

Combination Effect of Corrosion Inhibitors of  
 $\text{Na}_2\text{CrO}_4$  and  $\text{Na}_2\text{HPO}_4$  for Mild Steel in 3% NaCl  
Solution

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( Received March 2, 1985 )

The combination effects of inhibitor of  $\text{Na}_2\text{CrO}_4$  and  $\text{Na}_2\text{HPO}_4$  in 3% NaCl solution for 0.15% carbon steel were studied by weight loss tests during ten days and electrochemical tests.  $\text{Na}_2\text{CrO}_4$  prevents the initiation of deep pits.  $\text{Na}_2\text{HPO}_4$  protects most of the steel surface from the general corrosion attack but produces localized deep pits. When  $\text{Na}_2\text{CrO}_4$  and  $\text{Na}_2\text{HPO}_4$  are added together into 3% NaCl,  $i_{corr}$  becomes smaller than that for each inhibitor. Especially, adding 10 ppm  $\text{Na}_2\text{CrO}_4$ ,  $i_{corr}$  is almost the same regardless of the concentration of  $\text{Na}_2\text{HPO}_4$  (10-100 ppm). The combination of  $\text{Na}_2\text{CrO}_4$  and  $\text{Na}_2\text{HPO}_4$  stifles the disadvantage of individual inhibitor and thus provides much effective prevention of corrosion in sufficient concentration.

## 1. Introduction

The application of corrosion inhibitors in the liquid system is one of the corrosion prevention methods. Many types of corrosion inhibitors are used and generally are divided into three types.

The anodic inhibitor is absorbed on the anodic area of the corroding metal and reduces the metal dissolution reaction. This is usually organic compounds having N, S or O atom with free (donor) electron pairs. Several kinds of anodic inhibitors which cause a large shift in the corrosion potential are called passivating inhibitor. However, they cause pitting and sometimes an increase in corrosion rate if used in insufficient concentration, thus they are also called dangerous inhibitors. The examples of

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these are sodium chromate and sodium nitrite (1).

The cathodic inhibitors reduce the exchange current density for hydrogen evolution or the exchange current density for oxygen reduction. The examples of these are  $\text{As}_2\text{O}_3$ ,  $\text{N}_2\text{H}_4$  and sulphite, which are well known as oxygen scavengers (1).

Film forming inhibitor causes the precipitation of the solid film over the cathodic area. The examples are phosphates and hydrogen carbonates ions, which interact with hydroxide ions produced by oxygen reduction in order to precipitate phosphates or carbonates film over the cathodic area.

Anodic and Cathodic inhibitors usually control the only individual reactions. However, corrosion is proceeded by both anodic and cathodic reactions, so that an individual inhibitor is not sufficient in several environments. For example, increasing the concentration of chromate ion lowers corrosion rate but does not prevent localized attack for mild steel (2). Thus, a binary combination of anodic inhibitor and film forming inhibitor is commonly used. It was reported that the phosphate-chromate inhibitors stifle the intensified corrosion or pitting (2,3). However, the degree of inhibitor effect of binary combination as a function of concentration remained unclear.

In the present work, the combination effects of inhibitors of  $\text{Na}_2\text{CrO}_4$  and  $\text{Na}_2\text{HPO}_4$  in 3% NaCl solution for mild steel were studied by weight loss and electrochemical tests.

## 2. Experimental procedure

The test material was 0.15% carbon steel fully annealed at  $910^\circ\text{C}$  for 1 hour. Chemical compositions and Vickers microhardness are listed in Table 1. The test pieces of both weight loss tests and electrochemical tests were the disk, with a diameter of 20 mm and a thickness of 5 mm. The test surfaces were polished with 1200 grade emery paper. The test piece was then degreased and cleaned. The test liquid was 3% NaCl solution (made by adding 3 wt.% NaCl to ion exchanged water).  $\text{Na}_2\text{CrO}_4$  and  $\text{Na}_2\text{HPO}_4$  as corrosion inhibitors were added into 3% NaCl by various concentrations.

Weight loss tests were carried out by fully immersing the test piece in the beaker (800 ml) of the test solution during ten days. The temperature of test solution was kept at  $20^\circ\text{C}$ . After exposure to the solution, each test piece was rinsed in water by using supersonic cleaner, dried and then the weight loss was measured with a precision balance (sensitivity of 0.01 mg).

