

# CHAPTER II

## REVIEW OF PREVIOUS WORK

## **Review of Previous Work**

### **2.1. Organic corrosion inhibitors**

Many trials have been done to protect environment from pollution and restrict usage of inorganic anti-corrosive pigments. The use of organic corrosion inhibitors in the field of surface coatings is a very useful trend. It is recently used to improve corrosion protection efficiencies of the paints, consequently, decreasing the inorganic anti-corrosive pigments content in the paints, which are expensive and toxic <sup>(161)</sup>.

*Wang et al* <sup>(162)</sup> studied weight loss of carbon steel using both 2-mercaptothiazoline and cetylpyridinium chloride as corrosion inhibitors. They found that the corrosion inhibition of low carbon steel over wide concentration range of aqueous phosphoric acid solution gives good results.

*Da-quan Zhang et al* <sup>(163)</sup> used benzotriazole (BTA), 2-mercapto-benzoxazole (MBO) and 2-mercaptobenzimidazole (MBI) as inhibitors for copper corrosion in (0.5 mol L<sup>-1</sup> HCl). The tests of weight loss measurements, potentiodynamic polarization curves and electrochemical impedance spectroscopy revealed that the (MBI) was shown to be the most effective inhibitor among those tested. It is may be due to that (MBI) has larger  $\pi$ -electron density. The obtained results of potentiodynamic polarization revealed that the three compounds act as anodic inhibitors, particularly (MBI) strongly suppressed anodic current densities

*Quraishi et al* <sup>(164)</sup> synthesized a new corrosion inhibitor namely 4-amino-3-butyl-5-mercapto-1, 2, 4-triazole (ABMT) and investigated its inhibitive performance toward the corrosion of mild steel in 1N sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) by weight loss and potentiodynamic polarization techniques. The obtained results of

potentiodynamic polarization measurements clearly reveal that the (ABMT) is a good inhibitor for mild steel.

*Adriana et al* <sup>(165)</sup> studied the inhibiting effect of 2-mercaptobenzo-thiazole (MBT) regarding the corrosion of carbon steel in diluted ammonia solution at room temperature. They demonstrated the effects of the inhibitor by using weight loss and electrochemical measurements. It was found that the increase of the inhibitor concentration leads to a decrease in the corrosion rate and in the corrosion current. Also the microscopic analysis of the surface of the carbon steel showed a decrease of the corrosion spots with the increase of the (MBT) concentration.

*Abd-El-Nabey et al* <sup>(166)</sup> used 4-amino-3H-5-mercapto-1, 2, 4-triazoline and some related compounds as corrosion inhibitors for mild steel in sulphuric acid solutions. The obtained results of polarization curves of these compounds indicated that the inhibitors act as mixed-type. Also the measurements of mass loss indicated that the rate of corrosion of mild steel rapidly increases with temperature over the range 25-60 °C both in the absence and in the presence of inhibitors.

*Hui-Long Wang et al* <sup>(167)</sup> synthesized 4-salicylideneamino-3-phenyl-5-mercapto-1, 2, 4-triazole (SAPMT), and investigated its corrosion inhibition for mild steel in 1.0 M hydrochloric acid (HCl). The obtained results revealed that (SAPMT) can be used as excellent corrosion inhibitor for mild steel in HCl solution.

*Quraishi et al* <sup>(168)</sup> synthesized three long chain fatty acid oxadiazoles namely 2-undecane-5-mercapto-1-oxa-3, 4-diazole (UMOD), 2-heptadecene-5-mercapto-1-oxa-3,4-diazole (HMOD) and 2-decene-5-mercapto-1-oxa-3,4-diazole (DMOD) in the laboratory, and evaluated their influence on the inhibition of corrosion for mild steel in 15% HCl at  $105 \pm 2^\circ\text{C}$  by weight loss method. Inhibition tests were also carried out on N-80 steel under similar

conditions in 15% HCl containing 5000 ppm of (UMOD). The obtained results indicated that the (UMOD) was found to be the best corrosion inhibitor; it exhibited 94% inhibition efficiency for N-80 steel and 72% inhibition efficiency for mild steel. The potentiodynamic polarization of (UMOD) at room temperature on mild steel in 15% HCl, and on N-80 in 15% HCl showed that all the investigated compounds are of mixed type inhibitors.

