

Chapter II

CORROSION INHIBITORS

CHAPTER - 2

CORROSION INHIBITORS

2.1. Definition :

The terms 'inhibitor', from the Latin 'inhibere', to check or 'corrosion retardants' describe substances which retard corrosion velocity in the corrosive media. These substances can be considered, as it were, as negative catalysts in respect of corrosion processes.^{1,2} The studies on corrosion inhibitors are closely linked to the problem of passivity. In many cases inhibitors exhibit the properties of classical passivators.³ If we consider that corrosion is the degradation of a metallic material through the passage of its constitutive elements to a state of combination with surrounding materials, making particular reference to corrosion phenomena in electrolytic conductors, we can define corrosion inhibitors as substances that inhibit one or more of the partial processes of the corrosion process as a whole.

2.2. Classification of inhibitors :

Inhibitors were for a long time used exclusively in liquid media, but successful attempts have been made to add them to gaseous media in the form of volatile inhibitors, as to solid and semi-solid materials such as paint films, packing materials and protective greases.

Attempts to classify inhibitors according to their chemical composition and structure are known.^{4,5} Depending on the mechanisms of inhibitor action, it is advantageous to classify the inhibitors into various types. A number of criteria are used for this purpose. On the basis of their chemical nature, inhibitors are divided into 'inorganic' and 'organic' categories. According to the nature of their polarizing or other actions, they are classified as 'anodic', 'cathodic' and 'mixed' or as 'shielding inhibitors', 'adsorption inhibitors' and 'diffusion inhibitors'. They are divided into 'brine inhibitors', 'pickling inhibitors', 'water inhibitors', 'antifreeze inhibitors', 'volatile inhibitors' etc. depending on the corrosive medium in which they are employed. If the influence of the cathodic reaction is greater than that of the anodic, the inhibitor can be classified as 'harmless' ; if however, the influence of the inhibitor on anodic reaction is greater, then it belongs to the 'dangerous' ones. Inhibitors which decrease the rate of corrosion in some solutions, may not affect, or may even accelerate corrosion in other solutions. It should be pointed out that there is a great deal of overlapping among the various types of inhibitors. A different classification has also been presented depending on mode of action viz. into those which form a protective layer, possibly monomolecular, on the metal surface called 'Type A', and those which reduce the aggressiveness of the medium called 'Type B'.⁶

Classification of inhibitors as 'anodic' or 'cathodic' can be made on the basis of the charge on the metal surface - that is on the so-called null-charge potential on the surface of the anodic and cathodic sections of the corroding metal.^{7,8} (Ch. 5.3.5 and Ch. 5.3.6).

Owing to the exceptional diversity in the chemical nature of corrosion inhibitors and in the conditions under which they are used, a rational classification of the inhibitors is, however, quite difficult and only constitute a convenient tool for studies of a general nature.

2.3. Organic inhibitors of corrosion :

2.3.1. Introduction :

Ever since Speller⁹ reported the use of hydrochloric acid containing an organic inhibitor for cleaning out badly scaled water pipes, there has been increasing interest in the study of organic inhibitors of corrosion. Different types of organic substances, including pure chemicals, plant products, animal products, intermediates and dyes and industrial by-products, have been investigated or proposed as corrosion inhibitors since the middle ages.^{10,11} Numerous low-molecular-weight organic compounds with polar molecules, containing elements of the fifth and sixth groups of the periodic table, are in commercial use as corrosion inhibitors. Of these, compounds containing nitrogen, oxygen and sulphur are most common. There

are several comprehensive reviews of the literature on earlier work.¹²⁻¹⁹

2.3.2. Applications :

Organic inhibitors find wide application in acid pickling of metals, de-rusting, de-scaling and phosphating processes, as well as in many chemical plants and in sour oil wells. They are also extensively used in the protection of metal containers for storage and transportation of acids, cleaning of industrial plants, dissolution and removal of encrustations in heat-exchangers and evaporators and in recent times for the protection of steam boiler installations from corrosion by feed water and steam and for decontamination of nuclear reactors. More recently, volatile and vapour phase inhibitors have been finding wide application both in aqueous solutions and also in non-aqueous solvents.

There are number of other special applications of corrosion additives. Organic inhibitors are added to crude oil and to refined petroleum products transported in pipe lines. Lubricating oils usually contain a number of organic additives including agents to prevent corrosion in bearings. Corrosion inhibitors are often added to cutting oils. Oil-water emulsions are generally used as coolants for cutting tools, and the emulsifying agents added may also act as corrosion inhibitors. A list of recommended corrosion inhibitors with their fields of

application has been given by Tomashov.²⁰

2.4. Inhibitors in acid solutions :

2.4.1. Nitrogen containing inhibitors :

The nitrogen-containing inhibitors are by far the commonest, including aliphatic amines, aromatic amines,²¹⁻²⁷ cyclic imines,²⁸ products of the reaction of aldehydes with ammonia and amines,²⁹ azoles,³⁰ pyridine derivatives,³¹⁻³⁶ quinoline bases,³⁷ naphthoquinoline bases,³⁸ and quaternary ammonium salts.³⁹ The 'onium' compounds of arsenic, phosphorus and sulphur have also found application as inhibitors in acid media.^{40,41}

