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THE CORROSION BEHAVIOUR OF LEAD IN SODIUM HYDROXIDE SOLUTIONS CONTAINING TUNGESTATE IONS

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ABSTRACT

The effect of tungestate ion on the potential of lead electrode was measured in different concentrations of sodium hydroxide solutions and the steady state potential vs. pH of the solution showed that lead behaves as Pb / PbO couple.

The corrosion rate of lead was measured also in the pure alkali and containing different concentrations of tungestate ion. The results showed that the corrosion rate and potential decreases with increase of tungestate concentrations indicating the deceleration of cathodic reaction.

Anodic polarisation measurements showed that increase of tungestate ion concentration delays the onset of passivity.

Cathodic polarisation curves were also measured; the results confirmed the decelaration of the cathodic reaction with increase of tungestate concentration.

INTRODUCTION

Brasher (1962) suggested that some anions are corrosive when present in large dilution and become inhibitive at high concentrations. In testing this theory the corrosion behaviour of lead in sodium hydroxide solutions containing sodium phosphate and sodium chromate were previously studied. Awad and El-Hady (1969) and Awad, Kamel, and El-Hady (1972).

In this work we studied the corrosion behaviour of lead in alkaline tungestate solutions.

EXPERIMENTAL

The polarisation measurements on the lead electrode were carried out in a cell described in an earlier publication Awad (1962). This cell is constructed from the arsenic-free hard borosilicate glass, Hysil, and thus it permits the vigorous purification of the solutions under investigation through pre-electrolysis.

For this purpose we used a platinum electrode (2 cm^2 platinum sheet weldet to a platinum wire sealed to glass).

The electrode were prepared from extra–pure lead ods 3 mm in diameter (Shering Kahlbaum Company). The electrode area was 1 cm^2. Each run was carried out with a new electrode. All solutions were prepared from A.R. materials. Before each run, the cell was cleaned with a mixture of nitric and sulphuric acids (A.R.) and thoroughly washed with conductance water.

Determination of the corrosion rate was carried out using the weight-loss technique. Experiments were performed on pieces of lead of area 6.25 cm^2 and 0.8 mm thick, cut from analar lead sheet.

The test pieces were first degreased with acetone, washed with conductivity water, dried in alcohol and ether, and then weighed.

Corrosion tests were carried out in a wide 30 ml. Jar, in which the specimen was suspended for 2 hours in the test solution. The specimen was then removed, rinsed with conductivity water and finally dried and weighed.

All corrosion tests were carried out in aerated, unstirred solutions, results were duplicated and the mean was computed.

For measuring the corrosion potential, the potential of the lead electrode was followed as a function of time over a period of 3 hours. In all solutions studied the potential became constant within Ca. 3 hours. All measurements were carried out a 30°C in an air thermostate controlled to ± 5°C.

RESULTS AND DISCUSSION

The potential of the lead electrode was measured in 0.2–2M sodium hydroxide solutions.

In Fig. (1) the steady state potentials, observed three hours after immersion, are plotted as a function of the pH values of the solutions. The dotted lines in this figure represent the theoretical potential / pH relations of the Pb / PbO and Pb / $HPbO_2^-$ systems. These systems are characterised by standard potentials (at 1M OH) (7) Latimer (1952). of –0.580 and –0.540 volt respectively. It is clear from Fig. (1) that the experimental values coincide fairly with that of the Pb / Pb Ocouple. Hence the anodic reaction is represented by

