1. Introduction

1.1. The history of packaging science

Millions of years ago people hunted for food and ate it at once. Soon they realized they could keep their food longer if they protected it, so they made packets from animal skins and large leaves, and kept water in containers made from coconut shells and dried vegetable skins. Today, we use lots of different packaging and containers to keep food and drink clean and fresh, so we don't waste it.

At Egyptian and Roman times, containers were being made of clay and other materials. Later, glass, metal and paper were introduced. In Victorian times, butter and cheese were kept in baskets, vinegar in barrels, and tea in chests and grain in sacks.

The first can was developed to solve the problem of keeping food fresh for the troops during the Napoleonic Wars. In 1795, Napoleon offered a prize to anyone in France who could come up with an idea which would keep food safe for his soldiers. Nicholas Apart, a chef from Paris, took up the challenge and invented a method of preserving food by heating it in a sealed container. Meanwhile, scientists in England discovered that steel covered with a very fine layer of tin, made an ideal packaging material to keep food fresh. By the Second World War, the steel can looked like cans we have today. It was lighter than the original version, opened at the end of a can opener, and contained a wide variety of foods – from spaghetti, mushy peas and pilchards, to sardines, evaporated milk and soft drinks. The space age brought new challenges. Food for astronauts not only needs to be tasty and crumb-free, but also light - which led to the discovery that freeze-drying foods such as meat and vegetables *reduces their weight. A special non-spill drinks can made from steel was also developed for space, fitted with a special mouthpiece which closed once the astronaut had drunk enough.*

Nowadays, packaging may be very different, but its main functions are still to make food and other products easy to transport, and to protect it until we are ready to eat or to use, which reduces the amount we waste. After the nano technology revolution; the polymer-inorganic nanocomposites, when applied as coating materials, are expected to improve the barrier properties without sacrificing the mechanical and the thermal properties, and thus solve one of the most challenging problems existing in current food and beverage packaging using paper barrier coating. Furthermore, a stable polymer composite suspension in an aqueous form has many other advantages such as better environmental concern, easier manipulation and better energy saving.; nano polymer composite of protective coatings and suitable packaging by the food industry has become a topic of great interest because of their potentiality for increasing the shelf life of many food products (Ahvenainen, 2003; Coles, McDowell, & Kirwan, 2003; Giles & Bain, 2001; Hernandez, Selke, & Cultler, 2000), and their mechanical and barrier properties.

Nanoparticles photo semiconductors were suggested for use in food package, after appropriate embedding within, or depositing them on a thin carrier foil [1,2,3,4]*. One also could use this concept in antimicrobial foils for sterilization purpose in medicine as plasters and bandages, to reduce the incidence of bacteria and viruses in wounds and to suppress the growth of fungi. Sunlight as well as indoor fluorescence UV lamps are sufficient to activate the antimicrobial efficiency. The strong UV absorption with* *simultaneous transparency for visible light makes thin layers of such photo semiconductors, embedded in a suitable carrier foil, useful to prevent sunburn of surfaces of fruits and vegetables which otherwise would damage the fruit tissue and lead to the development of disease symptoms* [5].

1.2.Nanotechnology

Nanotechnology is the science of the small; the very small. It is the use and manipulation of matter at a tiny scale. Generally nanotechnology deals with structures of the size 100 nanometers or smaller, and involves developing materials or devices within that size (One nanometer (nm) is one billionth i.e.; 10^{-9}*, of a meter). At this size, atoms and molecules work differently, and provide a variety of surprising and interesting uses. A nanometer is a billionth of a meter, or to put it comparatively, about 1/80,000 of the diameter of a human hair. Nanotechnology should not be viewed as a single technique that only affects specific areas. It is more of a 'catch-all' term for a science which is benefiting a whole array of areas, from the environment, to healthcare, to hundreds of commercial products. Although often referred to as the 'tiny science', nanotechnology does not simply mean very small structures and products. Nanoscale features are often incorporated into bulk materials and large surfaces.*

Nanotechnology has the potential to create many new materials and devices with wide-ranging applications, such as in medicine, electronics, and energy production.

1.2.1.Nanocomposite polymer[6]

In materials research, the development of polymer nanocomposites is rapidly emerging as a multidisciplinary research activity whose results could broaden the applications of polymers to the great benefit of many different industries. Polymer nanocomposites (PNCs) are polymers (thermoplastics, thermosets or elastomers) that have been reinforced with small quantities (less than 5% by weight) of nano-sized particles having high aspect ratios (L/h >300) (Denault and Labrecque, 2004).

PNCs represent a radical alternative to conventional filled polymers or polymer blends – a staple of the modern plastics industry. In contrast to conventional composites, where the reinforcement is on the order of microns, PNCs are exemplified by discrete constituents on the order of a few nanometers. The value of PNC technology is not solely based on the mechanical enhancement of the neat resin nor the direct replacement of current filler or blend technology. Rather, its importance comes from providing value-added properties not present in the neat resin, without sacrificing the resins inherent processibility and mechanical properties, or by adding excessive weight. PNCs contain substantially less filler (1-5 vol %) and thus enabling greater retention of the inherent processibility and toughness of the neat resin (Vaia and Wagner, 2004).

There are three main material constituents in any composite: the matrix, the reinforcement (fiber), and the so-called interfacial region. The interfacial region is responsible for communication between the matrix and filler and is conventionally ascribed properties different from the bulk matrix because of its proximity to the surface of the filler (Vaia and Wagner, 2004).

In almost every case, nanoparticles are added to the matrix or matrix precursors as 1-100 µm powders, containing an association of nanoparticles.

Polymer/layered nanocomposites in general, can be classified into three different types, namely (i) flocculated nanocomposites, (ii) intercalated nanocomposites, and (iii) exfoliated nanocomposites (see figure 1.1) (Wypych and Satyanarayana, 2005; Ray and Okamoto, 2003).

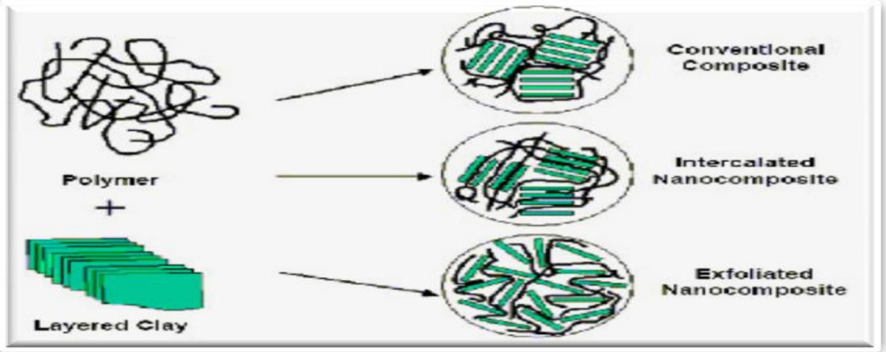


Figure (1.1): *Polymer-layered nanocomposites (Denault and Labrecque, 2004).*

1.2.2.Nanoparticles, Methods of preparation[6]

Nanoparticles are obtained from available natural resources and generally they need to be treated . The poor physical interaction between the organic and the inorganic components leads to poor mechanical and thermal properties. In contrast, strong interactions between the polymer and the inorganic particles nanocomposites lead to the organic and inorganic phases being dispersed at the nanometer level. As a result, nanocomposites exhibit unique higher properties than conventional composites .

Solids with nanosize particle size cannot be prepared or treated by traditional methods simply because the reactants are not mixed on the atomic scale. . All the alternative methods, e.g., hydrothermal, sol-gel, Pechini, chemical vapor deposition, and microwave, address this problem by achieving atomic scale mixing of reactants, in gas, liquid, or even solid phases. Most of these are low temperature methods, although finally firing may be required at high temperatures especially for ceramic-type products.

1.2.3Techniques of nanocomposite formulation[6]

1.2.3.1 In situ intercalative polymerization

Polymer is formed (initiation of polymerization by heating or radiation or by diffusion) between the layers by swelling the layer hosts within the liquid monomer or monomer solution (see figure 1.2).

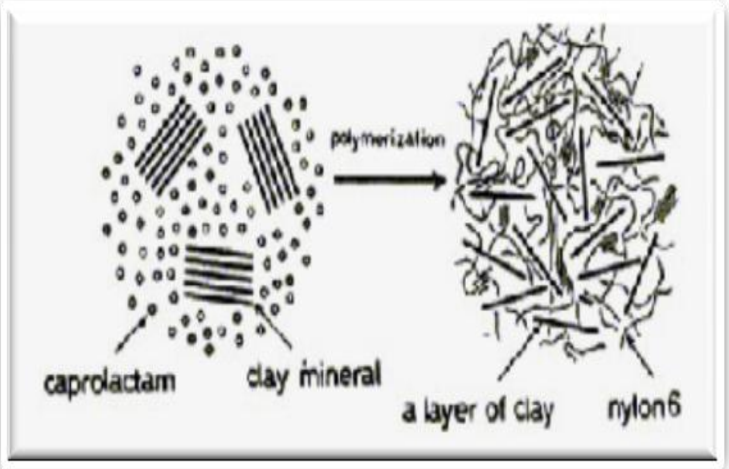


Figure (1.2): *Schematic illustration for synthesis of Nylon-6/clay nanocomposites (Ray and Okamoto, 2003).*

1.2.3.2 Melt intercalation

This method, an environmentally benign one, uses all types of polymers as well as being compatible with practicing polymer industrial processes such as injection molding, being the most popular procedure to prepare nanocomposites for industrial applications. In this method, polymers, and layered hosts are annealed above the softening point of the polymer (see figure 1.3).

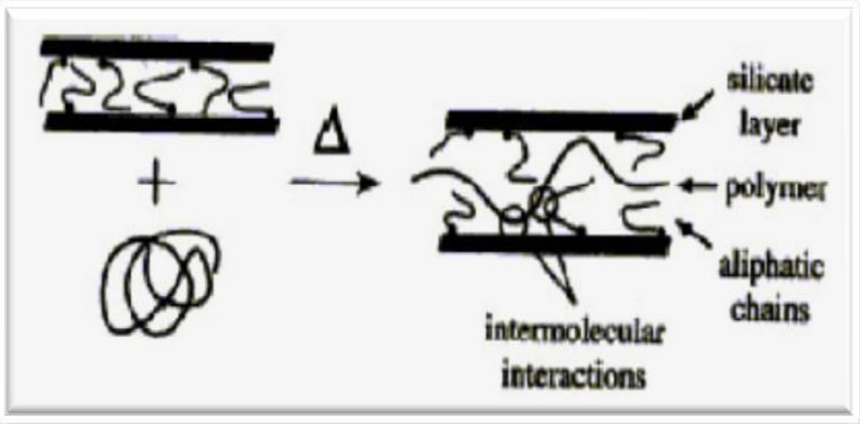


***Figure (1.3)**: Schematic depicting the intercalation process between a polymer melt and an organic modified layered silicate (Ray and Okamoto, 2003).*

1.2.3.3.Template synthesis

In situ layered double hydroxide (LDH) based nanocomposites can be obtained in a template of polymer aqueous solution for the formation of host layers and usually employed for water-soluble polymers.

1.2.3.4.Intercalation of prepolymer from solution

The layered host is to be swelled in a solvent (water, toluene ,etc.) followed by its mixture with polymer or prepolymer, whereby the chains of the latter intercalate while displacing the solvents used for swelling. Polymer layered nanocomposite results when the solvent within the interlayer is removed.

1.3. corrosion

1.3.1.Simplified theory of corrosion

Corrosion may be defined as the destruction of metal by chemical or electrochemical reaction with its environment . Most of the common metals are unstable , or chemically active in some environments and tend to revert to more stable combinations . The metallic ores are familiar examples of these stable combination .

