on the open circuit potentials of the brass at 25 ^oC was investigated. Some examples are given in Fig 3 and 4. The obtained data reveal that in make-up water (in absence of inhibitors) the potential decreases rapidly and finally reaches a steady state value Es with the time. This variation of open circuit potential with the time reflects the corrosivity of water towards the brass. However, in the presence of either of these inhibitors, the electrode potential fluctuates till a steady state is attained. It is seen that the presence of these inhibitors shifts the steady state potentials to more noble direction to an extant depends upon the type and the concentration of the inhibitor. The more positive the steady state potential the better is the inhibition efficiency.

The steady state potentials Es varies with the inhibitor concentrations according to the equation:

$$Es = a + b \log C \quad …………………..(5)$$

The linear dependence of Es vs log C is given in Figs 5 and 6. It is observed that in water containing hydrazine, the presence of inhibitors shifts Es to more noble values than in hydrazine – free water . On The other hand, the presence of 0.005 M Na_2SO_3 in water with the inhibitors leads to a negative potential more than in sulphite free water. These results confirm the suggestion that the sulphite ions accelerate the corrosion of brass and its acceleration influence exceeds the inhibition activity of the cited inhibitors.

4. Conclusion

It can be concluded that (PVP) of average molecular weights 10,000 and 40,000, (BIA) and (AMP) acts as corrosion inhibitors for brass in the cooling water system. Investigation of these inhibitors was performed using weight loss method and open circuit potential measurements.

It was found that the inhibition efficiencies of these inhibitors enhance with increasing inhibitor concentrations. The inhibition efficiency of these inhibitors decrease in the order: BIA > PVP 10,000 > PVP 40,000 > AMP. The protection efficiency was improved when 2% N_2H_4 was added to these inhibitors solution.

5- Acknowledgment

Table 1: Typical Make up- water Analysis.

	Units	Concentration
pH		8.2
Temperature	^oC	25
Alkalinity (HCO_3^-)	ppm	130
T.D.S.	ppm	400

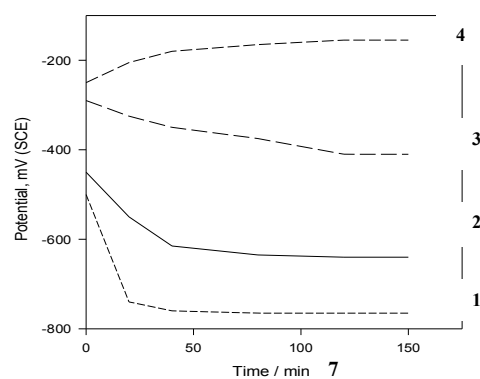| Calcium Hardness	ppm	6.0
Magnesium Hardness	ppm	2.7
Total Hardness	ppm	8.7
Chloride (Cl$^-$)	ppm	143
Sulphate (SO$^-_4$)	ppm	97
Copper (Cu)	ppm	0.00
Zinc (Zn)	ppm	0.11
Sodium	ppm	23
Potassium	ppm	2.6
Langelier Index (Is)		-0.53 (corrosive)
Ryznar Index SI		9.3 (corrosive)

Table 2: Inhibition efficiencies of inhibitors obtained under weight loss conditions.