$$Pb + 2\ O\overline{H} \rightleftarrows PbO + H_2O + 2e^- \qquad (1)$$

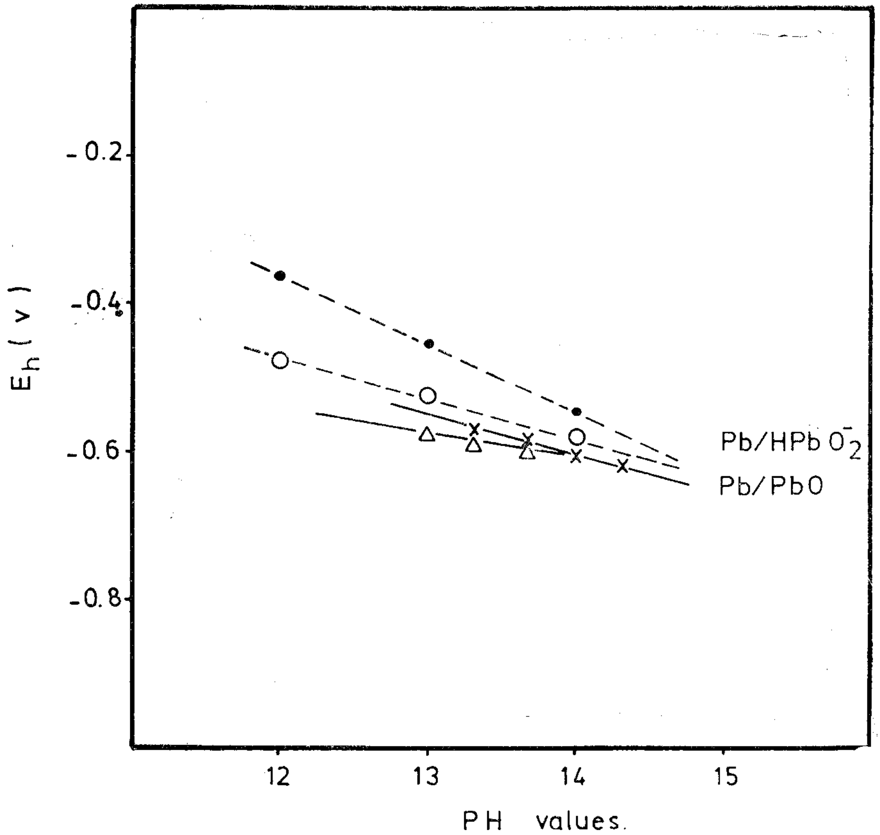

Fig. 1. Effect of pH on the potential of Pb x Pure NaOH △ 0.5 WO_4^{-2}

The corrosion rate of the metal, Vcorr, was measured in the pure alkali solutions and the results were given in Fig. (2). It is clear that the metal corrodes, although slightly, in these solutions. One can therefore conclude that the oxide is not quite protective, due to most probably, to dissolution in the alkaline solutions forming plumbite according to

$$PbO + O\bar{H} \rightleftarrows HPbO^-_2 \quad (2)$$

Effect of WO_4^{--}:

To test the effect of tungestate on the corrosion potential of lead, the potential was measured in (0.2–2M) NaOH, containing (0.0001–0.5M) Na_2WO_4. In Fig. (3), the steady state potentials are plotted as a func-