Ordinary , iron and steel corrode in the presence of both oxygen and water , and corrosion usually does not take place in the absence of either of these . Rapid corrosion may take place in water , the rate of corrosion is accelerated by the velocity of the acidity of the water , by motion of the metal , by an increase in temperature or aeration , by the presence of certain bacteria , and by other less prevalent factors . On the other hands corrosion is generally related by protective layers (or films) consisting of corrosion products or absorbed oxygen , high alkalinity of the water also retards the rate of corrosion . Water and oxygen, however are almost always the essential factors and the amount of corrosion is controlled by one or the other . For instance, *corrosion of steel does not occur in dry air and is negligible when the relative humidity of the air is below 60 % . At normal or lower temperature prevention of corrosion by dehumidification is based upon this fact. As a matter of fact, water on the other hand , readily takes a small amount of oxygen from the atmosphere , for example into solution and oxygen may become highly corrosive . When the free oxygen dissolved in water is removed , the water is practically became non corrosive unless it becomes acidic or unless an aerobic bacteria incite corrosion . If oxygen free water maintained neutral or slightly alkaline , it will be non-corrosive to steel . Thus steam boilers and water supply systems are effectively protected .*

1.3.2.The chemistry of corrosion reactions[6]

Corrosion reactions are electrochemical in nature. They involve the transfer of charged ions across the surface between a metal and the electrolyte solution in which it is immersed. There are two types of electrode reaction occurring at the metal surface: anodic and cathodic .

Anodic reactions involve oxidation: electrons appear on the right hand side of the equation. For example metallic iron can produce ferrous ions by the anodic reaction:

$$Fe \rightarrow Fe^{+2} + + 2e^{-} \ (1)$$

In a solution with higher pH, the anodic reaction produces a surface film of ferric oxide according to reaction .

$$2Fe^{+2} + 3H_2O \rightarrow Fe_2O_3 + 6H^{+} + 6e^{-} \ (2)$$

Cathodic reactions involve electrochemical reduction: electrons appear on the left hand side of the equation. In corrosion processes *the most common cathodic reaction is the electrochemical reduction of dissolved oxygen according to the equation:*

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \ (3)$$

Hence the reduction of oxygen at an electrode will cause a rise in pH due to hydroxide ion production. This can be important in some corrosion processes as will be explained later. The potential difference E across the interface between a metal and a solution is the key factor controlling both the products of an electrode reaction and rate at which they are formed. The potential difference itself is caused by layers of charges at the surface: electrons in the metal and excess anions or cations in the solution, as shown in Figure 1.4. This arrangement of charges is known as the double layer or the Helmholtz layer. It is found not only on metal surfaces but also on other surfaces in contact with solutions such as colloids and proteins. The state of charging of the Helmholtz layer and hence the magnitude of the potential E can be changed as a result of using an external electrical current or by electrode reactions such as those shown in equations (1) to (3). For example, in the presence of a high concentration of oxygen, the cathodic reaction will remove electrons from the metal surface hence making the metal more positively charged and increasing the potential E.

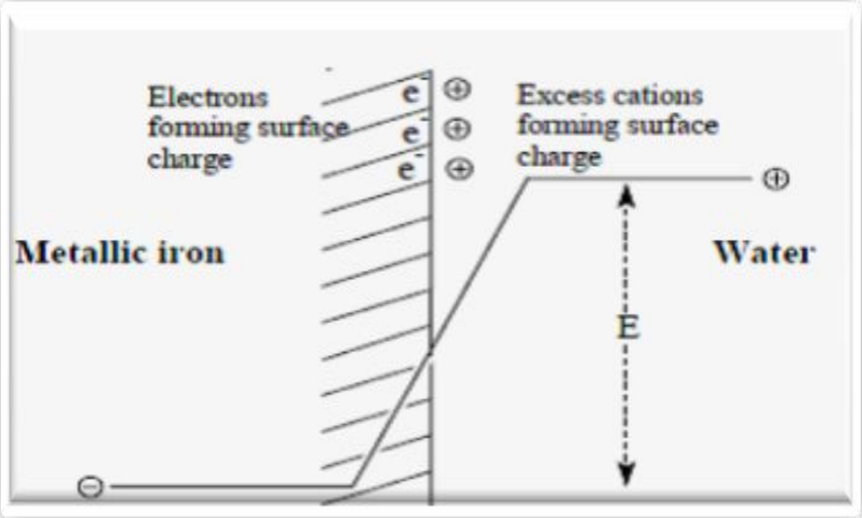


Figure (1.4): *Electric double layer at a metal surface*

The surface charge on the metal (electrons) is equal and opposite to the excess charge in the solution (cations). The potential difference, E, at the surface is created by the double layer.

The role of the electrode potential E in defining the products of corrosion reactions can be readily seen in Figure 1.5. This figure shows the corrosion products as a function of electrode potential and pH for iron at room temperature in the presence of water as solvent. At negative potentials metallic iron itself is the stable form hence in this region no corrosion is possible, and this is referred to as the immunity condition. At higher potentials and acidic pH values ferrous ions will form giving rise to active corrosion. Ferric ions are produced only at high potentials above 0.7 V.

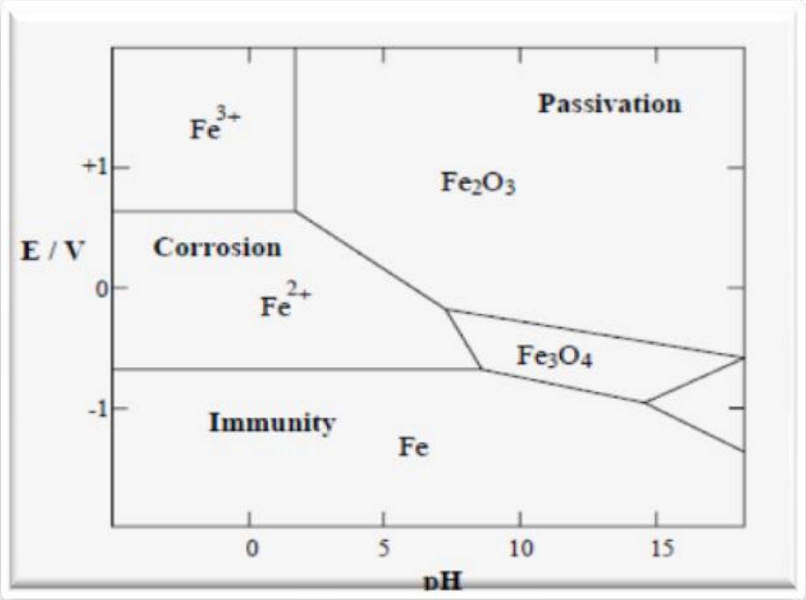


Figure (1.5): *Iron equilibrium diagram*

The diagram shows the stable forms of the element as a function of E and pH.

If the pH lies on the alkaline side of neutral then insoluble surface oxides will form. The oxide Fe_3O_4 *, known as magnetite or black iron oxide, is produced at low electrode potentials. Low potentials are found in relatively stagnant conditions with a low oxygen partial pressure as in soil or inside boilers which have been treated to remove oxygen. The characteristic black surface of iron under these conditions is due to magnetite. At more positive potentials the oxide formed is* Fe_2O_3 *and this is usually present as a thin adherent film. Since this oxide forms at the surface, its presence acts to block the surface reactions and hence corrosion rates are reduced. This is called passivation and the oxide film on the surface is known as a passive layer. The corrosion rate is very low in the passivation* *region of the diagram. Diagrams of the type shown in Figure5 are widely used in corrosion technology to predict the corrosion products which may be formed from a given metal under conditions specified by the axes of the figure. However the diagram does not tell the rate of corrosion which may be the most important information required in a practical situation.*

In order to understand the rate of the corrosion process we must examine the electrochemical polarisation curves of the electrode reactions which take place on the metal surface. Figure 1.6 shows the polarisation curve of iron in an acidic solution at room temperature. The rates of the electrode processes are controlled by the value of E. Thus, for a cathodic process in acidic solution producing hydrogen gas by the reduction of hydrogen ions, the more negative the electrode potential the greater the surface concentration of electrons and the faster the reaction rate.

$$2H^+ + 2e^- \rightarrow H_2(g) \quad (4)$$

Since the reaction rate is proportional to the flow of electrons (measured as a current I) the diagram shows the magnitude of I as a function of E.

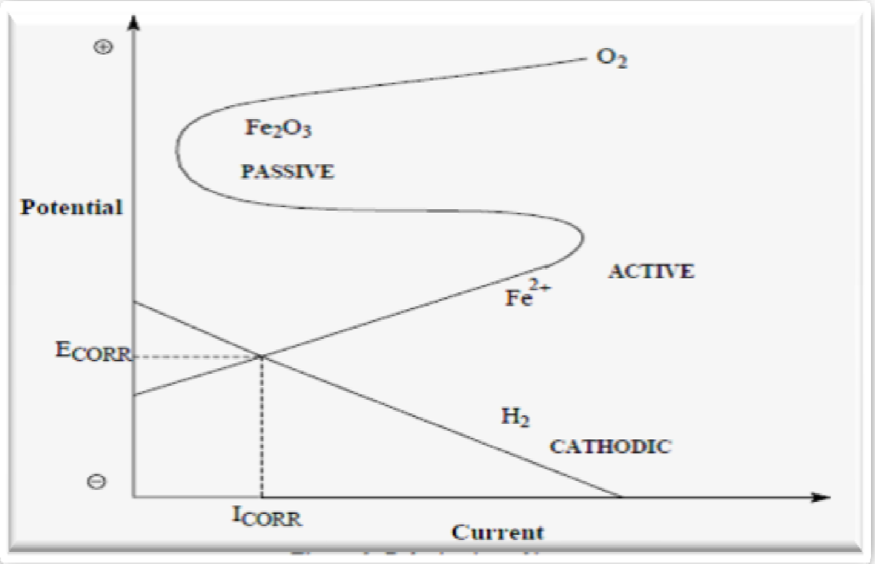


Figure (1.6): *Polarization current of iron*

The diagram shows how the potential, E, of the metal determines the electrochemical reaction rate and corrosion products.

Anodic reactions are accelerated by increasing potential in the positive sense as shown in the diagram. Ferrous ions are produced in the active state and this is the region in which corrosion will take place freely. At higher potentials the reaction passes into the passivation region (as shown in figure 1.5) and passivation occurs. This is observed as a very small current flowing in this region. The metal is protected by the passive film of ferric oxide on the surface. We see at very positive potentials that the passive electrode surface will act as an anode to oxidize water to oxygen gas, but this does not occur in normal corroding systems. To find the corrosion rate under normal conditions we look for the point on the diagram where the anodic and cathodic reactions intersect. At this point the rates of the anodic and cathodic reactions are equal and the system is behaving as a closed circuit with all the electrons produced in the anode *reaction being consumed in the cathodic reaction. This is the situation for an electrically isolated structure made from the mrtal. The polarisation diagram can be used to predict changes of corrosion rate as will be discussed in the next section; the following table illustrates all types of corrosion*[7] *(Table 1.1).*

Table (1.1): *Types of corrosion*

Type	***Characteristic***	***Examples***
1 . Uniform (or almost uniform)	*All areas of the metal corrode at the same (or similar) rate*	*Oxidation and tarnishing; active dissolution in acids; anodic oxidation and passivity; chemical and electrochemical polishing; atmospheric and immersed corrosion in certain cases*
2.Localized	*Certain areas of the metal surface corrode at higher Rates than others due to 'heterogeneities' in the metal, the environment or in the geometry of the structure as a whole. Attack can range from being slightly localized to pitting*	*Crevice corrosion; filiform corrosion ;deposit attack; bimetallic corrosion intergranular corrosion weld decay*

3. Pitting	*Highly localized attack at specific areas resulting in small pits that penetrate into the metal and may lead to perforation*	*Pitting of passive metals such as the stainless steels, aluminum alloys, etc., in the presence of specific ions ,e.g. Cl^- ions*
4.Selective dissolution	*One component of an alloy (usually the most active) is selectively removed from an alloy*	*Dezincification;* *dealuminification;* *graphitisation*
5. Conjoint action of corrosion and a mechanical factor	*Localized attack or fracture due to the synergistic action of a mechanical factor and corrosion*	*Erosion—corrosion, fretting corrosion, impingement attack, cavitation damage; stress corrosion cracking, hydrogen cracking, corrosion fatigue*

1.3.3. Protection of metals against corrosion using coatings[8]

Five mechanisms for protecting metals against corrosion through the use of coating as follows :

1.3.3.1 Barrier effect

Barrier coatings are some of the oldest anti-corrosion methods known. The coatings vary significantly in composition, some common *barrier coatings are organic paints and lacquer , metallic coatings (hot dip) heavy mastics and masonry . They vary in thickness from a few microns up to several centimeters.*

Generally , the lower the moisture vapour transmission rate of the coating , the more effective in preventing oxygen and moisture from reaching the metal substrate.

