Studies on Corrosion Inhibitor for Aluminum in Alkaline Media IV.

β -Diketones as Corrosion Inhibitors for Aluminum in Alkaline Media.

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Received Oct. 14 (1965)

The protective action of β -diketones on aluminum in alkaline media was studied through the measurement of the corrosion potentials. Benzylacetone, trifluoroacetone, 1-(2-furoyl)-3,3,3-trifluoroacetone, and 1-(2-thenoyl)-3,3,3-trifluoroacetone were used. In alkaline media of pH < 10.5, β -diketones showed a remarkable inhibitive action on aluminum. β -Diketones are considered to form aluminum chelate compounds, which covers the surface of the metal. Among β -diketones, the compounds which possess large hydrophobic and electronegative groups show higher corrosion resistivity.

1. Introduction

In an attempt to explain the mechanism of the corrosion inhibitive action of organic compounds, a physical-adsorption theory was reported by Mann¹⁾, and a chemical-adsorption theory by Hackerman²⁾. The authors of this paper have reached the conclusion that the corrosion inhibition is due to the formation of a film of a metal chelate compound on the surface of the metal by the chelating agents.

o-Hydroxyazo compounds³⁾ and 8-hydroxyquinoline derivatives⁴⁾ form hardly soluble films of metal chelate compounds on the surface of aluminum metal, and a remarkably inhibitive action is shown by them.

In this paper, the inhibition effect of some β -diketones is reported.

2. Experimentals

2.1 Specimens and Reagents

Aluminum of 99.8% purity, 0.3 mm thick and 2×3 cm in area, was treated as described in the previous paper, and used as specimen. β -diketones as listed in Table 1 were chosen as reagents, having structures capable of forming metal chelate compounds with aluminum. For comparison, methyl-n-propylketone was used as a reagent having a structure which enables it to form any chelates. All reagents used are of commercial grade.

2.2 Equipments and Measurements

The measurements of corrosion potential and corrosion current density were carried

Table 1 β -diketones (X·CO·CH₂·CO·Y)

Designation	Name	Structure		mp (°C)	bp (°C)
		X	Y		
AA	Acetylacetone	CH ₃ -	CH ₃ -	-	133
BA	Benzylacetone	C ₆ H ₅ -	CH ₃ -	57	135 (14mmHg)
TAA	Trifluoroacetylacetone	CH ₃ -	CF ₃ -	-	107
FTA	1-(2-furoyl)-3,3,3-trifluoroacetone		CF ₃ -	19	89 (14mmHg)
TTA	1-(2-thenoyl)-3,3,3-trifluoroacetone		CF ₃ -	42.5	103 (9mmHg)
M-n-P	Methyl-n-propylketone	CH ₃ ·CO·C ₃ H ₇		-	-

Table 2 Corrosion Potential.

Additive		Electrode potential of aluminum (V)			
Designation	Amount %	at pH 7	at pH 9	at pH 10.5	at pH 12
AA	0.01	-0.21	-0.66	-0.79	-1.22
	0.03	-0.46	-0.68	-0.42	-1.18
	0.05	-0.24	-0.15	-0.34	-1.17
BA	0.01	-0.12	-0.30	-0.41	-1.21
	0.03	-0.14	-0.15	-0.44	-1.23
	0.05	-0.17	-0.20	-0.44	-1.18
TAA	0.01	+0.03	-0.12	-0.74	-1.23
	0.03	-0.10	-0.12	-0.64	-1.19
	0.05	-0.17	-0.12	-0.58	-1.20
FTA	0.01	-0.13	-0.17	-0.47	-1.20
	0.03	-0.10	-0.18	-0.32	-1.26
	0.05	-0.22	-0.17	-0.24	-1.15
TTA	0.01	-0.11	-0.09	-0.36	-1.31
	0.03	-0.10	+0.04	-0.23	-1.27
	0.05	-0.12	+0.03	-0.14	-1.29
M-n-P	0.01	-0.09	-0.22	-1.41	-1.27
	0.03	-0.10	-0.19	-0.97	-1.26
	0.05	-0.15	-0.18	-0.99	-1.19
no additive	-	-0.02	-0.30	-0.80	-1.25

- S.C. Standard cadmium cell
- G Galvanometer
- P Potentiometer
- A Ammeter (μ A, mA)
- B₁ Battery (4V)
- B₂ Battery (6V)
- r₁ Variable resistance (1 k Ω)
- r₂ Variable resistance (100 Ω)
- r₃ Variable resistance (1 k Ω)
- r₄ Variable resistance (100 k Ω)
- RS₁, RS₂, RS₃ Rotary switch
- SW Switch
- C.E. Calomel electrode
- Al Specimen plate of aluminum
- Pt Platinum plate.