*Morales et al*<sup>(169)</sup> studied four types of inhibiting heterocyclic molecules namely {2-mercaptobenzoimidazole (MBI), 5-mercapto-1-tetrazoleacetic sodium salt (MTAc), 1-hydroxybenzotriazole (HBT) and benzimidazole (BIA)} on the corrosion susceptibility of steel pipeline samples grade API 5L X52 in 1 M H<sub>2</sub>SO<sub>4</sub> by electrochemical testing analysis. The obtained results showed that there was an optimum inhibitor concentration at which the maximum inhibiting efficiency has been occurs. Further, the (MBI) displayed the best inhibiting characteristics for this system, with maximum inhibition efficiency (IE) of approximately 99% having added only 25 ppm. It is shown that this compound can affect both the anodic and cathodic processes, thus it can be classified as a mixed-type inhibitor for API 5L X52 steel corrosion in sulphuric acid.

*Bensajjay et al*<sup>(170)</sup> tested 1-phenyl 5-mercarpto 1,2,3,4-tetrazole (PMT) as an inhibitor for the corrosion of steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 1/3 M H<sub>3</sub>PO<sub>4</sub> by weight loss and electrochemical methods. The obtained results showed that the inhibition efficiency of (PMT) increased with the increase of inhibitor concentration and reached an optimum value 98 % at 10<sup>-3</sup> M in H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> solutions.

*Quraishi et al*<sup>(171)</sup> synthesized 5-mercapto-2-Hydroxyphenyl-1-oxa-3, 4-diazole, 5-mercapto-2-phenyl-1-oxa-3, 4-diazole, and 5-mercapto-2-cinnamyl-1-oxa-3, 4-diazole in the laboratory and investigated their influence on the corrosion inhibition of mild steel in 1N HCl and 1N H<sub>2</sub>SO<sub>4</sub> by weight loss and

potentiodynamic polarization techniques. The inhibition efficiency of these compounds was found to vary with concentration.

*Lebrini et al* <sup>(172)</sup> studied a new class of thiadiazole derivatives, namely 3,5-bis(2-thienyl)-1,3,4-thiadiazole and 3,5-bis(3-thienyl)-1,3,4-thiadiazole as corrosion inhibitors for mild steel in 1M hydrochloric acid. The measurements of weight loss, polarization curves and AC impedance current methods showed that the thiadiazole derivatives were very good inhibitors for mild steel in 1 M HCl.

*Ozcan et al* <sup>(173)</sup> studied the influence of thioacetamide, thiourea and thiobenzamide on the corrosion inhibition of mild steel in 0.1M H<sub>2</sub>SO<sub>4</sub> solution. They suggested that the (-CS-NH<sub>2</sub>) group is the common main group for these compounds and they differ only having different groups on the other side of the thiocarbonyl group. The results of electrochemical impedance spectroscopy and polarization resistance measurement techniques showed that these compounds revealed a good corrosion inhibition.

*Lgamri et al* <sup>(174)</sup> investigated the effect of organic compounds containing heteroatoms such as nitrogen and sulphur on the corrosion behaviour of iron. The recorded electrochemical data showed that the corrosion resistance was greatly enhanced in the presence of inhibitor; it acts on both anodic and cathodic electrochemical processes and its effect depended on its concentration. These results were confirmed by the impedance tests where it was observed that the effect of inhibitor addition appears by an increase in the corrosion resistance.