2.4.2. Sulphur containing inhibitors :

Organic substances containing atoms of both nitrogen and sulphur in the molecule have also found application in pickling treatments. Among these are thiourea and its derivatives substituted on the nitrogen atom with aliphatic chains or aromatic rings.⁴²⁻⁴⁹

Numerous organic substances with sulphur atoms in the molecule have been reported as inhibitors of the acid corrosion of iron and steel. Hugel⁵⁰ has tested the effectiveness of a homologous series of mercaptans, while other authors⁵¹⁻⁵⁵ devoted their attention particularly to sulfoxides. The inhibition of the acid corrosion of stainless steel has been

studied by Carassiti⁵⁶ using decylamine, quinoline, phenylthiourea and dibenzyl sulfoxide.⁵⁷

2.4.3. Oxygen containing inhibitors :

Of the oxygen containing inhibitors there are the aldehydes^{58,59} with formaldehyde being quite common, various ketones, some carboxylic acids⁶⁰ and some polyhydric alcohols.⁶¹ Other compounds that have been tested are propargyl alcohol,^{62,63} 2-butyne-1, 4-diol⁶⁴, ethynyl cyclohexanol.^{65,66} Lists of organic compounds to be used as corrosion inhibitors have been given by Gatos⁶⁷ and by Eldredge and Warner.⁶⁸ The properties desired in an inhibitor have been summarised by Warner.⁶⁹

2.5. Methods of studying inhibitors :

2.5.1. Corrosion rate measurements :

The gravimetric method which determines the weight losses of metal specimens in the corrosive medium in the presence and absence of the inhibitors, is generally used to evaluate corrosion phenomenon. This is, however, valid for generalised and uniform corrosion processes and is the method used in the present investigation for evaluation of corrosion rate for determining inhibition coefficient of a particular inhibitor. (Ch. 6.8, p. 142.)

Sometimes, depending on the nature of the corrosive system, the corrosion rates are measured by gasvolumetric procedures or through microscopic observations.

2.5.2. Electrochemical methods :

At the present time, it may be considered that the electrochemical methods form the means most widely used for the study of the behaviour of inhibitors.⁷⁰⁻⁷²

Polarization techniques have been applied to the study of inhibition in a wide variety of environments^{44,64,73-99} and these usually reveal the anodic and cathodic nature of the inhibitors, their stability on the metal surfaces and perhaps the importance of their concentration changes.

Other electrochemical techniques available to investigations on inhibition phenomena are those described in connection with the determination of the potential - dependence of the adsorption of organic compounds. Thus depression of polarographic maxima¹⁰⁰⁻¹⁰³ and depression of electro-capillary curves¹⁰⁴⁻¹⁰⁶ have been applied in order to investigate correlations between adsorption and inhibition by different workers.¹⁰⁷⁻¹¹¹ Determination of differential capacity of the double layer were carried out both on mercury electrodes¹¹²⁻¹¹⁶ and on solid electrodes¹¹⁷⁻¹²² in order to determine from

capacity lowering, the range of potentials corresponding to the adsorption of the organic inhibitors.

In the present investigation on inhibition phenomena, the effect of different oxygen and sulphur containing organic compounds in depressing the electrocapillary curve on mercury has been utilised to show that the effectiveness of certain physical inhibitors of the acid corrosion of metals is connected with the reduction of surface tension at the mercury-solution interface at the potential corresponding to the corrosion potential of the metal on the φ -scale of potentials.¹²³⁻¹²⁵
(Ch. 5.4, p. 118.)

2.5.3. Other methods :

Radiochemical methods with labeled inhibitors have made it possible to investigate the inhibition phenomena under conditions of extreme dilution and at various values of potentials imposed on the electrode.¹²⁶⁻¹³⁶ I.R.^{137,138} and U.V.^{57,73,74,139-141} spectroscopic analyses performed directly on the adsorbed products or on the substances desorbed from metallic electrodes have been found to be particularly advantageous for the interpretation of inhibition phenomena. The application of mass spectrometry^{142,143} and electron spin¹³⁷ and nuclear magnetic measurements¹⁴⁴ have been found useful for the interpretation of the action of organic corrosion inhibitors. Studies on adsorption phenomena of inhibitors by

electron microscopy⁶⁴ and by thermogravimetric analysis¹⁴⁵ have also been attempted. The various techniques that have been employed in the study of corrosion inhibitors have been reviewed by Subramanyan.¹⁴⁶

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* This type of inadvertent repetition of a few references has taken place here as well as in some other chapters of this thesis.