Fig. 1 Experimental apparatus.

out by the apparatus shown in Fig. 1.

Measurement of corrosion potential:
Using N/10 calomel electrode, a potential-time curve was obtained using the method described in the previous papers.

Measurement of corrosion current density:
3 hrs. after the immersion of the aluminum

specimen into the alkaline medium, and when the potential was almost steady, a current density-potential curve was obtained by using a platinum electrode, through the same method as described in the previous papers.

3. Results and Discussions

3.1 Corrosion Potential

The results obtained are listed in Table 2.

At pH 12: The potential was stabilized within 1 hr., but the plots of the potential showed no effect of inhibition, and especially in the case of TTA addition the plots showed the promotion of corrosion.

In this region of pH, β -diketones take enol structure and easily form chelates with the metal, while the latter is extremely soluble to form Al^{+++} ions. Metal chelate compounds are formed in the solution in the neighborhood of the metal and suspend in the solution, and thus the effect of inhibition is not observed in this case.

At pH 10.5: By the addition of β -diketones, the potential shifted to the nobler side with increasing concentration, but in the case of AA and TAA the potential shifted to the more active side. At this pH range, the addition of β -diketones was effective in inhibition of corrosion. The order of inhibitive effect from the measurement of corrosion potential was TTA>FTA>BA>AA, TAA>no addition>M-n-P.

As at this pH the metal dissolved rather slowly and the formation rate of Al^{+++} ions was very slow, the chelating agent could combine with the metal on its surface. The small effects of AA and TAA were due to the narrow area covered with them, and the effect of M-n-P was due to its adsorption.

At pH 9: By adding β -diketones the corrosion potential generally showed a little shift to the nobler side, but in the case of AA addition the potential shifted to the more active side. The order of the inhibitive effect was

TTA>FTA>TAA>BA>M-n-P>no addition, AA.

At pH 7: By adding β -diketones the corrosion potential shifted to the more active side and proved to rather promote corrosion.

3.2 Corrosion Current Density

Corrosion current densities obtained from the polarization curves are listed in Table 3.

At pH 12: By the addition of β -diketones corrosion current density was tremendously decreased but corrosion was not significantly inhibited.

At pH 9~10.5: With the presence of β -diketones the inhibition effect was very much observed. In this case the polarization was anodic but the cathodic polarization increased with increasing amount of additive. The order of the inhibitive effect was

TTA>BA, FTA>TAA, AA>M-n-P>no addition.

At pH 7: By the addition of β -diketones, the corrosion current density was increased compared with that in the case of no addition. A tight oxide film on the surface of metal may be dissolved by adding β -diketones.

Table 3 Corrosion Current Density

Designation	Additive	Corrosion current density ($\mu A/cm^2$)			
	Amount %	at pH 7	at pH 9	at pH 10.5	at pH 12
AA	0.01	2.9	2.2	3.8	120
	0.03	3.8	1.6	3.1	82
	0.05	3.9	1.6	2.7	50
BA	0.01	0.2	1.3	3.0	80
	0.03	0.4	0.8	2.0	85
	0.05	0.5	0.7	1.5	45
TAA	0.01	0.9	2.0	4.0	140
	0.03	0.9	1.4	3.9	140
	0.05	0.2	1.0	2.2	48
FTA	0.01	0.4	1.6	3.2	44
	0.03	0.5	0.6	1.3	32
	0.05	0.5	0.3	1.8	30
TTA	0.01	0.4	0.4	0.9	17
	0.03	0.2	0.3	1.4	30
	0.05	0.2	0.2	1.6	30
M-n-P	0.01	0.4	1.0	12.0	310
	0.03	0.5	1.9	6.2	220
	0.05	0.4	1.3	1.6	150
no additive	-	0.1	2.3	7.4	1350

4. Conclusion

From the results obtained by the experiments and their discussions, β -diketones were concluded to form chelate compounds with aluminum in a medium of pH 10.5, and in this way to inhibit the corrosion of aluminum in this pH range.

Literature:

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