*Quraishi et al* <sup>(175)</sup> synthesized a new corrosion inhibitor namely 4-salicylideneamino-3-hydrazino-5-mercapto-1,2,4-triazole, and studied its influence on the corrosion inhibition of tubular steel (N-80) and mild steel in 15% hydrochloric acid solution under boiling condition by using weight loss method. The obtained results of potentiodynamic polarization clearly revealed

that the investigated inhibitor may inhibit the corrosion of both the steels by blocking the active site of the metal.

*Fouad et al* <sup>(176)</sup> studied the effect of isomers of 3-pyridyl-substituted 1,2,4- and 1,3,4-thiadiazoles (3-PTHD and 3-PTH) on the corrosion inhibition of mild steel in acidic media (1M HCl and 0.5M H<sub>2</sub>SO<sub>4</sub>) by using weight loss measurements and electrochemical techniques. It was found that the (3-PTHD) was the best inhibitor in both media, and its behaviour is better in 1M HCl than in 0.5M H<sub>2</sub>SO<sub>4</sub>.

*Hui-Long Wang et al* <sup>(177)</sup> investigated the effect of some mercaptotriazole derivatives containing different hetero atoms and substituents in the organic compounds on the corrosion and hydrogen permeation of mild steel in 1.0 M HCl by weight loss and various electrochemical techniques. The obtained results revealed that all the mercaptotriazole derivatives performed excellently as corrosion inhibitors for mild steel in 1.0 M HCl. Also the potentiodynamic polarization studies showed that all these compounds suppress both the anodic and cathodic process and they behave as mixed-type inhibitors.

*Garcia-Ochoa et al* <sup>(178)</sup> investigated the effect of 3-amino-1, 2, 4-triazole as a corrosion inhibitor for mild steel in acidic media by means of potentiodynamic polarization curves and electrochemical impedance spectroscopy. It was found that this compound inhibits mild steel corrosion by affecting both cathodic and anodic reactions.

*Tan et al* <sup>(179)</sup> studied the effect of substituted benzenethiol (BT) molecules, X-C<sub>6</sub>H<sub>4</sub>-SH (where X = meta-NH<sub>2</sub>, ortho-NH<sub>2</sub>, para-NH<sub>2</sub>, para-NHCOCH<sub>3</sub>, para-F, para-CH<sub>3</sub> and para-CH(CH<sub>3</sub>)<sub>2</sub>), as corrosion inhibition on the modified Cu surfaces in a sulfuric acid solution by electrochemical characterization. They found that the protection afforded by the substituted

functional groups on BT is strongly influenced by the type and the position of the substituents on the benzene ring.

*Zheludkevich et al*<sup>(180)</sup> evaluated 1, 2, 4-triazole, 3-amino-1, 2, 4-triazole, benzotriazole and 2-mercaptobenzothiazole as corrosion protection of the aluminum alloy in neutral chloride solutions. They found that the corrosion protection to the alloy performed by forming a thin organic layer on the substrate surface, and the inhibitors decreasing the rate of both the anodic and cathodic processes. The obtained results showed that the benzotriazole and 2-mercaptobenzothiazole offer better corrosion protection in comparison with 1, 2, 4-triazole, 3-amino-1, 2, 4-triazole.

*Chetouani et al*<sup>(181)</sup> studied the effect of corrosion inhibition of new synthesized pyridazine compounds on pure iron in 1M HCl by weight loss, electrochemical polarization and electrochemical impedance spectroscopy measurements. The obtained results revealed that these compounds are efficient inhibitors. It was found that the inhibition efficiency increases with the increase of inhibitor concentration and reached 98% at  $10^{-4}$  M for 5-benzyl-6-methyl pyridazine-3-thione. Also the results of potentiodynamic polarization clearly revealed that the presence of pyridazines does not change the mechanism of hydrogen evolution and that they act essentially as cathodic inhibitors.