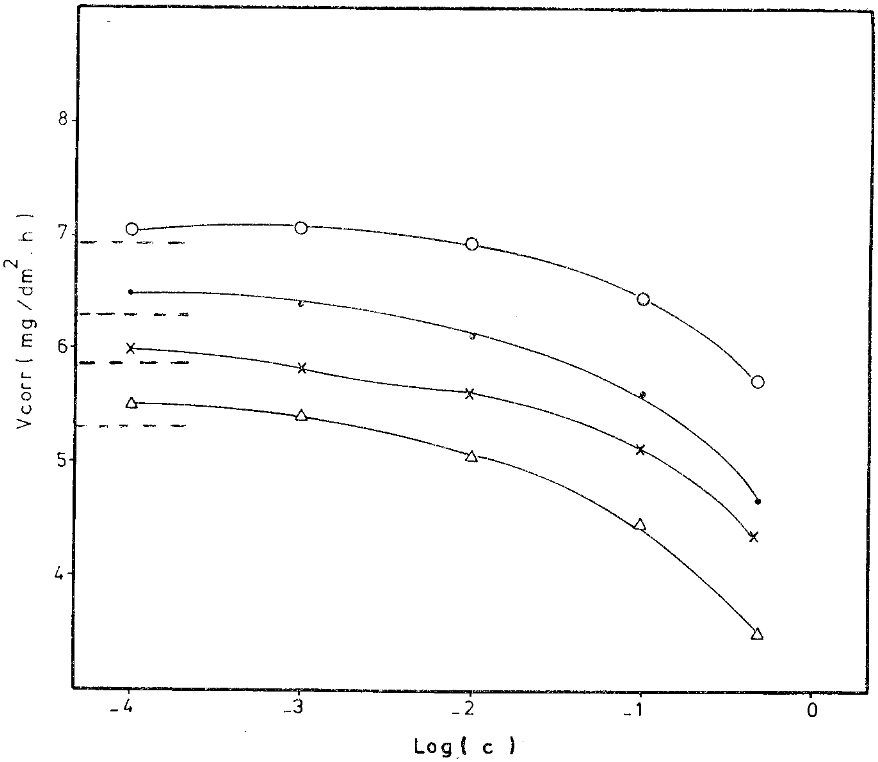

Fig. 2. Rate of corrosion of lead in Na$_2$WO$_4$ solution containing (θ 2M NaOH, ● 1M NaOH, x 0.5MNaOH and △ 0.2 MNaOH).

tion of the logarithm of the molar concentration of tungestate, for the different alkali solutions.

In this figure the steady state potentials in the corresponding free NaOH solutions are represented by dotted lines; these are taken as reference values to those obtained in presence of WO_4^{-2}. From Fig. (3) it is clear that (except in 2M NaOH) the potential decreases slightly with increase of tuntestate concentration.

Corrosion rate measurements were also carried out in the various alkali solutions, containing different tungestate concentrations. The results showed that addition of tungestate is accompanied by decrease in the corrosion rate [c.f. Fig. (2)]. In the light of Evans diagram (Bockris (1972)) the decrease of both corrosion potential and corrosion rate indicates that it is the cathodic reaction which is subjected to decelerati-

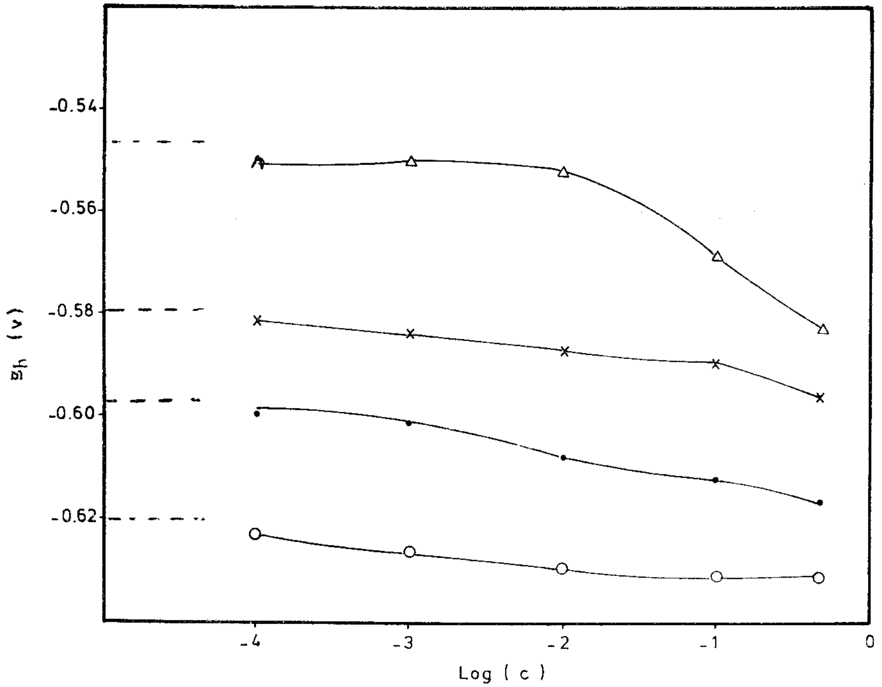

Fig. 3. Effect of concentration of Na$_2$WO$_4$ solution containing (θ 2M NaOH, ● 1M NaOH, x 0.5 M NaOH and △ 0.1M NaOH) on the potential of lead.

on. Such inhibiting action might be attributed to adsorption of tungstate ions on the cathodic centers in the oxide–free areas of the surface.

Anodic polarisation :

In order to throw light on the corrosion behaviour of lead in the tungestate solutions, anodic polarisation measurements were carried out in 0.1M NaOH containing 0.1, 0.01 and 0.001M tungestate. The results are given in Fig. (4). Polarisation was conducted within the current density range 10^{-4}–10^{-1} A / cm^2.