Type of Inhibitor	C_{inh} (ML^{-1})	Weight Loss mg cm^{-2} day^{-1}	θ	P %
Blank (Pure H$_2$O)	-	0.220	-	-
PVP M. Wt. = 10000	2 x 10^{-5}	0.110	0.5000	50.00
	8.5 x 10^{-5}	0.100	0.5455	54.55
	8.5 x 10^{-4}	0.088	0.6000	60.00
	4.3 x 10^{-3}	0.078	0.6455	64.55
PVP M.Wt. =10000 With 2 % N$_2$H$_4$	2 x 10^{-5}	0.057	0.7409	74.09
	8.5 x 10^{-5}	0.054	0.7545	75.45
	8.5 x 10^{-4}	0.050	0.7727	77.27
	4.3 x 10^{-3}	0.047	0.7864	78.64
PVP M.Wt. =10000 With 0.005M Na$_2$SO$_3$	2 x 10^{-5}	0.290	-	-
	8.5 x 10^{-5}	0.280	-	-
	8.5 x 10^{-4}	0.280	-	-
PVP M.Wt. = 40000	2 x 10^{-5}	0.120	0.4545	45.45
	8.5 x 10^{-5}	0.113	0.4864	48.64
	8.5 x 10^{-4}	0.105	0.5227	52.27
	4.3 x 10^{-3}	0.100	0.5455	54.55
PVP M. Wt. = 40000 With 2 % N$_2$H$_4$	2 x 10^{-5}	0.068	0.6909	69.09
	8.5 x 10^{-5}	0.064	0.7091	70.91
	8.5 x 10^{-4}	0.060	0.7273	72.73
	4.3 x 10^{-3}	0.057	0.7409	74.09
PVP M.Wt. =40000 With 0.005M Na$_2$SO$_3$	2 x 10^{-5}	0.310	-	-
	8.5 x 10^{-5}	0.310	-	-
	8.5 x 10^{-4}	0.310	-	-
BIA In Pure H$_2$O	2 x 10^{-5}	0.050	0.7727	77.27
	8.5 x 10^{-5}	0.054	0.7864	78.64
	8.5 x 10^{-4}	0.037	0.8318	83.18
	4.3 x 10^{-3}	0.030	0.8636	86.36
BIA With 2% N$_2$H$_4$	2 x 10^{-5}	0.010	0.9545	95.45
	8.5 x 10^{-5}	0.010	0.9545	95.45
	8.5 x 10^{-4}	0.010	0.9545	95.45
	4.3 x 10^{-3}	0.010	0.9545	95.45
BIA with 0.005 M Na$_2$SO$_3$	2 x 10^{-5}	0.180	0.1818	18.18
	8.5 x 10^{-5}	0.160	0.2727	27.27
	8.5 x 10^{-4}	0.150	0.3182	31.82
AMP In Pure H$_2$O	2 x 10^{-5}	0.130	0.4091	40.91
	8.5 x 10^{-5}	0.124	0.4364	43.64
	8.5 x 10^{-4}	0.115	0.4772	47.72
	4.3 x 10^{-3}	0.110	0.5000	50.00
AMP with 2 % N$_2$H$_4$	2 x 10^{-5}	0.070	0.6818	68.18
	8.5 x 10^{-5}	0.068	0.6909	69.09

	8.5 x 10^{-4}	0.064	0.7091	70.91
	4.3 x 10^{-3}	0.060	0.7273	72.73
AMB with 0.005 M Na_2SO_3	2 x 10^{-5}	0.200	0.0909	9.09
	8.5 x 10^{-5}	0.190	0.1364	13.64
	8.5 x 10^{-4}	0.190	0.1364	13.64

Table 3 : The Equilibrium Constant of Adsorption (K) for each inhibitorin the absence and presence of 2% N_2H_4

Inhibitor Symbol	K (without N_2H_4)	K (with 2% N_2H_4)
BIA	0.9734	0.9549
PVP (10000)	0.8344	0.8498
PVP (40000)	0.6639	0.7930
AMP	0.6246	0.7749
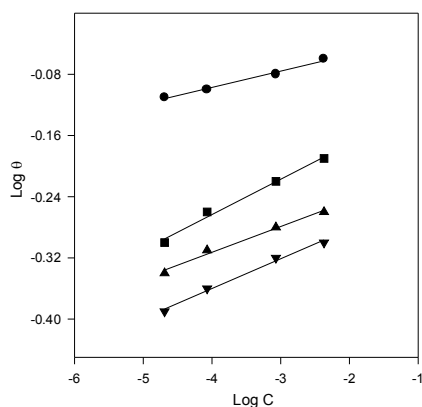
Fig.1. The relation between the surface coverage θ and the molar concentrations of the organic inhibitors in cooling water at 25°C, (1) BIA,
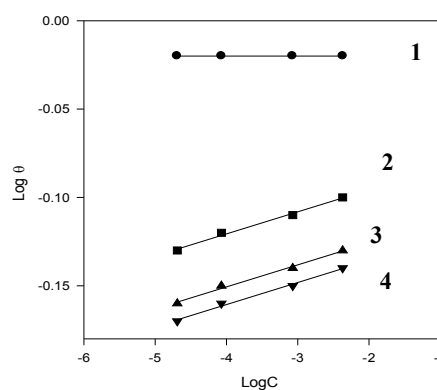
Fig.2. The relation between the surface coverage θ and the molar concentrations of the organic inhibitors in cooling water containing 2% NH_2 at 25°C, (1) BIA, (2) PVP-10, (3) PVP-40 and (4) AMP
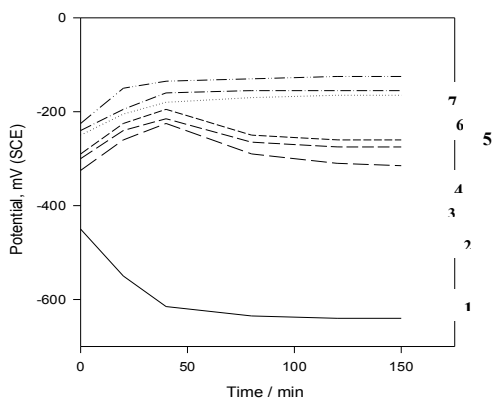
Fig.3. Potential vs time plot for brass in cooling water in the absence and in the presence of BIA with and without N_2H_4: (1) Pure cooling water, (2) $2X10^{-5}$ M BIA, (3) $8.5X10^{-4}$ M BIA, (4) $4.3X10^{-3}$ M BIA, (5) $2X10^{-5}$ M BIA + 2% N_2H_4, (6) $8.5X10^{-4}$ M BIA + 2% N_2H_4 and (7) $4.3X10^{-3}$ M BIA + 2% N_2H_4.