The barrier [9] film prevents corrosion by increasing the electrical resistance of the path of currents generated by slight differences in electrochemical potential between adjacent areas of the metal surface or between the underlying metal and another metal having a different potential. Paint films are not completely impermeable to the concentration of water and oxygen, and transmission of both is normally high enough so that prevention of the cathode reaction is impossible [10,11,12]. Penetration by water and oxygen does not produce a resistance low enough to maintain a corrosion current , and though most paint films take up water relatively quickly , they take up ion solution only very slowly [13]. This keeps the electrolyte resistance relatively high and the corrosion low; since corrosion is dependent upon ionic flow. However, even when the electrical resistance of penetrating moisture is reduced by absorption of ions , the resistance of a good barrier film remains high enough to achieve an important reduction in the magnitude of the corrosion current .

Inorganic (ion producing) materials found under film (particularly chlorides and sulphates) that are left after poor surface preparation can be dissolved as ion–free water, penetrate the film , from conductive electrolytes , and increase corrosion .

Also, under conditions of immersion, differences in ionic concentration between liquids beneath and outside the film give rise to osmotic migrations of water into the film . This promotes blistering and eventual film rupture .Further degradation and loss of protective value can result from electroendosmosis generated by differences in the electrochemical potential on the metal surface at and around the film disruption.

Unlike well cured films, insufficiently cured films allow the penetration of much more ionic material [14,15].

Polymer groups such as carboxyls and hydroxyls tend to foster ionic penetration [16,17,18,19]. *As pigment volume concentration (P.V.C)* is increase, these factors are overwhelmed because interstitial penetration dominates. Good barrier films , therefore; are high molecular weight films with uniform crosslink density , cured uniformly , formulated well below the critical pigments volume concentration (C.P.V.C.) ** with low water solubility pigments.*

Lammeller pigments (leafing type aluminum) dramatically reduce ionic transmission rates. Care must always be taken in using metal flakes (such as copper or stainless steel), to ensure complete pigment encapsulation to avoid unwanted galvanic effects.

**Ratio of the volume of pigment to the volume of total non-volatile material (i.e. pigment and binder) present in a coating*

*** Level of pigmentation where just sufficient binder is present to fill the voids between pigments particles in the dry film*

Similarly, tiecoats should be used to improve adhesion between such metallic barrier films and zinc-rich primers.

All things being equal in atmospheric service, thicker barrier system give better protection [20].

In general . the more sever the environment , or the longer the requirement for protection , the greater will be the coating dry film thickness required .

Thick films (particular those of rigid thermosets) are less able to provide the necessary flexibility to Vehicle choice for barrier is also important. High molecular weight thermoplastics (e.g. vinyls and chlorinated rubbers) are effective particularly at high builds. Thermosetting systems such as epoxy/ phenolics and certain polyesters are also effective vehicles, as are the coal tar epoxies . Vehicles with high hydroxyl or carboxyl contents (oils, alkyds, acrylics, etc.) tend to attract water into the film.

High- build vinyl and chlorinated rubber systems of 8 mils(1mils=25microns) and more make excellent barrier systems. One hundred mils of coal-tar on buried pipelines or immersed structures used in combination with impressed current cathodic protection can reduce current requirements for cathodic protection ten thousand fold as compared to requirements for bare steel[21].

1.3.3.2 The barrier pigment effect [22]

Pigments are commonly thought of a coloring agents ; however , many pigments serve special purposes, including *participating in metal protection . Most pigments produce some barrier effect; structurally reinforcing the film and reducing permeability . Some , such as micaceous iron oxide , or metallic flakes such as bronze or aluminum are called " Lameller" pigments in a paint film their plate-shaped particles align parallel to the substrate , blocking water and oxygen with a "well" of flat m, thin particles, thus the water is forced to take a long , circuitous path to the substrate; Figure (1.7) illustrates the barrier pigment effect.*

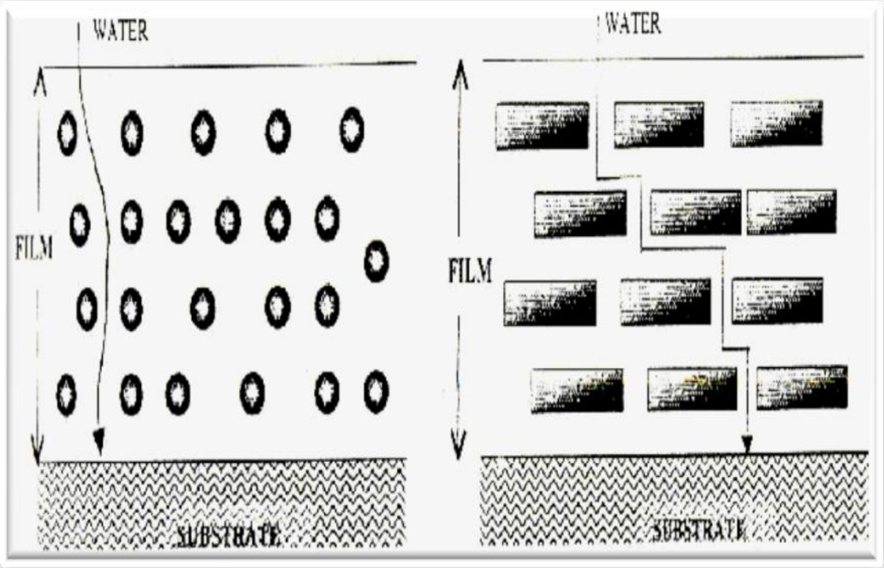


***Figure (1.7)** Barrier pigment effect(Barrier pigment effect . water takes a straight path through an unreinforced film , but is forced to take an extended path through lamellar of a metallic flake or mica reinforced film) .*

In the inhibitive primer , pigments are incorporated to provide a source of corrosion inhibitive ions which can be carried to the metal interface as water penetrates the film.

Here they modify anode and/or cathode reactions driving the steel potential into its passive region [23].

There are two principal to such inhibition , (a) direct inhibition relies on a controlled dissolution of ions from the pigments itself . At the interface , the ionic solutions passivate the metal by increasing the polarization of the anode by increasing the polarization of the cathode , (b) by thickening the natural oxide layer and increase the electrical resistance across anode and cathode .

Perhaps the most efficient direct inhibitive are the salts of hexavalent chromium . In paint films, chromate inhibition is provided from such pigments as zinc potassium chromate, strontium chromate, etc. Pigment solubility is most important . Highly soluble pigments (calcium chromate) are rapidly depleted, while those with very low solubility (lead chromate) provide too few hexavalent chromate ions for protection . Zinc chromate offers a moderate solubility and is extensively used . other less toxic inhibitors, the molybdates, phosphates, phosphosilicates, borates, and borosilicates also protect by similar mechanisms. However, as the environmental awareness increased, the toxicity of those compounds received universal attention and their overall adverse effect on human health is being closely monitored.

The ratio of the primer`s pigment volume concentration (P.V.C.) to the critical pigment volume concentration (C.P.V.C.) of the pigment system is equally important .Very low ratios (low pigment content) give overly tight films and increase the tendency of the primer to blister. Filiform corrosion of the substrate can occur. Too high ratio provides rapid dissolution of the inhibitor , and allows corrosive ions such as chlorides from the environment to penetrate the film.

Chlorides and other depassivators complete with inhibitive ions from anodic absorption , and can nullify inhibition , or at least increase the quantities of inhibitor needed . Inhibitive primers are best restricted to environments where the penetration of chloride ions is limited . Their use in immersion condition is definitely not recommended because of the danger of the osmotic blistering . The best pigment volume concentration; critical pigment volume concentration ratio is determined experimentally , but a level near 9:1 is often used[24].

Some binder media, for example, such as chlorinated rubber , polyesters and epoxies, form a film that is chemically resistant to acids , some such as coal tar epoxy resins and polyamide epoxies are highly resistant to water. Others demonstrates resistance to abrasion, weather, alkalis, salts and other corrosive environments.

The addition of pigments , help coatings to protect metal surfaces by reinforcing film structure and reducing permeability . Pigments also add color, hiding ability, gloss retention and opacity to paint.

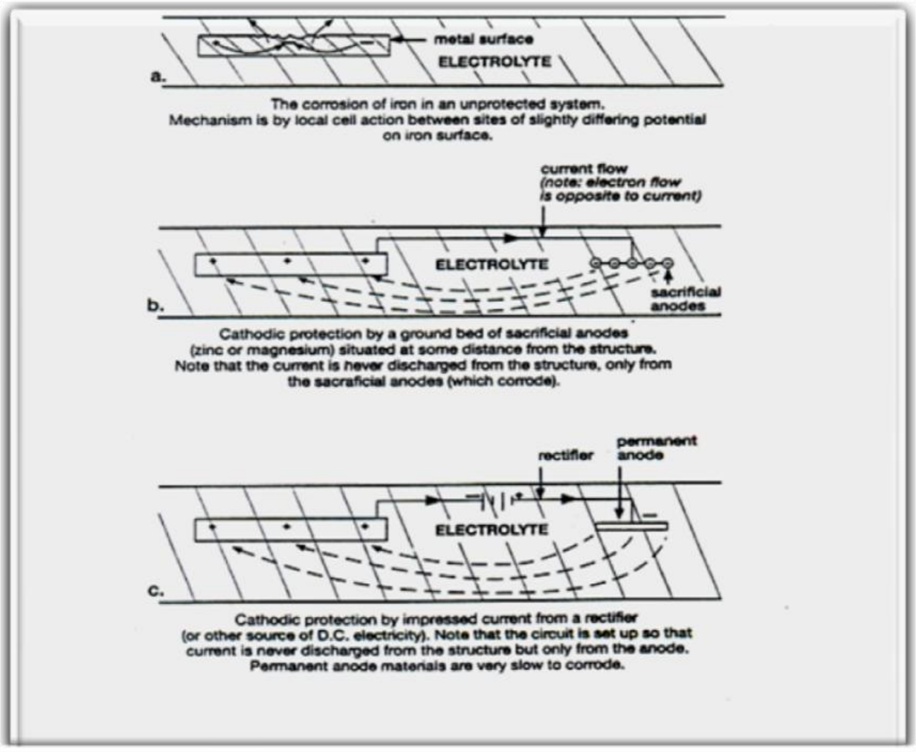
Barrier[25] type vehicles are less effective with inhibitive primers than the more permeable vehicles (oils, alkyds, etc.). Oils and alkyds do not , however ; have the alkali resistance of vinyls and this is a disadvantage.

Alkali generated at the cathode can rapidly saponify alkali-sensitive coatings. Alkali attack occurs at cathode areas adjacent to or surrounding corroding areas (anodes).

1.3.3.3Cathodic (Zinc-Rich) protection[26]

A somewhat different technique is to alter the nature of the operating cell by providing a new more active anode in electrical contact with the metal sensitive to attack . The presence of this anode sets up a powerful bimetallic cell which overrides all local cell activity on the sensitive metal itself .In this way , the small potential differences between the local anodes and cathodes of the sensitive metal are all overridden by the much larger potential difference that exists across the new artificial cell between the new anode (which is thereby slowly sacrificed) and the metal itself , which now becomes totally cathodic .