Generally, the polarisation curves exhibit a region of stationary potential. Which extends up to a certain current density, dependent on the tungestate concentration. The potential then exhibits a linear logarithmic relation, with a slope of about 0.03V. At higher currents, the potential shows rapid increase with the current density indicating the onset of passivity.

As obvious from Fig. (4), the polarisation curve is shifted to more negative potential with increase of the tungestate concentration. This is consistent with the results of measurements of corrosion potential [c.f. Fig. (3)]. The observed Tafel slopes are almost equal to the previously obtained for the anodic dissolution of lead in pure alkali solutions. Those results Awad, El Hady and Kamel (1986) had been taken to indicate that the metal dissolves in two successive steps as follows:

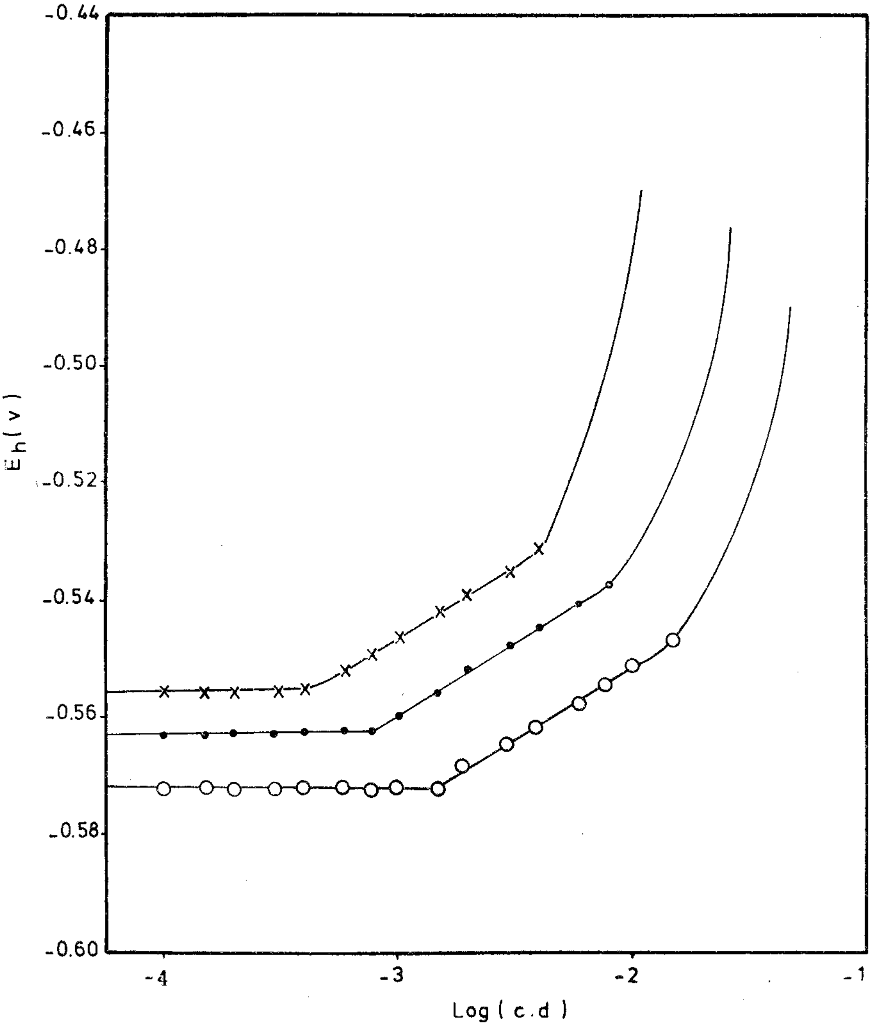

Fig. 4. Anodic polarisation of lead in 0.1M NaOH containing θ 0.1M WO_4^{-2} ● 0.01M WO_4^{-2} x 0.001M WO_4^{-2}

$$Pb + O\bar{H} \rightleftarrows PbOH + e \qquad (3)$$

$$2\ PbOH \rightarrow PbO + Pb + H_2O \qquad (4)$$

The second reaction is the rate–determining step. The observation of the same Tafel slope in the presence of tungestate, indicates that this ion does not change the mechanism of the anode reaction. However, as evident from Fig. (4), the linear logarithmic part is extended to higher currents as the tungestate concentration is increased, a fact which means that increase of WO_4^{-2} concentration delays the onset of passivity.