*Awad et al*<sup>(182)</sup> investigated the effect of alkyl and aryl substituents in triazoline compounds on the corrosion inhibition efficiency. They suggested that the adsorption of the sulphur-containing inhibitors to the surface occurs through the C-S centre. It was showed that the aryl-substituted triazoline are more reactive inhibitors than the alkyl ones; this may be due to smaller energy separation between the highest occupied molecular orbital-lowest unoccupied molecular orbital levels. And the electrophilic group showed the highest charge density on the sulphur atom and the highest protection efficiency due to its polar interaction with a metal surface.

*Popova et al*<sup>(183)</sup> investigated five heterocyclic compounds, having a five atom ring, fused with the benzene ring (indole, benzimidazole, benzotriazole, benzothiazole and benzothiadiazole), as corrosion inhibitors for mild steel in 1 N HCl by using impedance and polarization resistance methods. It was found that four of these compounds exhibit inhibition properties, while one of them, benzothiadiazole, stimulates the corrosion process.

*Bouklah et al*<sup>(184)</sup> studied the influence of 5-(2-chlorobenzyl)-6-methylpyridazine-3(2H)-thione (P1) and 5-(4-chlorobenzyl)-6-methylpyridazine-3(2H)-thione (P2) on the corrosion of steel in 0.5M H<sub>2</sub>SO<sub>4</sub> solution by using weight loss measurements at various temperature. They found that the inhibiting action is more pronounced on using (P1) than (P2). And the inhibition efficiency increases with (P2) concentration to attain the maximum value of 100% at  $5 \times 10^{-4}$  M.

*Cruz et al*<sup>(185)</sup> studied the effect of 1-(2-ethyl-amino)-2-methylimidazoline (imidazoline), N-[3-(2-amino-ethylaminoethyl)]-acetamide (amide) and its derivative 1-(2-ethylamino)-2-methyl-imidazolidine (imidazolidine), as corrosion inhibitors by using potentiodynamic polarization curves and electrochemical impedance spectroscopy techniques. The experimental results suggested that (imidazoline) is a good corrosion inhibitor at different concentrations whereas (amide) showed low efficiency values. The theoretical results indicated that imidazoline is the more efficient corrosion inhibitor because of its two very active sites (two nitrogen atoms) and the plane geometry of the heterocyclic ring, thus promoting coordination with the metal surface.

## **2.2. Anti-corrosive pigments**

*Blustein et al*<sup>(186)</sup> studied the properties of three anti-corrosive inorganic phosphate pigments in solvent-based and water-borne paints. They investigated the behaviour of these pigments in anti-corrosive paints formulated with different

binders, by accelerated (salt spray cabinet and humidity chamber) and electrochemical tests (corrosion potential and ionic resistance measurements). It was found that the accelerated and electrochemical tests allowed to differentiating the anti-corrosive performance of the three pigments.

*Amirudina et al*<sup>(187)</sup> investigated the inhibition efficiencies of zinc chromate, barium metaborate, calcium silicate, amino carboxylate, calcium barium phosphosilicate, aluminum triphosphate and a modified zinc phosphate on the corrosion of steel and zinc by using polarization experiments. They found that zinc phosphate and zinc chromate gave the best inhibition efficiencies.

*Kalendova et al*<sup>(188)</sup> studied the properties of non-toxic anti-corrosion pigments of varying chemical composition such as (zinc phosphate, zinc phosphate modified with an organic corrosion inhibitor, zinc–aluminum polyphosphate, calcium metaborate, calcium ferrite, and strontium chromate) in epoxy ester paints. They prepared two types of paints, the first type comprised an anti-corrosion pigment with a pigment volume concentration (PVC) of 10% while the other type comprised an anti-corrosion pigment with a PVC = CPVC (critical pigment volume concentration). Anti-corrosion efficiency was derived from tests in a salt spray cabinet and chemical resistance of pigmented coatings. The evaluation of anti-corrosion efficiency of inorganic non-metal pigments was carried out by means of comparison with anti-corrosion efficiency of metal dust.