In coatings application , cathodic protection **Figure (1.8)** *is derived from several sources , including the use of galvanizing zinc metalizing , electro deposited zinc plating and coating with zinc rich metal primers.*



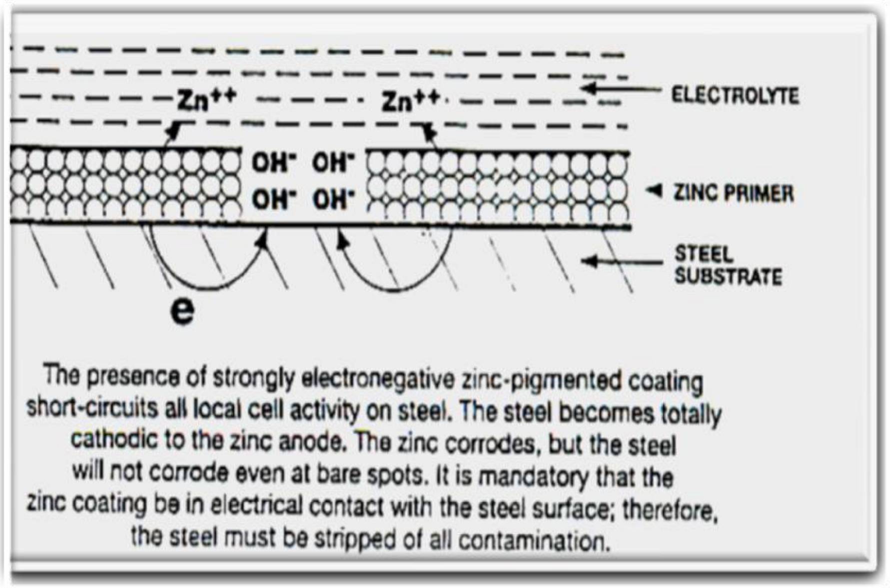
The corrosion of iron in an unprotected system.
Mechanism is by local cell action between sites of slightly differing potential on iron surface.

Cathodic protection by a ground bed of sacrificial anodes (zinc or magnesium) situated at some distance from the structure. Note that the current is never discharged from the structure, only from the sacraficial anodes (which corrode).

Cathodic protection by impressed current from a rectifier (or other source of D.C. electricity). Note that the circuit is set up so that current is never discharged from the structure but only from the anode. Permanent anode materials are very slow to corrode.

Figure (1.8): *The corrosion of iron& the cathodic protection by sacrifial anode impressed current*

The essential protective mechanism of all these films is the same . The iron is coated with an electrically conductive zinc coating that will act as a sacrificial anode , corroding instead of the iron , and thereby protecting the iron , which acts as the cathode of a large galvanic cell Figure (1.9).



The presence of strongly electronegative zinc-pigmented coating short-circuits all local cell activity on steel. The steel becomes totally cathodic to the zinc anode. The zinc corrodes, but the steel will not corrode even at bare spots. It is mandatory that the zinc coating be in electrical contact with the steel surface; therefore, the steel must be stripped of all contamination.

Figure (1.9): *Mechanism of cathodic (Zinc-Rich) protection*

1.3.3.4 Zinc-Rich primers[27]

Zinc employed in coating films at loadings that insure the film conductivity , will form an efficient anode of a galvanic couple with steel , sacrificially corroding itself , and overriding local cell activity on the steel , which becomes entirely cathodic and protected .

The concept is easily adaptable to practical coating system , and such primers are the most efficient of all. Zinc-rich primers based on both organic and inorganic vehicle are widely and successfully employed .

1.3.3.4.1. Organic Zinc-Rich primers

The organic zinc-rich primer may be considered a special case of a high pigment volume concentration (PVC) paint. It must maintain *zinc particle to zinc particle contact within its continuum and contact between pigment and substrate to ensure electrical conductivity within the film and across the interface . These requirements translate to a paint formulated at a pigment volume concentration slightly above the (CPVC) figure (1.10). The film must also display sufficient adhesion at these loadings to anchor the system to the steel, because of cathodic alkali generation at the interface , the vehicle must resist alkalis .*

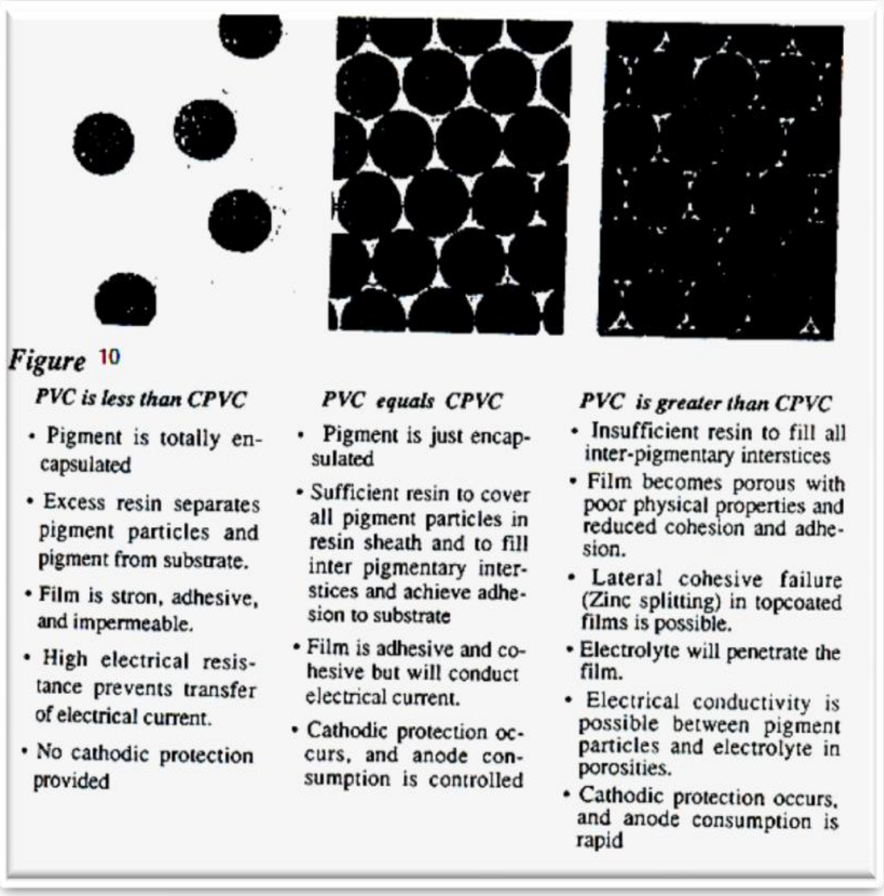


Figure 10

PVC is less than CPVC

- Pigment is totally encapsulated
- Excess resin separates pigment particles and pigment from substrate.
- Film is stron, adhesive, and impermeable.
- High electrical resistance prevents transfer of electrical current.
- No cathodic protection provided

PVC equals CPVC

- Pigment is just encapsulated
- Sufficient resin to cover all pigment particles in resin sheath and to fill inter pigmentary interstices and achieve adhesion to substrate
- Film is adhesive and cohesive but will conduct electrical current.
- Cathodic protection occurs, and anode consumption is controlled

PVC is greater than CPVC

- Insufficient resin to fill all inter-pigmentary interstices
- Film becomes porous with poor physical properties and reduced cohesion and adhesion.
- Lateral cohesive failure (Zinc splitting) in topcoated films is possible.
- Electrolyte will penetrate the film.
- Electrical conductivity is possible between pigment particles and electrolyte in porosities.
- Cathodic protection occurs, and anode consumption is rapid

Figure (1.10): *Schematic illustrate the role of the ratio between (PVC) to (CPVC)*

Chlorinated rubber , epoxy/polyamides , high molecular weight linear epoxies and epoxy ester systems are used as binders . Epoxy esters do not have quite the alkali resistance of other vehicles , but certain specific vehicles (high epoxy content) offer acceptable compositions . Primer films will vary and reflect the properties of the vehicle type .

This provides enough film and film/substrate conductivity for good protection . up to 15% mica has been effectively used in this way[28] *The use of conductive extenders (di-iron phosphide) is not related to (PVC) effects, and high zinc replacements have been achieved with this types of pigments*[29].

1.3.3.4.2. Inorganic Zinc-Rich primers

Inorganic zinc-rich primers, unlike the organics depart radically from conventional paint technology . These vehicles (generally silicates) do not bind zinc as do the organics, but chemically react with zinc ions on zinc particle surfaces forming primary bonded zinc silicate matrices .

Vehicles may generally be classed as either alkaline silicates (water solutions of sodium, potassium, lithium or quaternary ammonium silicates) or alkyl silicates which may be ethyl silicate (the most common) or higher alkyd or alkoxy homologues .

The inorganic films show better performance than most organics. Their films are strong , hard, and resistant to impact and abrasion . They are quite resistant to heat. The matrix of the inorganic primer film is not subject to age-related deterioration as are organic primers.

Weathering may actually improves its physical properties . Zinc rich primers are normally applied at approximately 75 microns. The porosity of zinc-rich films (particularly the inorganic) can lead to problems because of air occlusion on top coating. The resultant bubbling and pin holing of applied top coats may necessitate the use of mist coats, thinned finish coats of tiecoats before finish coat application [30]. *Carefully tailor finish coats for bubble free application over the zinc-rich primers*[31].

1.3.3.5Intermediate and finish coats for steel

The vehicle binder of the finish must bear the brunt of the environmental attack.

Most design decision should be based on the polymer chemistry of the vehicle involved . An empirical awareness of the effects of UV, moisture , oxygen , chemical attack, microbiological attack, high and low temperature , abrasion and impact, etc.

1.3.3.5.1 Lacqers, Thermoplastic coating

A lacquer is simply a coating that forms its film by solvent evaporation alone. Vinyls are the most common lacquers used in anti-corrosive maintenance finishes . Solution of high molecular weight , vinyl chloride/vinyl acetate copolymers or terpolymers with vinyl alcohol or maleic acid , are used. Vinyl are distinguished by excellent acid and alkali resistance. Their backbone being exclusively carbon/carbon bonds. Vinyl films are attacked by the solvents from which they were cast (ketones, esters, etc.) . Also by concentrated organic acid, and softened by aromatics they have low water and *oxygen transmission rates, and are suitable for water immersion service .*

Acrylic films have a better resistance to ultraviolet than the vinyls, and show long-term gloss and color retention as well as good weatherability in exterior environments . They are more suitable for polymer modification than the vinyls.

Chlorinated rubber coatings have perhaps even lower moisture and oxygen transmission properties than the vinyl and the absence of pendent ester groups provides better chemical resistance than the acrylics. Solvents resistance is not as good as the vinyls , but chlorinated rubber has better compatibility with other film formers than have the unmodified vinyls[32].

1.3.3.5.2 Latex

Latex systems show every possibility of expanding into the maintenance painting area as technologies develop. Unlike lacquers, latex are dispersions (not solution) of thermoplastic polymers in water . Molecular weights are not restricted by solution viscosities , and much higher solids of very high molecular weight polymers are possible . Film formation involves evaporation of water followed by coalescence of discreet particles of polymer (micelles) dispersed in the water. Total coalescence has never been achieved[33] *and systems give higher moisture and oxygen transmission rates than their lower molecular weight analogues cast from solution.*

1.3.3.5.3. Oxidizing system

Oxidizing systems are thermosets which convert to three-dimensional polymeric networks by absorption of atmospheric oxygen. Such systems are based on vegetables oils (esters of glycerol and vegetable oil, fatty acids).

Alkyds are oxidizing system , and have limited applications in heavy-duty maintenance. Chemical resistance is poor, and they are not suitable for immersion service .

Alkyds make an excellent choice of vehicle in light-duty environments. Thirty percent silicon modification provides finish coats that have excellent ultraviolet light resistance and exceptionally good weathering properties .

More alkali-resistant oxidizing vehicles are obtained with the phenolic varnishes and epoxy esters (epoxy resins esterfied with oil fatty acids). Both vehicles have better chemical resistance than either the unmodified oil or the analogous alkyd, and as phenolic or epoxy content of such resins increases , so does their chemical resistance . Epoxy esters are hard, resistant to abrasion in aromatic and even aliphatic hydrocarbons.

1.3.3.5. Chemically curing thermosets

Oxidizing system are a special case of thermosetting vehicle , where the activator is supplied by the environment . In other cases, water from the air will cure the vehicle . In backing finishes (e.g. alkyd/amino) both reactive oligomers are added to one can ; but are *selected so that the reaction will only occur when the system is applied as a film and subjected to high temperatures (180-400° F) depending on vehicle type.*

More commonly, maintenance painting systems are designed so that reactions occur at room temperature .Reactive vehicle are packaged separately and combined in the field just before applications of these two package systems, the two most important are epoxies and polyurethanes . the properties of both system are related to the chemical constitution of the reactants . Epoxies are less complex than polyurethane because of the more limited choice of reactants . Epoxies are available in molecular weights ranging from materials which are liquid at room temperature to high molecular weight materials which may themselves be used without crosslinking as lacquers . The epoxy resin is most commonly cured in the field with polyamines or polyamides . With a given epoxy polyamines produce a tighter crosslinked film having greater chemical resistance , hardness , and cure response than the same resin cured with a polyamide. The polyamides give better flexibility , water resistance and exterior durability.