The onset of passivity is usually ascribed to the incomplete removal of the oxide as plumbite.

Hence, the oxide accumulates on the anode surface, leading to rapid increase of potential. Accordingly, one expects that increase of the alkali concentration (at a given tungestate content), delays the onset of passivity. Therefore, potential–current density relations were–measured in 0.1, 0.2 and 0.5M NaOH, in presence of 0.5M Na_2WO_4. As evident from Fig. (5), the current density at which the metal is passivated, increase, although slightly, with increase of the alkali concentration.

Cathodic polarisation

Cathodic polarisation measurements were carried out in 0.1M NaOH solution, in presence of 0.001, 0.01 and 0.1M Na_2WO_4, and the results are shown in Fig. (6). It is evident that the potential remains stationary within a current density range, that increases with increase of the tungestate concentration. Then the potential decreases markedly with the current density. The stationary potential decreases with increase of tungestate concentration, in good agreement with the result of Vcorr measurements [c.f. Fig. (2)].

The observed stationary potentials in Fig. (4) ranges from –0.556 to –0.572. These values are markedly less negative than the standard potential for hydrogen evolution from alkaline solution (–0.84V). Hence, the cathodic reaction is not the evolution of hydrogen. It is probable that the tungestate ions are reduced to the pentavalent state as molybdate ion which take standard potential in acid solution as 0.4V Latimer (1952), the potential in alkaline solutions amounts to –0.44V.

The observed stationary potential are comparable with this value.