The potentiostatic method was used in order to measure  $i_{corr}$ .

Table 1 Chemical compositions (%) and hardness

C	Si	Mn	P	S	Cu	Ni	Cr	Hardness Hv
0.15	0.25	0.47	0.015	0.013	0.14	0.04	0.18	135

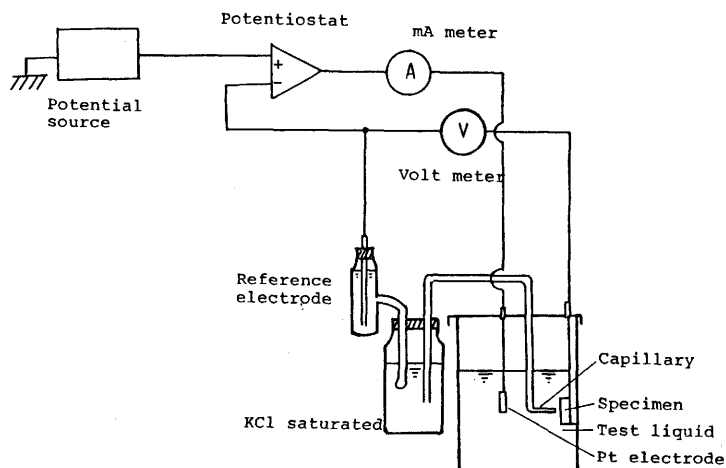


Fig.1 Test apparatus of potentiostatic method

electrochemically. Figure 1 shows the test apparatus of the potentiostatic method. The test piece was used as a working electrode, calomel as a reference electrode and Pt foil as an auxiliary electrode. The test solution was aerated by using bubbling pump during test and kept at room temperature.

A scanning electron microscope (SEM) and a Talysurf 10 surface profilometer were used to observe the corroded surface exposed to the test solutions.

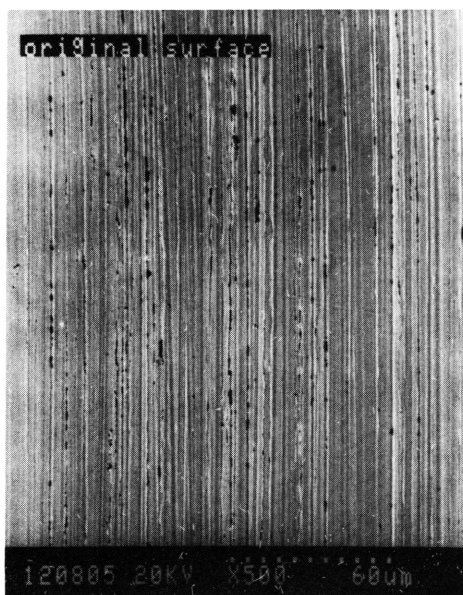
### 3. Experimental results and discussion

Figure 2 shows the SEM photographs of the corroded surface of the mild steel specimens exposed to various test solutions during ten days. Fig. (a) is a original surface before test. In 3% NaCl, general corrosion attack occurs uniformly (Fig. (b)). In 3% NaCl with 10 ppm  $\text{Na}_2\text{CrO}_4$ , the surface is slightly corroded over the

whole surface (Fig.(c)). In 3% NaCl with 100 ppm  $\text{Na}_2\text{HPO}_4$ , large pits occur but the other surface is not corroded (Fig.(d)). Fig.(e) shows the damage at the combination of 10 ppm  $\text{Na}_2\text{CrO}_4$  and 100 ppm  $\text{Na}_2\text{HPO}_4$ . The original surface can be seen and thus corrosion of the surface is negligible. From these observations, it was found that each inhibitor and combination of them stifle the corrosion in different way.