In general, epoxies show excellent adhesion ,good chemical resistance, especially to alkalis and good solvent resistance , Epoxies have less acid resistance than vinyls and chlorinated rubbers , but show good abrasion and impact resistance .Exterior durability is hampered only by a tendency to chalk and yellow , which is not progressive and does not affect resistance properties . Chalk resistance epoxies with good color retention are now available[34]*.*

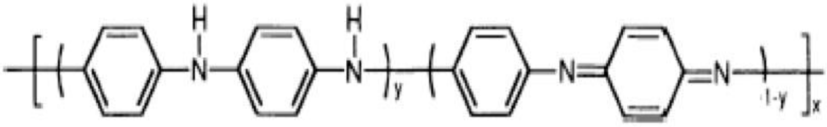
With certain coal-tar pitches, epoxy systems give synergistically improved coatings, which at 16-20 mils dry or so, give good protection against moisture and oxygen transmission , chemical attack and physical abuse. They are ideal coatings for areas with restricted access after application.

Polyurethane systems have an even wider variety of possible reactants. While polyisocyanates are generally limited to adducts of toluene di isocyanate or hexamethylen- di- isocyanates, polyols used in the formulation are exceptionally varied . Almost any resinous material having di or poly-functionality based on a hydrogen donor will react with isocyanates , although –OH functionality is most widely used in coatings.

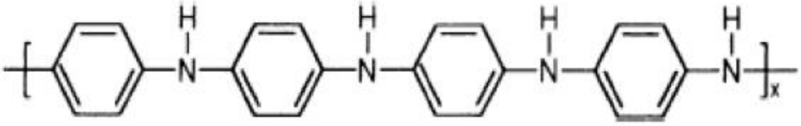
The urethane may range from hard chemically resistant finishes to soft rubbery finishes having good abrasion resistance . Toluene diisocyanate coating give exceptional chemical and abrasion resistance ,while hexamethylene-di-isocyanate systems have exceptional light and weather resistance . Urethane show better curing properties at low temperatures than do most epoxies, but specific properties will depend greatly upon the type of modifier selected[35].

1.4. Polyaniline

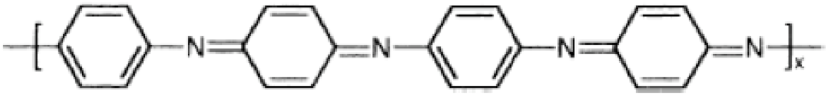
The name polyaniline refers to a family of polymers that have taken on much importance upon the discovery of their conducting abilities when doped. A polyaniline takes on the general structure:



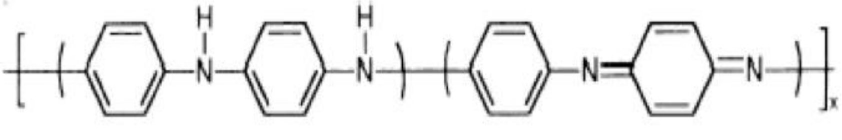
Polyanilines were first reported in 1862 and in 1910 – 1912 it was first proposed that polyaniline had three stable insulating oxidation states namely leucoemeraldine, ermeraldine, and pernigraniline [36]. *Leucoemeraldine is the fully reduced state and takes on the general structure:*



Where in reference to the general structure above leucoemeraldine would be described by $y = 1$*, where the fully oxidized state, pernigraniline, would be described by* $y = 0$ *and represented by the structure below.*



The half oxidized or partially oxidized state emeraldine has $1 < y < 0.5$ *and with the structure below.*



The emeraldine state can be protonated to form the conducting emeraldine salt.

Upon complete protonation of the imine nitrogen results in delocalized poly semiquinone radical cation, increasing conductivity to the order of 1010 S/cm [36 - 37]*. Emeraldine was first noticeably doped in aqueous HCl solution with pH= 0 in which the H+ dopes the nitrogen. It has also been found to dope well with various sulfonic acids including: dodecyl benzene sulfonic acid (DBSA), camphor sulfonic acid (CSA), phenyl sulfonic acid (PSA), toluene sulfonic acid (TSA), and methyl sulfonic acid (MSA)* [38- 39]*. It is also possible to oxidatively dope the fully reduced leucoemeraldine base to be like the conductive emeraldine salt. The more complete the protonation of the emeraldine the higher the observed conductivity* [40]*. The formation of secondary structures within the emeraldine state has been proposed one of a polaron and/or bipolaron as can be seen below in Figure 1.11* [40, 41]*.*

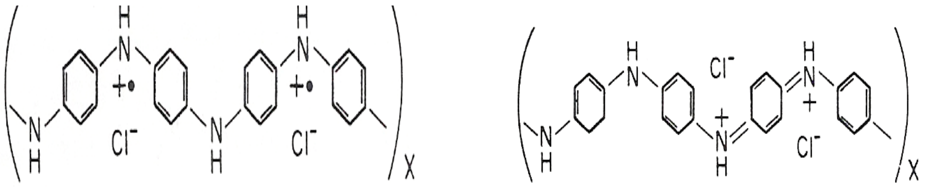


Figure (1.11): *Schematic representation of the proposed of the left, polaron structure and right, bipolaron structure of polyaniline* [41]*.*

Polyaniline has been a significant interest due to its high conductivity, good redox reversibility, swift change in film color with potential and high stability in air. Polyaniline can be used for batteries [42,43]*, electrochromic devices*[44,45] *photoelectrochemical conversion of light to electricity*[46,47]*, light-emitting diode* [48]*and immobilization of enzymes* [49,50]*. Polyaniline can be synthesized by* *the electrochemical polymerization or chemical polymerization of aniline.*

1.5. Zinc phosphate

Zinc phosphate ($Zn_3(PO_4)_2$*) is an inorganic chemical compound used as a corrosion resistant pigment on metal surfaces either as part of an electroplating process or applied as a primer pigment. The anticorrosive properties of zinc phosphate depend in a large degree, on the distribution of the particle size.*

Natural forms of zinc phosphate include minerals hopeite and parahopeite ($Zn_3(PO_4)_2 \cdot 4H_2O$*). A somewhat similar mineral is natural hydrous zinc phosphate called tarbuttite(* $Zn_2(PO_4)(OH)$*). Both are known from oxidation zones of Zn ore beds and were formed through oxidation of sphalerite by the presence of phosphate-rich solutions. The anhydrous form was not found naturally yet.*

1.6. Literature Review

Whereas the interest in providing new corrosion protection systems for different metals and metal alloys is related to restrictions to the use of chromium (VI) compounds owing to their environmental problems; coatings for corrosion protection of different metals considering intrinsically electronic conducting polymers have become important mainly. polymer amines; such as polyaniline have been studied as an efficient corrosion inhibitor for iron and other metals; for example; ***Ogurtsov et al.***[51] *studied the corrosion inhibition of Al alloy by pure undoped PANI (emeraldine base) and PANI doped with p-toluene-sulfonic, camphorsulfonic and dodecylbenzenesulfonic acids in aqueous 3.5% NaCl and 0.1 N HCl solutions where the results indicated that corrosion protection of the bare aluminum alloy surface resulting from a defect of the PANI coating is in line with an increase of the thickness of the oxide layer protecting the aluminum alloy surface.* ***Özyılmaz et al.***[52] *prepared polyaniline film on copper electrodes from monomer, then the corrosion performance of polyaniline coated samples were investigated in 3.5% NaCl solutions, and it was shown that PANI coating could provide important protection against corrosion of copper in an aggressive medium. The polymer film behaved like a barrier against the attack of the corrosive environment. It was also found that the polymer film by its catalysing effect led to the formation of protective copper oxides on the surface.* ***Souza***[53] *studied the electrochemical behavior of blend formed from camphor sulphonate-doped polyaniline and poly(methyl methacrylate) which was used for iron, copper and silver corrosion protection in acidic environments with or without chloride ions. It was observed that the* *protection depends on the formation of a passive film between the polymeric coating and the metallic substrate. Raman spectroscopy revealed that the degree of redox conversion of camphor sulphonate-doped polyaniline strongly depends on the reducing power of oxidizable metals, showing a galvanic coupling between the metal and polyaniline. After that, metallic cations form a passivating complex with the dopant anion (camphorsulphonate), which improved the barrier property of different metals modified polyaniline coating system.* ***Fang et al.*** *[54] prepared polyaniline coatings by electrochemical deposition on substrates of stainless steel and platinum The corrosion protection of the PANI coatings and their failure were investigated in strong acid solution. It was observed that the protection depends on the formation of a passive film between the polymeric coating and the metallic substrate.*

Some researchers studied the corrosion inhibition of different metals by using the polyaniline and its dervative; such as ; ***Bereket et al.*** *[55] studied the using of polyaniline (PANI), poly(2-toluidine) (PT) and poly(aniline-co-2-toluidine) (co-PT) for corrosion protection of stainless steel (SS) The results of this study reveal that PANI, PT, and co-PT acts as corrosion protective coatings on SS and every coating gives protection efficiency of greater than 80% after 48 h of immersion in corrosive test solution.* ***Sathiyanarayanan et al.*** *[56] who studied the inhibitive action of ortho-methoxy substituted polyaniline, on the iron in acidic chloride solution ; where Double-layer capacitance studies indicate a strong adsorption of polymer following the Temkin adsorption isotherm is largely responsible for its inhibitive action.* ***Brusic et al.*** *[57] also worked on a number of* *polyaniline derivatives are studied, including the unsubstituted parent polymer and the substituted poly-o-phenetidine both nondoped and doped, with several different protonic acids. The polymers are readily soluble in organic solvents and can be applied as thin coatings onto the metal surface. The corrosion protection of the resulting structure is determined by electrochemical and inductively coupled plasma techniques using water as an electrolyte and under varied conditions of temperature, humidity. It is found that polyaniline could either enhance the corrosion rate or produce significant corrosion protection depending on the chemical nature of the polymer backbone and the conditions in which the material is processed and doped .* ***Quraishi et al.*** *[58] studied the corrosion inhibition of poly(aniline-formaldehyde) on mild steel in 1.0N HCl. Results showed that poly(aniline-formaldehyde) is a mixed inhibitor and it inhibits mild steel corrosion through adsorption mechanism.*