*Feliu et al*<sup>(189)</sup> studied the effectiveness of chromate and phosphate that accompany lacquer as corrosion inhibitors for hot galvanized steel by using continuous immersion tests in 3% NaCl and ultra-violet (UV) tests in a climate cabinet, electrochemical impedance spectroscopy (EIS) techniques. The obtained results showed that the rapid loss of adhesion of the lacquer/phosphating reagents system during the (UV) test, due to water adsorption phenomena at the metal/lacquer interface as a result of the presence of soluble species in it.

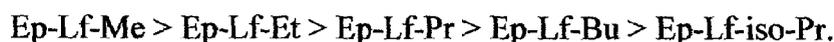
*Amo et al* <sup>(59)</sup> studied anti-corrosive paints formulated with zinc phosphate and vinyl binders. The anti-corrosive performance of the paints evaluated by using accelerated tests (salt spray and humidity chambers) as well as film adhesion and electrochemical measurements. The obtained results were compared with a reference paint containing zinc chromate. It was established that paints formulated with an acid resin, containing 30% zinc phosphate by volume and a PVC/CPVC ratio of 0.8-0.9 showed good anti-corrosive behaviour.

### **2.3. Inhibitors in water-borne coatings**

*Badran, B.M. et al* <sup>(190)</sup> used the reaction products of epoxidized fatty materials with aliphatic amines as corrosion inhibitors for carbon steel in HCl solution. They found that the efficiency of the prepared adducts increased by decreasing the aliphatic chain length of the used amines, and their efficiencies were found to be in the order: Methylamine > Ethylamine > Butylamine.

*El -Sawy et al* <sup>(191)</sup> studied the adducts resulted from the reaction of the epoxydized linseed oil free fatty acids (Ep-Lf-) with different aliphatic amines (methyl, ethyl, propyl, iso-propyl and butyl amines) as corrosion inhibitors for carbon steel. They found that the optimum concentration ranges of methyl adduct and butyl adducts as corrosion inhibitors are the same and equal to 0.4-0.7 %.

It was found that the protective action of the prepared inhibitors decreases by increasing branching of the alkyl groups, so their protective properties can follow the descending order:



*Badran, B.M. et al* <sup>(192)</sup> investigated the performance of emulsified corrosion inhibitors of different amines with epoxidized soybean oil in various water-borne coating systems. The superior corrosion protection performance of such organic inhibitors to the anti-corrosive pigments emphasized their reliability

as alternatives to the toxic anti-corrosive pigments in formulating water-borne anti-corrosive paints.

*Zhigiang* <sup>(193)</sup> found that emulsion alkyd coatings including imidazolidinone organic inhibitors showed an outstanding corrosion protection behavior for phosphated cold rolled steel after 200 hours of exposure in salt spray tests.

*Müller, B. et al* <sup>(194)</sup> used amino-phenols in inhibiting zinc pigments reactions occurring in aqueous alkaline media. They concluded that the addition of such organic inhibitors could prevent hydrogen evolution from zinc reaction, and hence better pigment stability was observed.

*Braig* <sup>(195)</sup> demonstrated the performance of Schiff's base as an organic corrosion inhibitor in water-borne acrylic coatings. The good results of such coatings observed during accelerated tests were attributed to the complete surface coverage of the adsorbed inhibitor at the metal/coating interface.

*Jackson* <sup>(146)</sup> investigated the performance of water-borne epoxy coatings employing different types of anti-corrosive pigments and blends of organic inhibitors (zinc salt of nitro-compound). The accelerated corrosion results showed that the best performance was obtained with calcium-strontium-phosphosilicate pigment and a blend of zinc phosphate and organic nitro-compound respectively.