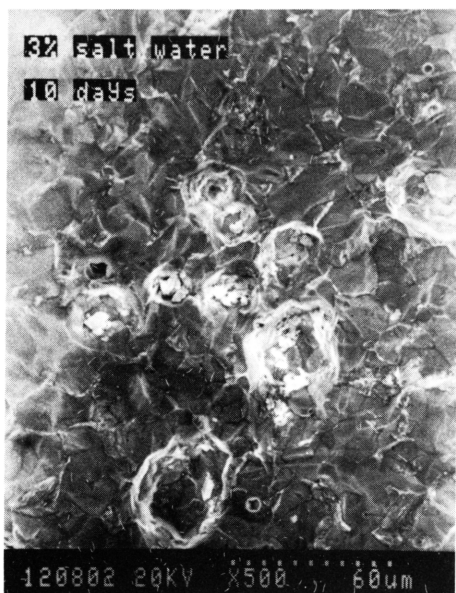
To study inhibitor effects as a function of concentration in the various test solutions,  $i_{corr}$ . of the specimens were measured by the potentiostatic method. Figure 3 shows the examples of the extrapolated curves of anodic and cathodic polarization in the various test solutions. The corrosion potential and  $i_{corr}$ . is obtained at the intersection of anodic and cathodic curves.  $i_{corr}$ . in 3% NaCl with inhibitor is smaller than that in 3% NaCl. The combination of 10 ppm  $\text{Na}_2\text{CrO}_4$  and 100 ppm  $\text{Na}_2\text{HPO}_4$  much decreases  $i_{corr}$ .

From these polarization curves,  $i_{corr}$ . are plotted as a function of the concentration of  $\text{Na}_2\text{CrO}_4$  and  $\text{Na}_2\text{HPO}_4$  in Fig.4 (a) and (b), respectively.  $i_{corr}$ . decreases sharply when only  $\text{Na}_2\text{CrO}_4$  is



(a) original surface

Fig.2 SEM photographs of corroded surface exposed to the various solutions during ten days



(b) 3% NaCl solution

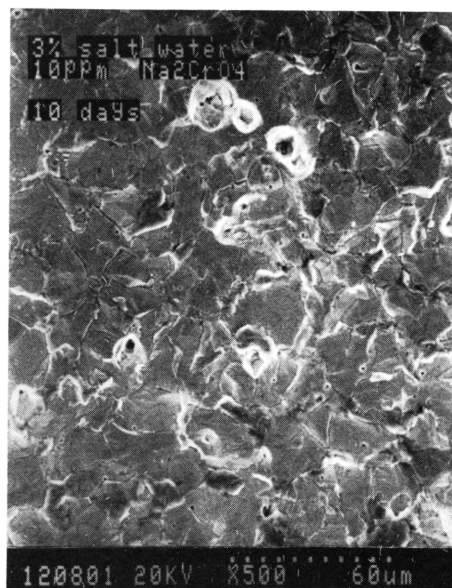
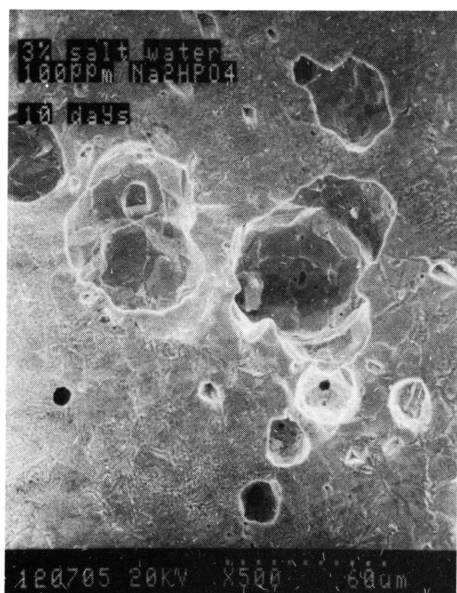
(c) 3% NaCl with  
10 ppm  $\text{Na}_2\text{CrO}_4$ (d) 3% NaCl with  
100 ppm  $\text{Na}_2\text{HPO}_4$ (e) 3% NaCl with 10 ppm  $\text{Na}_2\text{CrO}_4$   
and 100 ppm  $\text{Na}_2\text{HPO}_4$ 

Fig.2 SEM photographs of corroded surface exposed to the various solutions during ten days