As using steel is wide spread; most of researchers concern about finding the best procedure for protecting it from corrosion; so some used polyaniline with additives and others used it with other polymer as composite. For example; ***Lu et al.*** *[59] coated smples of mild steel with polyaniline deposited from solution, and overcoated with an epoxy barrier paint, when scratched to expose precise areas of bare metal, exhibited corrosion rates in aqueous* ***3.5%*** *NaCl solutions 2 times less, and in 0.1 N HCI solutions, 100 times less than observed on identical samples coated with epoxy paint alone and this is due to the formation of passivating iron oxide (γ - Fe_2O_3 and Fe_3O_4) surface layers.* ***Li et al.*** *[60] the ability of polyaniline to act as a protective coating for mild steel corrosion in saline and acid was* *investigated by electrochemical impedance spectroscopy . The effectiveness of the process, which also provides the repassivation of damaged films, is greater in acids. The performance of PANI is further enhanced by the presence of a top coat to increase the diffusional resistance for the corrosion.* ***Malik et al.*** *[61] studied the ability of a polyaniline film, into which highly dispersed platinum microparticles were introduced at a fairly low level to protect stainless steel against corrosion in strong acid solution (2 M H_2SO_4) , where the study showed that the corrosion potential of stainless steel is stabilized within the passive range, and the rate of its dissolution is minimized. Also a low over potential for the reduction of protons seems to facilitate the active-to-passive transition of stainless steel.* ***Dhawan et al.*** *[62] designed a novel route to prepare water soluble polyaniline which is crystalline in nature. The water soluble polyaniline can be used as a corrosion inhibitor for iron in HCl medium. The results showed that double-layer capacitance studies indicate a strong adsorption of polymer following the Temkin adsorption isotherm is largely responsible for its inhibitive action.* ***Kilmartin et al.*** *[63] prepared polyaniline films by electrochemical deposition on stainless steel and its corrosion performance monitored by the open circuit potentials in acidic solutions it was shown that in 0.5 M H_2SO_4 the potential climbed to over 0.4 V , to values typical of the partially oxidised form of the polymer and of the metal substrate in a passive state with low rates of corrosion. In 0.5 M HCl, the steels were maintained in a passive state for some hours to days (lasting longer with a thicker polymer film), prior to a drop in potential to −0.15 V after the beginning of pitting corrosion* ***Sathiyanarayanan et al.*** *[64] studied the synergistic effect of halide* *ions on the inhibition of corrosion of iron in 0.5 M* H_2SO_4 *solutions by polyaniline has been studied by polarization and impedance methods. Addition of* 0.5×10^{-3} *M* I^- *ions enhanced the inhibition efficiency of polyaniline at 10 ppm from 53% to 90%. The results indicated that the synergistic effect is attributed to enhanced adsorption of polyaniline by the adsorbed halide ions which carry out increasing of high corrosion inhibition* ***Blackwood et al.*** *[65] deposited multilayered coatings, consisting of combinations of the conducting polymers polyaniline (PANI) and polypyrrole (Ppy) by galvanostatical process on to both carbon steel and stainless steel. Potentiodynamic polarisation was used to assess the ability of these copolymers to provide an effective barrier to corrosion in chloride environments. The results indicated that for carbon steel the performance of these multilayered coatings on carbon steel were not sufficiently better than for single PANI coatings to justify their more complicated deposition procedures. However, in the case of stainless steels the new multilayered coatings proved to be significantly better than previously reported single PANI coatings, especially at protecting against pitting corrosion. It was found that the degree of protection was a function of the deposition order of the copolymer, with films consisting of a PANI layer over the top of a Ppy layer yielding the best results.* ***Herrasti et al.*** *[66] used Electrodeposition methods to obtain polypyrrole and polyaniline polymer layers, bilayers and blends of these polymers on carbon steel by passivation of the steel surface in the electrodeposition solution (oxalic acid and monomer) between −0.5 and 0.3 V versus Ag/AgCl and subsequent electrodeposition using different techniques* **.** *The results obtained indicated that prepassivation gives rise to adherent polymer layers* *with excellent corrosion resistance. Of all the bilayers obtained, the best results are yielded with those in which polyaniline is deposited as the base for the deposition of polypyrrole.* ***Bereket et al.***[67] *prepared a stable and adherent polymer films of polyaniline and of poly(2-anisidine) on stainless steel by cyclic voltammetry in tetrabutylammonium perchlorate/acetonitrile solution containing perchloric acid , then the anti-corrosion behavior of polyaniline, poly(2-anisidine), and poly(aniline-co-2-anisidine) coated electrodes were investigated where; Poly(2-anisidine) film showed protection against corrosion stainless steel by passivating steel substrate in similar manner as has been observed for polyaniline. But anti-corrosion behavior was slightly poorer than that of polyaniline.* ***Sathiyanarayanan et al.***[68] *synthesized phosphate doped polyaniline from aqueous phosphoric acid containing aniline by chemical oxidation method using ammonium persulphate as oxidant. The corrosion resistant property of the polymer containing coating on steel was found out in 0.1 N HCl, 0.1 N* H_3PO_4 *and 3% NaCl for a duration of 50 days. The coating was able to protect the steel more in 0.1 N* H_3PO_4 *and 3% NaCl media than in 0.1 N HCl.* ***Gan et al.*** [69] *prepared a separate doped Polyaniline film electrode on a glass substrate to investigate the role of polyaniline (PANI) in the corrosion protection of stainless steel (SS) in oxygen-deficient acidic solution, the study showed that passivation is achieved because PANI film provides a large critical current at the early stage of coupling and a persistent passive current by its electrochemical dedoping/re-doping equilibrium activity with the acidic environment at the subsequent stage of coupling.* ***Venkatachari et al.***[70] *evaluated the performance of water soluble polyaniline as corrosion inhibitor* *for iron in 0.5M H_2SO_4. It was found that polyaniline is an efficient inhibitor, since the maximum efficiency of 84% has been observed at a concentration of 100 ppm, whereas the monomer has accelerated the corrosion, where polyaniline is strongly adsorbed on the iron surface and inhibits the corrosion effectively.* ***Jeyaprabha et al.***[71] *studied the performance of the polyaniline inhibitor for iron by the addition of halide ions or metal cations such as; cerium ions ; the study showed that the inhibition efficiency of polyaniline at 10 ppm has been increased from 53 to 88% and for 50 ppm from 71 to 90% in the presence of cerium ions and this is due to the higher coverage of polyaniline–cerium complex.* ***Sazou et al.***[72] *prepared Polyaniline films by electrodeposited on stainless steel polyaniline films provide protection to SS in chloride-containing 0.5 M H_2SO_4.*

Some researchers concern about evaluating polyaniline in adhesives; for example; ***Talo et al.***[73] *studied the polyaniline epoxy blend coatings on mild steel have been studied in neutral, acidic and alkaline solutions with various electrochemical methods. It has been found that coatings containing emeraldine base provide better corrosion protection in NaCl solution than coatings based on conducting polyaniline .* ***Mattos et al.***[74] *studied the anticorrosive properties of undoped polyaniline (PANI) casted onto mild- and galvanised steels by a classical methodology used for organic coatings. Pure PANI, as well as, PANI plus an epoxy topcoat were tested in total immersion conditions monitored by electrochemical impedance It was shown that undoped PANI did not have good barrier properties and adhesion to the substrates was very poor. Even with an epoxy topcoat, PANI coated samples had the worst* *performance in comparison with the other coating systems herein used as reference.* ***Spinks et al.***[75] *studied whether the dopant used with polyaniline emeraldine salt affected the corrosion rate of coated steel when the polyaniline was used as a primer with a polyurethane or epoxy topcoat. The results showed that epoxy topcoated systems showed adequate corrosion protection for up to 2 years during immersion in 3.5% saline solution. Quantitative analysis of iron-dissolution rates showed distinct differences between polyaniline doped with different ions when used with a polyurethane topcoat. However, the emeraldine base produced the lowest iron-dissolution rate over the period tested.* ***Armelin et al.***[76] *studied the protective behaviour of polyaniline (PANI) emeraldine salt and polypyrrole composite with carbon black as additives of an epoxy paint coating by the addition of a low concentration of conducting polymer (0.2–0.3%, w/w) was examined The results indicated that this conducting polymer might works as both corrosion inhibitor and adhesion promoter.* ***Kalendová***[77] *studied the adhesion, barrier, and anti-corrosion properties of the coatings containing PANI and selected chemically inorganic active pigments were studied as well as the combination of PANI with zinc dust. Epoxy resin of bisphenol type hardened with a polyamine-based curing agent was used as a binder The investigation of the total anticorrosion efficiency of coatings with the PANI + Zn-dust combination found out that the PANI combination with a volume concentration of 5% and Zn-dust achieves high anticorrosion.* ***Aleman et al.***[78] *studied the anticorrosive behavior of polyaniline emeraldine salt, polyaniline emeraldine base, polyaniline emeraldine salt composite with carbon black, polypyrrole composite with carbon black and poly(3,4-*

ethylenedioxythiophene) doped with poly(styrene sulphonate) dispersed in epoxy paint. Results indicate that the protection against corrosion imparted by the formulations modified by the addition of poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulphonate), polyaniline emeraldine salt and, especially, polyaniline emeraldine base is significantly higher than that of the unmodified paint. ***Roberto et al.***[79] *studied the corrosion protection behavior of different metals by using coatings based on acrylic blends formed by polyaniline and poly(methyl methacrylate). Results indicate that the degree of redox conversion of polyaniline, from emeraldine to leucoemeraldine state, strongly depends on the reducing power of metals showing a galvanic coupling between the substrate and polyaniline. On the other way, results reveal that PANI acts as an anion reservoir, which can release anions in a smart way when damage is produced on the surface of the coating forming a second physical barrier to avoid penetration of aggressive ions.* ***Gheorghe et al.***[80] *determined that the corrosion protection of carbon steel of acrylic dispersion based on PANI doped with anions containing phosphorus was improved .* ***Sathiyanarayanan et al.***[81] *studied the comparative corrosion protection performance of the coatings containing polyaniline and polyaniline–TiO2 composite (PTC) on steel in acrylic binder was evaluated by immersion test in 3% NaCl for 60 days and salt fog test for 35 days The better performance of PTC containing coatings may be due to uniform distribution of polyaniline which can form uniform passive film on the iron surface.* ***Laco et al.***[82] *studied the protection against corrosion for specimens of carbon steel coated with conventional thermoplastic polymers as a blend of poly(methyl methacrylate) with poly(butylmethacrlylate),* *phenoxy resin and a poly(vinyl chloride-co-vinyl acetate) 90/10 copolymer and compared with an alkyd resin containing 0.2, 0.4 and 0.6% (w/w) of polyaniline, a conductive polymer extensively investigated for its ability to protect metals against aqueous corrosion. The results indicated that the presence of conductive polymer in alkyd resin improve the protection against corrosion of the metal and the degradation resistance of the coating, improving the overall performance of the coated steel.* ***Torresi et al.***[83] *studied the electrochemical behavior of a polymeric blend formed by camphorsulphonate or phenylphosphonate-doped polyaniline (PANI) and poly(methyl methacrylate) used for iron corrosion protection in sulphuric acid solutions with or without chloride ions. Results indicate that these blends act by a two-step protection mechanism. First, a redox reaction between Fe and PANI takes place leading to PANI reduction and concomitant anion release. Then, iron cations form a passivating complex with the PANI doping anion (camphorsulphonate or phenylphosphonate) that simultaneously acts as a second physical barrier to avoid penetration of aggressive ions.* ***Radhakrishnan et al.***[84] *prepared hybrid composite coatings containing zinc oxide (ZnO) and polyaniline (PANI) as nano-additives dispersions were prepared with poly(vinyl acetate) (PVAc) as the major matrix. The steel plates dip-coated with these formulations were tested for corrosion protection by immersion in saline water over long periods . The coatings containing both ZnO and PANI showed improved corrosion resistance as compared to the single component coating.* ***Adhikari et al.***[85] *prepared polyaniline in the presence of methane sulfonic acid (MeSA) as dopant by chemical oxidative polymerization. The polymer was dispersed in* *polyvinylacetate and coated on carbon steel samples by a dipping method. The electrochemical behavior and anticorrosion properties of the coating on carbon steel in 3% NaCl were investigated .The results indicated that polyaniline maintains its oxidative state and provides corrosion protection for carbon steel throughout the investigated period.* ***Alam et al***[86] *studied the corrosion-protective performance of soya oil alkyd coatings using different loadings of PANI (0.5 wt%, 1.5 wt% and 2.5 wt%). The coatings were evaluated for their physico-mechanical properties, corrosion-protective efficiency as well as corrosion potential studies. The results showed that high performance of corrosion porotection.* ***Bhanvase and Sonawane***[87] *prepared a new alkyd coatings by addition of water-based polyaniline–4% CaCO3 (PAC) nanocomposites into alkyd resin as anticorrosive composite . Pure polyaniline (PANI) and PAC were synthesized using ultrasound assisted emulsion polymerization and added to alkyd resin to form nanocomposite coating. Nano CaCO3 was added in different percentage ranging from 0% to 8% of monomer during the synthesis of polyaniline shows that corrosion current (*I_{corr}*) was decreased when PAC nanocomposite was added to neat coatings. Positive shift of* E_{corr}*. Also indicates that PAC nanocomposite acts as an anticorrosive additive to alkyd coating. Presence of water repellant nano CaCO3 in PAC nanocomposite has exhibited dual effect, such as improvement in mechanical and anticorrosion properties. The experimental results have shown superiority of PAC nanocomposite over PANI when PAC nanocomposite added to alkyd coatings.*

1.7. Research Scope

The scope of this research is as listed below:

1- *Nano zinc phosphate tetrahydrate*

2- *Preparation polyaniline zinc phosphate nanocomposite.*

3- *Preparation of epoxy primer modified with polyaniline / Zinc phosphate nanocomposite.*

4- *Evaluation of the coated metallic substrates against corrosion. Special attention is paid into healing effect property.*

5- *Application of the prepared modified primer in the area of metallic package (tin-coat).*

1.8. Research Objective

The aim of work is to study the application of epoxy primer which modified with polyaniline-zinc phosphate nanocomposite in the field of metallic package (tin-coat). The healing effect is studied as it is an advantageous in the area of tin coat.