Fig. 4. Potential vs time plot for brass in cooling water in the absence and in the presence of PVP-10: (1) Pure cooling water, (2) $8.5X10^{-4}$ M PVP-10, (3) $8.5X10^{-4}$ M PVP-10+ 2% N_2H_4 and (4) $8.5X10^{-4}$ M
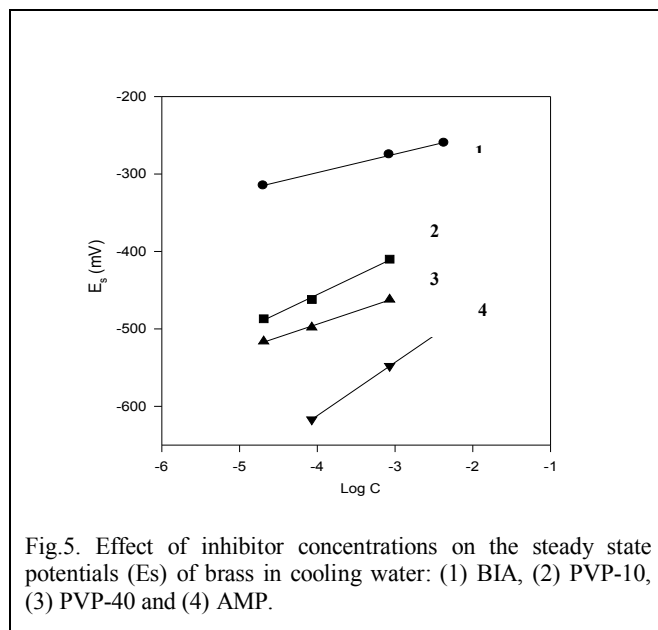
Fig.5. Effect of inhibitor concentrations on the steady state potentials (Es) of brass in cooling water: (1) BIA, (2) PVP-10, (3) PVP-40 and (4) AMP.
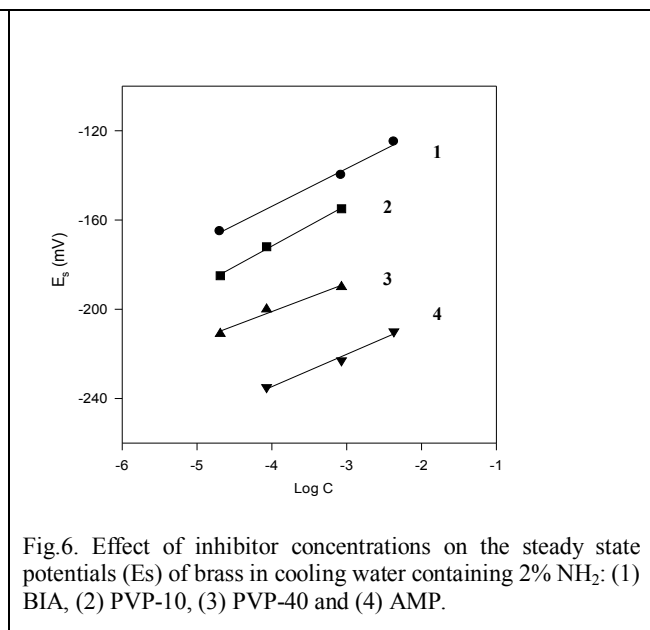

Fig.6. Effect of inhibitor concentrations on the steady state potentials (Es) of brass in cooling water containing 2% NH_2: (1) BIA, (2) PVP-10, (3) PVP-40 and (4) AMP.

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