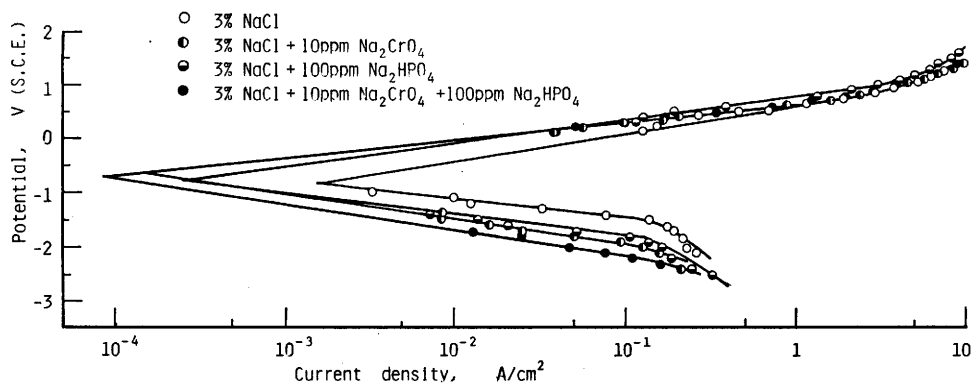


Fig.3 Polarization curves

added 1 ppm in 3% NaCl and then decreases smoothly with increasing  $\text{Na}_2\text{CrO}_4$  (Fig.4 (a)). On the other hand, the variation of  $i_{corr.}$  vs. the concentration of  $\text{Na}_2\text{HPO}_4$  shows the similar tendency as  $\text{Na}_2\text{CrO}_4$ . However, the effect of the inhibitor is smaller for  $\text{Na}_2\text{HPO}_4$  than  $\text{Na}_2\text{CrO}_4$ . When  $\text{Na}_2\text{CrO}_4$  and  $\text{Na}_2\text{HPO}_4$  are added together in 3% NaCl,  $i_{corr.}$  becomes smaller than that in each inhibitor. Especially, when 10 ppm  $\text{Na}_2\text{CrO}_4$  is added,  $i_{corr.}$  is almost the same regardless of the concentration of  $\text{Na}_2\text{HPO}_4$ . Therefore, the sufficient combination of both inhibitors is much beneficial in reducing  $i_{corr.}$ .

The corrosion rates were calculated from  $i_{corr.}$  using the relationship that 1 mdd corresponds to  $4 \times 10^{-7}$  A/cm<sup>2</sup> for  $\text{Fe} \rightarrow \text{Fe}^{2+}$ . Table 2 lists the corrosion rates for the typical four conditions, together with the results obtained by weight loss tests during ten days. Here, the inhibitor efficiency was defined as follows (4).

$$\text{inhibitor efficiency (\%)} = \frac{R_0 - R_i}{R_0} \times 100$$

$R_0$  : corrosion rate in absence of inhibitor  
 $R_i$  : corrosion rate in presence of inhibitor

Although the corrosion rates are much larger for weight loss tests than for potentiostatic method, inhibitor efficiency is almost the same between both methods except for the case in 3% NaCl with 100 ppm  $\text{Na}_2\text{HPO}_4$ . The combination of both inhibitors is the most beneficial in increasing inhibitor efficiency.

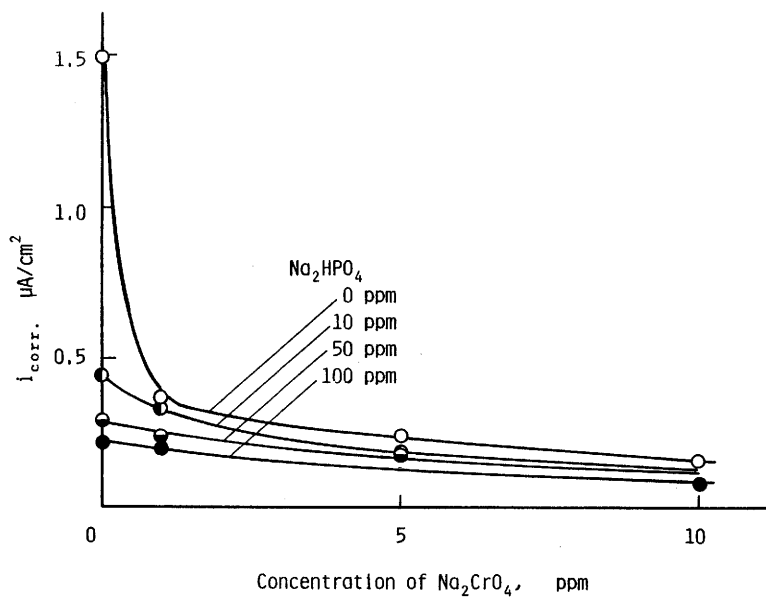


Fig.4 (a) Variations of  $i_{corr}$ . as function of concentration of  $\text{Na}_2\text{CrO}_4$