Synthesis & Characterization Techniques

2.1. Chemicals

- *Zinc nitrate $Zn(NO_3)_2.6H_2O$ (s d fine – chem. limited MUMBAI), Di-ammonium hydrogen orthophosphate (El Nasr Pharmaceutical Chemical Co.) .*
- *Aniline hydrochloride, $Zn_3(PO_4)_2.4H_2O$ particles , ammonium peroxodisulphate (APS) . Acetone (El Nasr Pharmaceutical Chemical Co.).*
- *Epoxy risen (Pachin Compony).*

2.2. Instrumentation

Samples were characterized by using the instruments as listed below:

2.2.1 Vibrational Spectra (FTIR)

Vibrational spectra of the samples were recorded with JASCO FT-IR-6100 Fourier transform infrared spectrophotometer using the KBr pellet disk method for transmittance measurements.

2.2.2 Determination of molecular weight by gel permeation chromatography (GPC)

The GPC measurements were performed on Gel permeation Chromatography type; Agillent 1100, Germany. The measurements were conducted at ambient temperature using tetrahydrofuran as the mobile phase at a flow rate of 1.0 ml/ min. Polyaniline samples were dissolved in the same solvent as the mobile phase at a concentration *of 5mg /ml in solution. The amount of each sample injection was 100µl.*

Polystyrene standards with a concentration of 1mg/ ml were used for calibration (molecular weight as follows: 393.4k, 233.2k, 114.4k, 44.1k. 13.2k, 3.68, 2.33k, and 820). The calibration curve was plotted with the logarithm of average molecular weight as a function of elution volume.

2.2.3 Thermogravimetry Analysis (TGA)

Thermogravimetry analysis of PANI and its composite were investigated by using Perkin Elmer thermogravimetric analyzer with nitrogen as purge gas. The heating rate was 10 ºC per minute from 50 ºC to 1000ºC.

2.2.4 X-Ray Diffraction (XRD)

*The X-ray diffraction of PANI and its composite nano Zinc phosphate in powder form were obtained from Diano X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å) The scanning range was between angle $2\ \theta$= 0 to 60 for polyaniline and its composite; and for nano zinc phosphate the scanning range was between angle 2Θ= 0 to 80 a scanning speed of 1 /s and sampling rate of 2 data /s; the crystallinity index of the polyaniline was calculated using **Bragg's Law** which was illustrated as :*

$$n\lambda = 2d \sin \theta, \text{ for } n = 1, 2, 3 \text{ etc}$$

2.2.5 Transmission Electron Microscope (TEM)

Morphology and particle size of nano-zinc phosphate tetrahydrate and polyaniline zinc phosphate nano composite were *determined using transmission electron microscope (TEM) (JEOL [JEM-1230 electron microscope]). The samples were prepared as follows: A fine powder of the samples were dispersed in water under ultrasonication, then one drop of the suspension was suspended and evaporated on a carbon coated copper grid and placed in the Phillips (CM / TEM).*

2.2.6 Energy Dispersive X-ray photoelectron spectroscopy (EDX)

Elements present in the composite were confirmed by using energy dispersive X-ray photoelectron spectroscopy (EDX) from OXFORD model(INCAX-Sight) and supplied with Scanning Electron Microscope JEOL JXA- 840 A Electron PROBE microanalyzer microscope.

2.2.7 Scanning Electron Microscope (SEM)

Scanning electron microscope (SEM) was used to observe the surface morphology of the steel after corrosion. Micrographs were obtained using JEOL JXA- 840 A Electron PROBE microanalyzer microscope. The samples were prepared by deposition of a thin gold film, sputtered using a Balzers SCD 050 deposition system.

2.2.8 Electrochemical technique

The electrochemical measurements [Potentiostatic polarization (Tafel polarization), Potentiodynamic anodic polarization (pitting polariztion)] were carried out using Meinsberger Potentiostate/Galvanostate (zum ps6 remote) with software for calculating the electrochemical parameters. All experiments were performed in natural aerated solution at 298ºK.

Polarization experiments were carried out in a three electrode conventional pyrex glass cell as shown in figure (2.1). It consists of a vessel of about 100ml capacity provided with three openings. Two of these openings are used for fitting the working electrode as shown in Figure (2.2) and the platinum counter electrode. The platinum counter electrode is fitted in a compartment separated from the main bulk of the electrolyte by means of G-4 sintered glass disc to affect the separation of the anodic and cathodic compartments.

The potential of the working electrode was measured relative to a saturated calomel electrode (SCE), which is fitted in the third opening of the glass cell. The reference electrode has a lugging capillary probe, which is placed very near to the surface of the working electrode. The electrolytic cell and their components were carefully cleaned, after each experiment to remove any foreign residues especially the metallic products formed during the measurements.

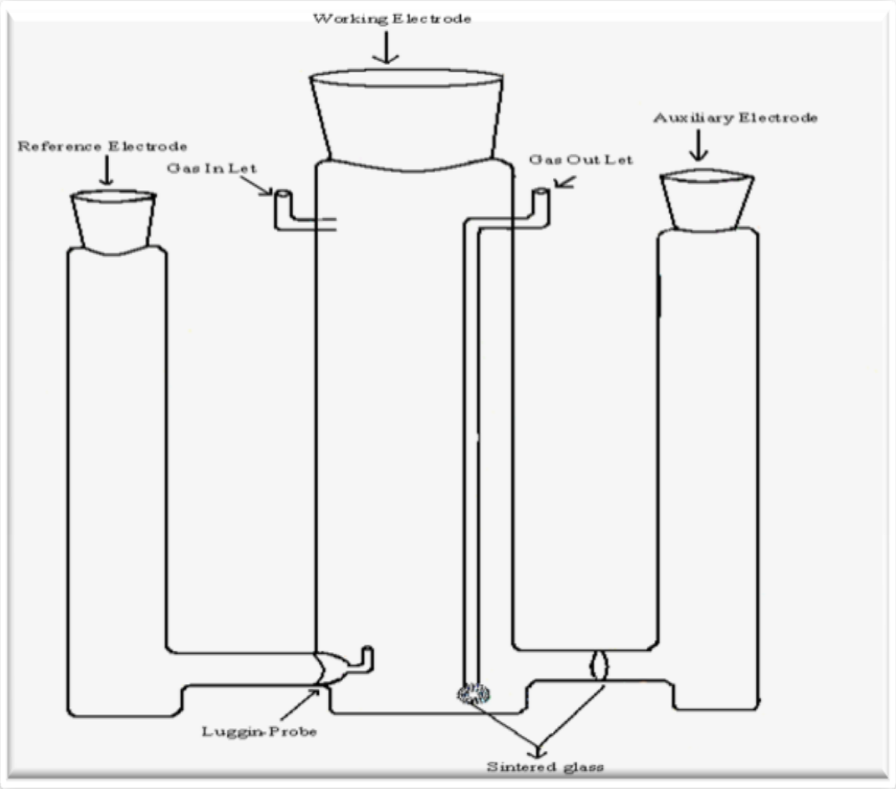


Figure (2.1): *Cell*

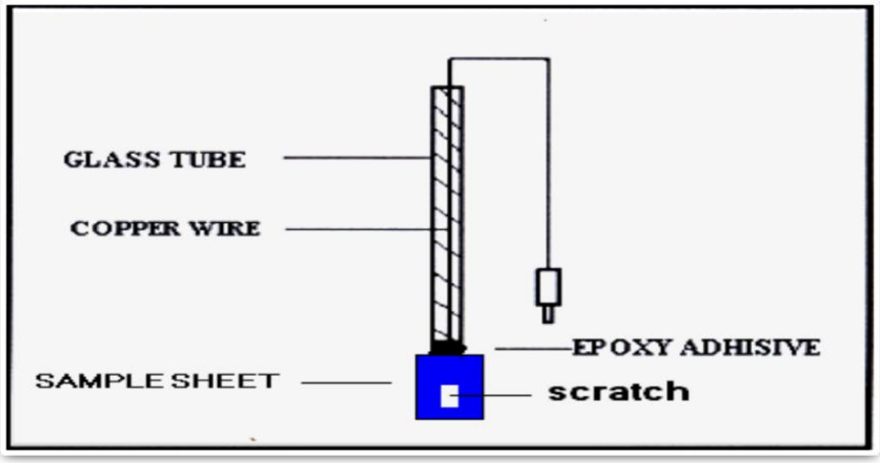


Figure (2.2): *Working Electrode*

2.2.9 Dielectric

The electrical properties of polyaniline, its composite, epoxy resin and blend desks of polyaniline with epoxy and polyaniline nano composite with epoxy by using the computerized LRC Bridge (Hioki model 3532 LCR Hi Tester). The bridge measures the capacitance from 19 pF up to 370 mF, the resistance from 100 mΩ *up to 200 M*Ω *and the dielectric less than (*δ*) from* 10^{-5} *up to* 10^{1}*. The a-c resistivity as well as the dielectric constant* $\in$ *for the investigated samples was carried out from room temperature up to ……..*^{o}*C at different frequencies ranging from 42Hz up to 5 MHz. The samples used in the measurement were in the form of pellets in the form of circular disk specimens of …..mm diameter and ……mm thickness, pressed using a pressure of …… Ton at room temperature. The surfaces of each pellet were carefully polished and then coated with silver paint (BDH). Figure* ***(2.3)*** *illustrate the diagram of (LCR Hi tester).*

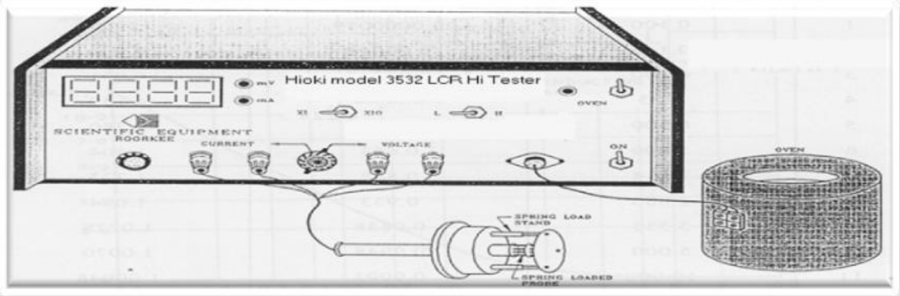


Figure (2.3) *Diagram of the LCR Hi Tester*

2.3. Synthesis

2.3.1 Preparation of nano particles $Zn_3 (PO_4)_2.4H_2O$

11.7g of Di-ammonium hydrogen orthophosphate was dissolved in 25 ml distilled water in100ml two-necked round-bottom flask equipped with a thermometer, stirrer with heating in water bath and stirring for 1h. 29.2g $Zn (NO_3)_2.6H_2O$ was dissolved in 25ml H_2O and then added to the reaction mixture drop wise. The resulting mixture was allowed to react for 3h with heating and stirring. The product was washed with distilled water for several times, and then sample was characterized by TEM.