*Paradini et al* <sup>(196)</sup> studied the performance of chestnut tannin, which contains polyphenols of vegetable origin, as a corrosion inhibitor in water-borne acrylic paint applied over rusted steel surfaces. The superior performance of such coatings during exposure was ascribed to the formation of a passivation layer of ferric tannate on iron surface. Similar results were obtained by

*Favre, M. et al*<sup>(197)</sup>, which formulated water-borne coatings with gallic acid as a corrosion inhibitor over rusty surfaces.

*Smiezek, E. and coworkers*<sup>(198)</sup> studied the effectiveness of mercapto-benzothiazole corrosion inhibitor in alkyd and acrylic emulsion coatings. The accelerated corrosion tests showed competitive performance to their solvent based counterparts.

*Badran, B.M. et al*<sup>(199)</sup> studied the replacement of anti-corrosive pigments, which are expensive and hazardous to the environment, by some new aromatic amine adducts as corrosion inhibitors in different paint formulations. The amine adducts (Ep-Lf-Ar) are prepared by the reaction of epoxidized linseed oil-free fatty acids (Ep-Lf) with some aromatic amines (-Ar) (aniline, o-, m-, p-anizidine, o-, m-, p-toulidine and o-,m-,p-chloroaniline) stoichiometric amounts. The efficiency of the prepared adducts could be arranged in the following sequence:

Ep-Lf-p-Az > Ep-Lf-m-Az > Ep-Lf-p-T > Ep-Lf-o-Az > Ep-Lf-m-T >  
Ep-Lf-o-T > Ep-Lf-An > Ep-Lf-p-Cl > Ep-Lf-m-Cl > Ep-Lf-o-Cl.

#### **2.4. Emulsion and emulsifier**

*Porrás et al*<sup>(200)</sup> prepared water-in-oil emulsions (water/mixed non-ionic surfactant/oil), and studied the emulsions formed by a condensation method. It has been proved that mixtures of surfactants as Span 20, Span 80, Tween 20 and Tween 80 can provide better performance than pure surfactants.

*George*<sup>(201)</sup> studied the effect of the addition of low molecular weight surfactants on the coalescence stability of emulsions stabilized by the protein b-lactoglobulin. It was found that only Span 80 able to displace the protein from the droplet interface, this lead to coalescence by spontaneous rupture of thin films between the emulsion droplets. He suggests that this mechanism of

coalescence is only enhanced if the adsorbed protein layer is displaced by a surfactant, another mechanism for coalescence in highly concentrated protein-stabilized emulsions, was reduced after the addition of sodium dodecyl sulphate (SDS) and Tween 20.

*Takahiro et al* <sup>(202)</sup> prepared water-in-oil-in-water (W/O/W) emulsions. He used polyoxyethylene sorbitan monolaurate (Tween 20) in the external water phase to stabilize oil droplets containing water droplets. And sorbitan monolaurate (Span 20), sorbitan monooleate (Span 80) and tetraglycerol polyricinoleate (TGPR) were tested as surfactants to stabilize the W/O emulsions. W/O/W emulsions were produced when using oleic acid or triolein as the oil phase and TGPR as the surfactant, while W/O/W emulsions could not be produced using Span 20 or Span 80 due to large water clusters and the low stability of the W/O emulsions.

*Chong et al* <sup>(203)</sup> prepared W/O/W multiple emulsions by using non-ionic surfactants of the Tween and Span types. The effect of droplet size and emulsion stability was investigated. It was found that the combination of (Tween 20/80 and Span 20/80) as a hydrophilic and lipophilic surfactant system produced the most stable multiple emulsion.

*Jeonghee et al* <sup>(204)</sup> studied the influence of pH on the stability of sodium caseinate stabilized oil-in-water emulsions by measuring particle size, microstructure, apparent viscosity, and creaming stability. It was found that the emulsions containing droplets stabilized by sodium caseinate (CAS) were prepared by homogenizing 10 wt% corn oil with 90 wt% aqueous CAS solution (1.0 wt%, pH 7.0).