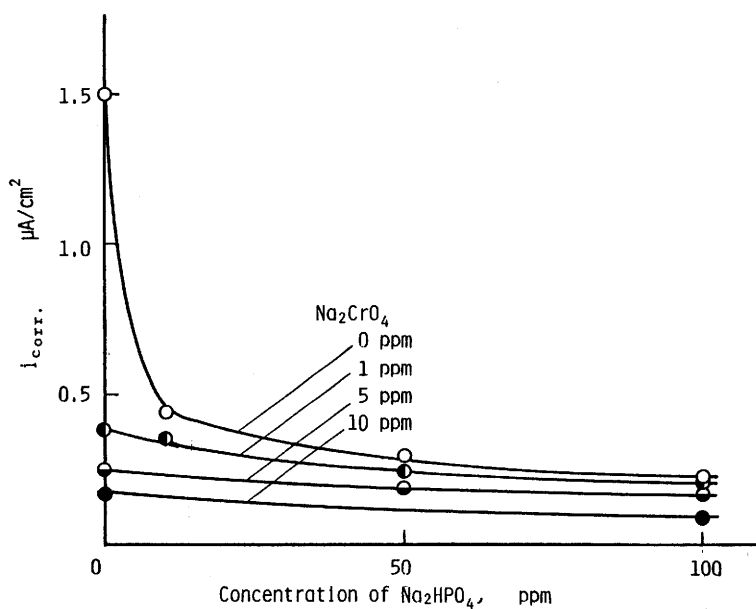


Fig.4 (b) Variations of  $i_{corr}$ . as function of concentration of  $\text{Na}_2\text{HPO}_4$

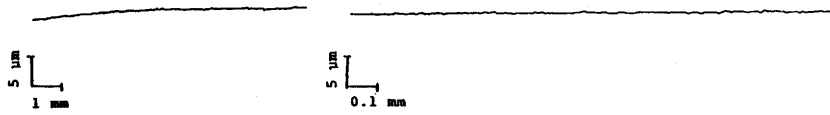
Table 2 Corrosion rates, inhibitor efficiencies and roughness of weight loss test specimens

Concentration of inhibitor (ppm)		Potentiostatic method		Weight loss test			
Na <sub>2</sub> CrO <sub>4</sub>	Na <sub>2</sub> HPO <sub>4</sub>	Corr. rate (mdd)	Efficiency (%)	Corr. rate (mdd)	Efficiency (%)	R <sub>a</sub> (μm)	R <sub>max</sub> (μm)
0	0	3.75	-	54.3	-	0.3	12.5
10	0	0.4	89.3	11.2	79.4	0.2	8.9
0	100	0.7	81.3	44.0	18.9	0.6	13.1
10	100	0.2	94.7	7.2	86.7	0.1	8.5

