TENSAMMETRIC STUDIES ON CORROSION INHIBITORS

Part I. Dicyclohexylamine Nitrite

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ABSTRACT

The study of adsorption by the alternating current polarographic method is known as 'tensammetry'. This technique has been extended to the study of the adsorption characteristics of organic corrosion inhibitors with a view to elucidate the mechanism of inhibition by such compounds. The usefulness of such studies in elucidating the mechanism of inhibition by dicyclohexylamine nitrite, which is now widely used as a vapour phase corrosion inhibitor, is brought out. For this purpose, results obtained by tensammetric studies have been compared with potential measurements on the one hand and direct corrosion tests on the other and discussed.

INTRODUCTION

A large number of organic compounds are known to inhibit corrosion in aqueous media.1-2 The mechanism of inhibition by these compounds has been studied by polarization measurements.3 Direct measurement of the extent of adsorption of the inhibitor on the metal surface has also been attempted.4 Direct studies on adsorption characteristics of organic corrosion inhibitors, however, involve the use of fine metal powders, the surface condition of which is generally difficult to reproduce. This difficulty may be overcome by studying the adsorption behaviour of organic compounds at the mercury surface. Among metals, mercury is unique in that it can be obtained in a highly pure chemical form and its surface characteristics are easily reproduced because of its liquid state. It is for this reason that mercury has been so widely used for the study of various metal-liquid interface phenomena including the changes in surface tension caused by capillary active substances. Electro-capillary data have been employed for the study of corrosion inhibitors.5 Purely electrochemical methods of studying adsorption using mercury surface have also been put forward. One approach that has
been made in this direction is that of Gatos based on the suppression of polarographic maximum by surface-active substances which are, otherwise, known as maxima suppressors. While this method appears to have been quite fruitful in regard to the behaviour of certain types of organic compounds having corrosion-inhibiting properties, it suffers from two important drawbacks. Firstly, the polarographic maximum is not an easily reproducible phenomenon and secondly, the mechanism of maxima suppression is not yet adequately understood. A more elegant approach to the study of adsorption of organic compounds on mercury surfaces is that of Proskurnin and Frumkin and Grahame who have made use of the capacity of the electrical double layer of mercury for following adsorption. They observed capacitance peaks when surface-active substances were desorbed at the metal-solution interface of a mercury electrode. The measurements were made by superposing a small low-frequency alternating voltage on to the direct potential applied to the electrode. Subsequently, Breyer and Hacobian and Doss and Gupta showed that the alternating current polarographic method can be used with advantage for this type of investigation. The technique consists in applying simultaneously a D.C. potential as well as a small A.C. voltage on the dropping mercury electrode of the type commonly used in polarography. The magnitude of the A.C. component of the pulsating current thus produced is a direct measure of the capacity of the electrical double layer. Percentage decrease in capacity values indicate the extent of adsorption. A new term “tensammetry” has been coined to denote studies of this kind.

The present paper deals with the relationship between adsorption measurements made in this manner, potential and polarization measurements and the corrosion inhibiting property of some inhibitors. The study has been particularly useful from the point of view of elucidating the mechanism of inhibition by dicyclohexylamine nitrite which is widely used as a vapour phase corrosion inhibitor.

**Experimental**

(a) **Compounds studied.**—(1) p-toluidine, (2) a-naphthylamine, (3) morpholine, (4) cyclohexylamine, (5) dicyclohexylamine, (6) dicyclohexylamine nitrite, and (7) sodium nitrite. Dicyclohexylamine nitrite is the active constituent of the trade product known as V.P.I. 260 and was obtained by recrystallisation from alcoholic solution of the trade product. The other chemicals were obtained from trade and used as such.

(b) **Capacity measurement.**—The method used was the same as that described in reference 10. Measurements were made in N/10 KCl solutions to which the inhibitor had been added. 0.1% solution of the inhibitor was