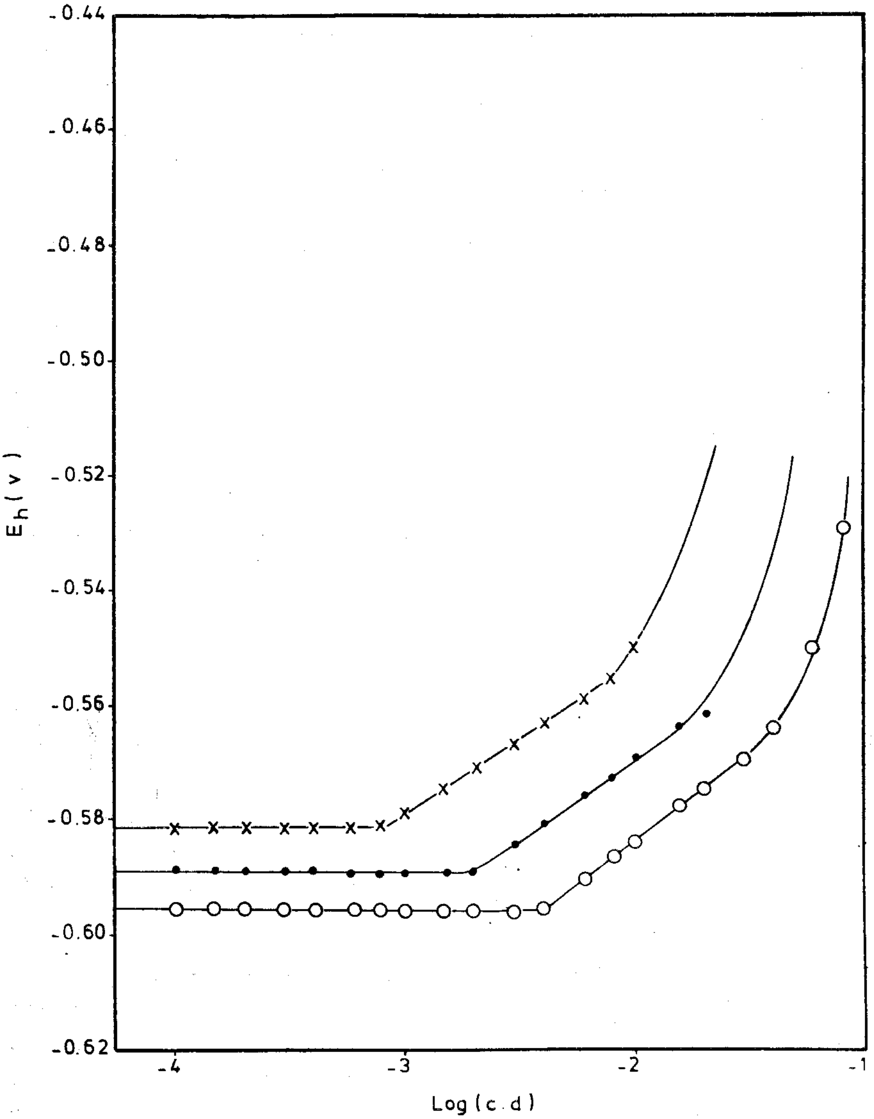

Fig. 5. Anodic polarisation of lead in 0.5M WO_4^{-2} containing θ 0.5M NaOH ● 0.2M NaOH x 0.1M NaOH.

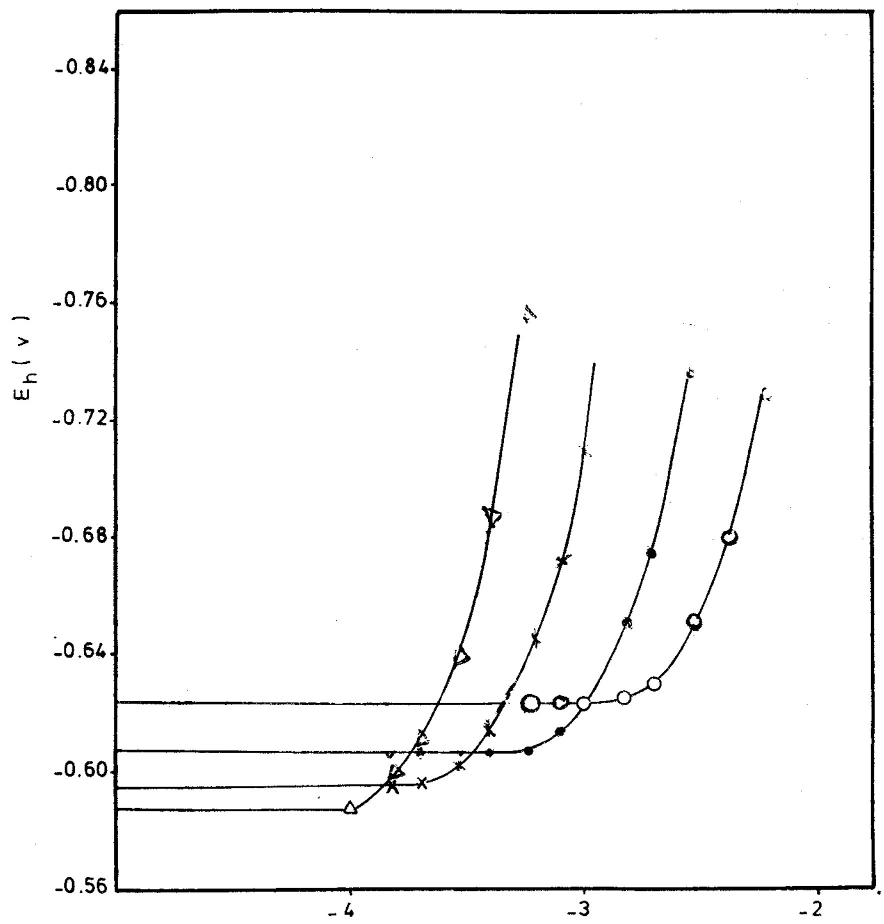

Fig. 6. Cathodic polarisation of Pb in 0.1N NaOH containing θ 0.5M WO_4^{-2} . 0.1M WO_4^{-2} x 0.01M WO_4^{-2} △ 0.001M WO_4^{-2}.

As mentioned above, (and in agreement with the corrosion potential measurements), the increase of tungestate concentration shifts the potential to more negative values. This points out that the cathode becomes less ready to deliver electrons to solution. It seems that the reduction product (containing the pentavalent state), forms with WO_4^{-2} ions a complex anion, which has higher affinity for adsorption on the metal surface. This causes the decrease of the bare cathodic areas. That is why corrosion of the metal is cathodically controlled.

Accordingly to this argument, the passivation current, at a given tungestate concentration, should increase as the alkali concentration is increased. This actually true as evident from Fig. (5) which shows polarisation curves in 0.1, 0.2 and 0.5M NaOH solutions containing 0.5M tungestate.

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