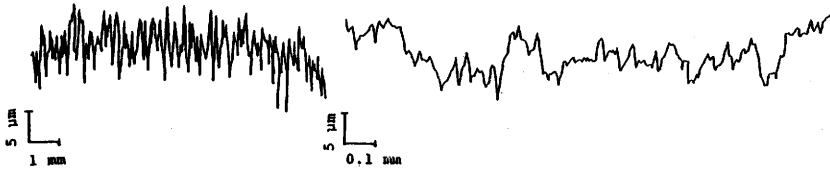
To make clear the mechanism of prevention of corrosion, the surface topographies were measured for the weight loss test specimen exposed to the test solution during ten days. Figure 5 shows the surface profiles. The profiles of right side were enlarged by ten times of those of left side in horizontal direction. The center line average roughness,  $R_a$ , and maximum roughness,  $R_{max}$ , were also measured and presented in the Table 2. In 3% NaCl, the metal surface are corroded uniformly and  $R_{max}$  of the pits are about 12 μm (Fig. (b)). In the 3% NaCl with 10 ppm Na<sub>2</sub>CrO<sub>4</sub>, the surface is slightly rough compared to that in 3% NaCl (Fig. (c)). The surface is prevented from corrosion because a considerable amount of passivative film is produced by adding CrO<sub>4</sub><sup>2-</sup> ion. However, the degree of prevention is not sufficient in this concentration. On the other hand, for the profile in 3% NaCl with 100 ppm Na<sub>2</sub>HPO<sub>4</sub>, the large deep pits, whose  $R_{max}$  is about 1.1 times larger than that in 3% NaCl, occur locally but the other surface is negligibly corroded (Fig. (d)). This is because Na<sub>2</sub>HPO<sub>4</sub> promotes the passivation due to the adsorption of oxide on the anodic area and thus most of the virgin surface is protected by passivative film. However, passive-active cell is formed locally at the area where the passivative film is incomplete, so that localized attack occurs. For the profile in 3% NaCl with 10 ppm Na<sub>2</sub>CrO<sub>4</sub> and 100 ppm Na<sub>2</sub>HPO<sub>4</sub>, general corrosion of virgin surface and initiation of deep pits are suppressed (Fig. (e)). Therefore, the combination of both inhibitors in sufficient concentration may stifle the disadvantage of individual inhibitors, so that inhibitor effect becomes remarkable.



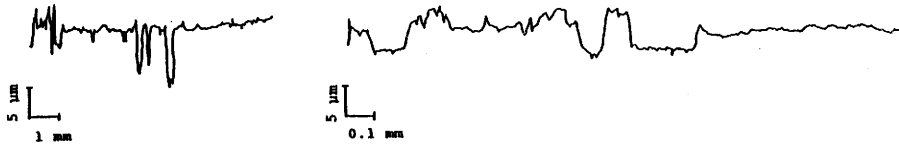
(a) original surface



(b) 3% NaCl solution



(c) 3% NaCl with 10 ppm  $\text{Na}_2\text{CrO}_4$



(d) 3% NaCl with 100 ppm  $\text{Na}_2\text{HPO}_4$



(e) 3% NaCl with 10 ppm  $\text{Na}_2\text{CrO}_4$  and 100 ppm  $\text{Na}_2\text{HPO}_4$

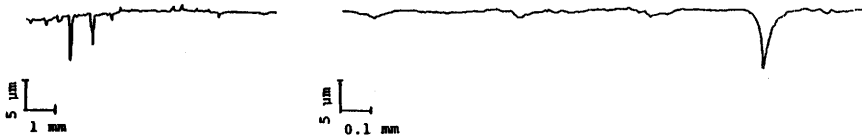


Fig.5 Profiles of corroded surface exposed to the various test solutions during ten days

#### 4. Conclusion

Inhibitor effects were studied in 3% NaCl solution for 0.15% carbon steel. The following conclusions are drawn.

- (1)  $\text{Na}_2\text{CrO}_4$  prevents the initiation of deep pits.
- (2)  $\text{Na}_2\text{HPO}_4$  protects most of the metal surface from general corrosion attack but produces deep pits.
- (3) The inhibitor effect is much larger for  $\text{Na}_2\text{CrO}_4$  than  $\text{Na}_2\text{HPO}_4$ .
- (4) The combination of 10 ppm  $\text{Na}_2\text{CrO}_4$  and 100 ppm  $\text{Na}_2\text{HPO}_4$  stifles the disadvantage of individual inhibitors and thus provides much effective prevention of corrosion damage in sufficient concentration.

#### Acknowledgments

The present study was performed in Fukui University from September 22, 1984 to December 11, 1984 as part of a joint research project on corrosion problem between LIPI (Indonesian Institute of Science) and JSPS (Japan Society for the Promotion of Science). The authors would like to express their gratitude to LIPI-JSPS and Fukui University that allowed them to do research, and also to Prof. T. Wakamatsu and Dr. Y. Nakahiro, Dept. of Mineral Science and Technology, Kyoto University, and Mr. K. Kanai, President of Kanai Gakuen, who have kindly assisted the first author. The authors are grateful to helpful suggestions of Prof. G. Kano, Dean of the Faculty of Engineering, and Dr. M. Takashima in the Dept. of Industrial Chemistry and Dr. S. Hattori and Mr. N. Maekawa in the Dept. of Mechanical Engineering, Fukui University.

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