The reaction of preparation was carried out as the following:

$$3Zn (NO_3)2 + 2(NH_4)_2HPO_4 + 4H_2O \longrightarrow Zn_3 (PO_4)_2\cdot 4H_2O + 4NH_4NO_3 + 2HNO_3$$

2.3.2 Preparation of Polyaniline- $Zn_3 (PO_4)_2.4H_2O$ Nanocomposite

To prepare PANI- $Zn_3(PO_4)_2.4H_2O$ of different ratio , the following weights were used 0.00,0.15,0.25,0.35,0.45 g from $Zn_3(PO_4)_2.4H_2O$ nano particles were added into a solution of 4gm aniline hydrochloride dissolved in 50ml H_2O in a set of reaction vessels. The mixtures were stirred with mechanical stirrers in ice water bath for 1h. To these mix, 5gm of APS dissolved in 50ml H_2O was added drop wise. The resulting mixtures were allowed to react in ice water bath for about 4h. From these reactions we get pure PANI or we can get PANI- $Zn_3 (PO_4)_2.4H_2O$ nanocomposite. The products *were filtered and washed with distilled water for several times and at last one washed with acetone to remove low molecular weight oligmers along with other impurities, then all samples were dried in an oven for 12 h. These samples were characterized by TEM.*

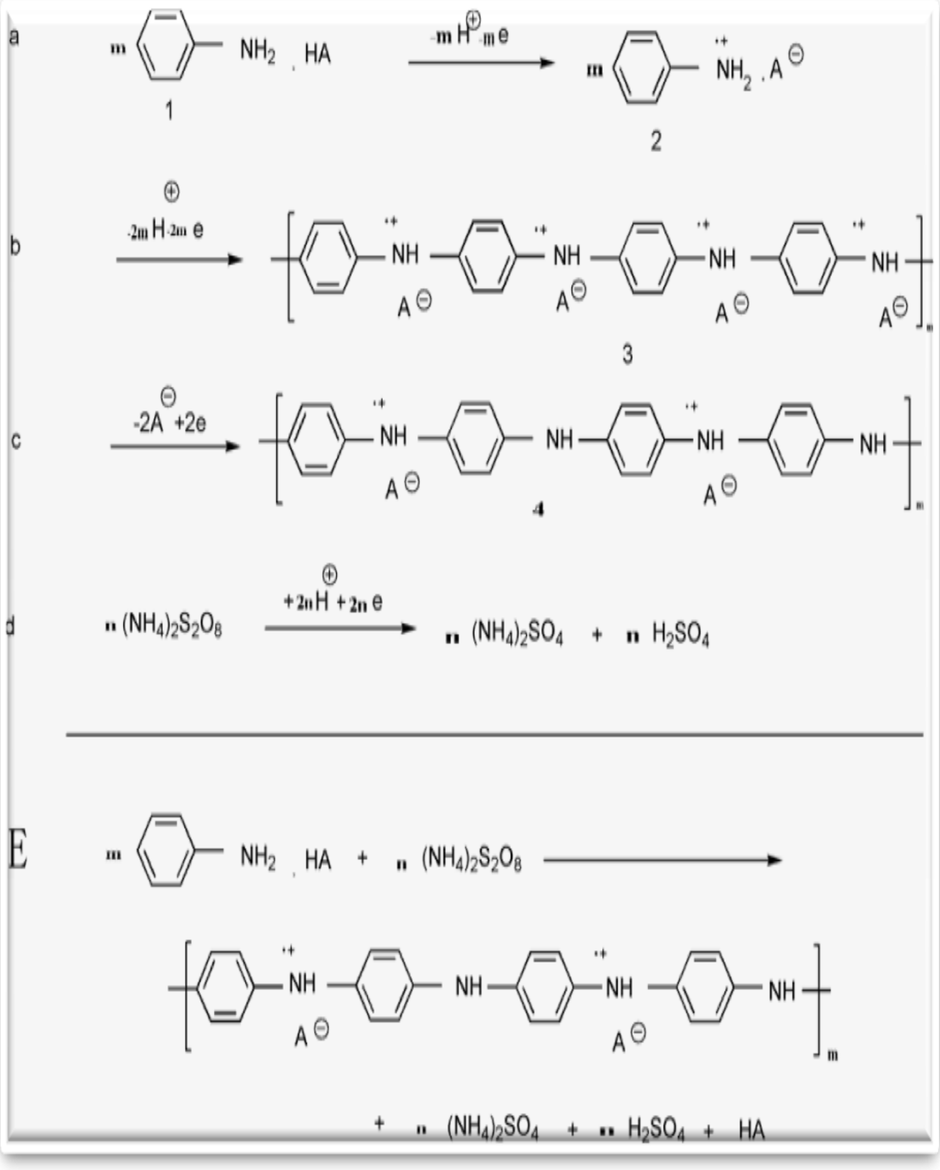


Figure (2.4): *Reaction mechanism of polyaniline*

2.3.3 Preparation of epoxy primer modified with PANI- Zinc phosphate nanocomposite

(2gm) of epoxy was dissolved in (20ml) solvent .PANI- $Zn_3(PO_4)_2.4H_2O$ *nanocomposite in the following ratios were added (0.0gm, 0.1gm, 0.2gm, 0.3gm, 0.5gm); then the hardener (0.25gm) was added to the mixture. The Stainless steel panels were coated by the pervious formulation prepared from different ratios of epoxy / PANI-* $Zn_3(PO_4)_2.4H_2O$ *using the wire-wound draw down bar and dried at room temperature for 7 days.*

2.4. Preparation of steel panels for testing purposes

1. *Remove the rust by sanding the panels.*
2. *The rust free panels wiped vigorously on both sides with a cloth wet with solvent (eg. methanol) to remove any film of oil present. The panels were then cleaned by solvent spray gun. The panels were then cleaned by solvent spray gun. The solvent consists of equal volumes of petroleum naphtha and xylene.*
3. *The panels were allowed to dry at room temperature (15minutes), and then rubbed briskly with a clean, lintless cloth to remove any adhering dirt or smut.*
4. *The panels were dipped in phosphoric acid (1:1) at 25°C for a minimum of 15 seconds.*
5. *The panels were dried at a temperature between 50°C - 100°C and coated immediately or stored in a desiccator for future use.*
6. *The panels should not be touched with the finger during the process of preparation.*

2.5. Methods of testing of painted film

2.5.1Fineness (D 1210 – 96)

This test method covers measurement of the degree of dispersion (fineness of grind) of the pigment in a pigment-vehicle system such as liquid coatings and their intermediates.

2.5.1.1Test Method

There are two technique for measuring the fineness degree:

***2.5.1.1.1 Tapered Gage:** The product is spread by means of a scraper figure (2.5) in a machined tapered path figure (2.6). At some point in this path, particles or agglomerates, or both, will become visible. A direct reading from the graduated scale is then made at the point where the particles from a definite pattern. When the single path gage is used it is also possible to rate "cleanliness".*

***2.5.1.1.2 Stepped Gage:** The product is spread by means of a scarper figure (2.5) on a stepped gage (2.7). There are two delimited sections on this gage, each of 1 inche^2 (6.5 cm^2) area, and of two different depth. A count is made of the particles deposited in the two delimited* *areas, and cleanliness (texture) reading is determined.*

Table (2.1): *Degree of fineness*

Hegman Scale[A]	***Depth, µm***[B]	***Depth, mils***[B]	***PC or FSPT Scale***[C]	***NPIRI Scale***[D]
0	*100*	*4*	*0*	*40*
1	*90*	*3.5*	*1¼*	*35*
2	*75*	*3*	*2½*	*30*
3	*65*	*2.5*	*3¾*	*25*
4	*50*	*2*	*5*	*20*
5	*40*	*1.5*	*6¼*	*15*
6	*25*	*1*	*7½*	*10*
7	*15*	*0.5*	*8¾*	*5*
8	*0*	*0*	*10*	*0*

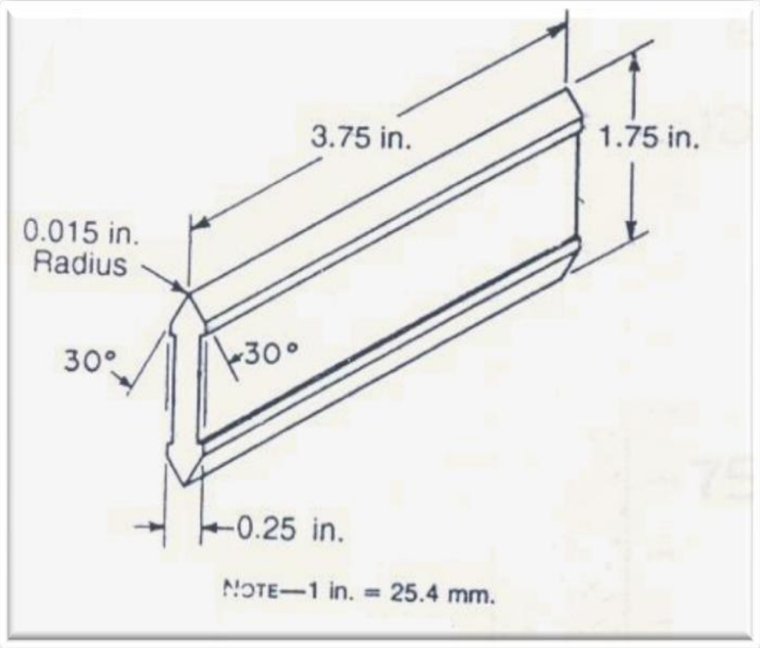
[A] *Sometimes referred to inche error as the North Standard scale.*

[B] *Rounded to nearest 5 µm or 0.5 mil.*

[C] *Federation of Societies for paint Technology scale.*

[D] *National Printing Ink Research Institute scale, 0 to 10 on NPIRI*

Production Grindometer, but extended on many gages to 20 or 30



Figure(2.5): *Scraper*

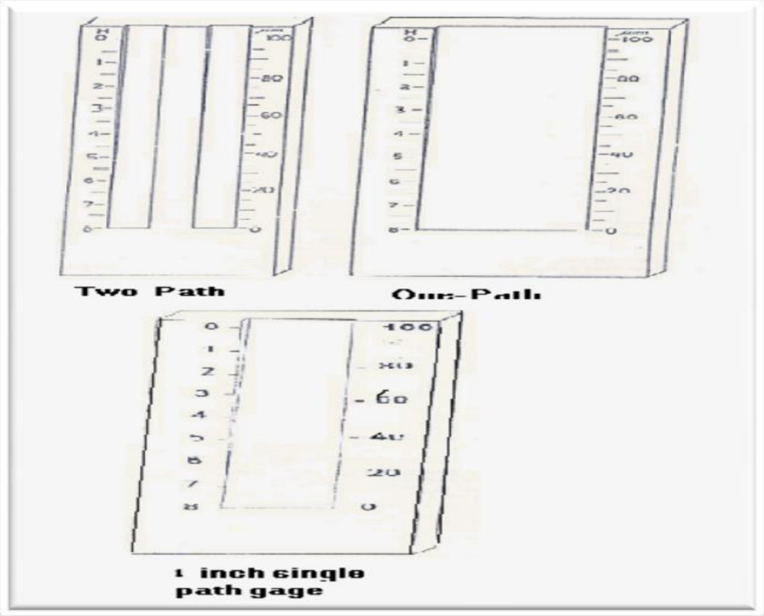


Figure (2.6): *Tapered Gage*

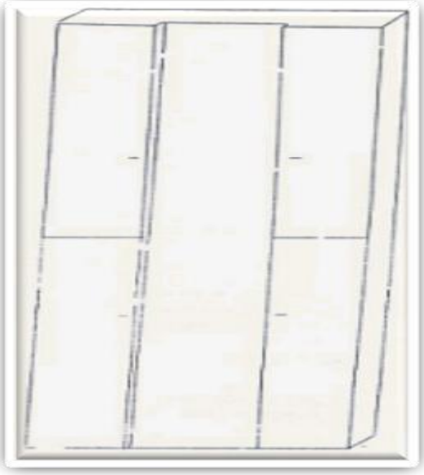


Figure (2.7): *Stepped Gage*

2.5.2 Drying time (D 1640 – 95)

To determine ***Set-To-Touch Time-Lightly Touch*** *the test film at point not less than15 mm from the film edges with the tip of a clean finger and immediately place the fingertip against a pieces of clean, clear glass. Observe if any of the coating is transferred to the glass. The film is consider to has set-to-touch when it still shows a tacky condition, but none of it adheres to the finger.*

Dry Time: With the end of the thumb resting on the testing on the test film and the forefinger supporting the test panel, exert a maximum downward pressure (without twisting) of thumb on the film.

2.5.3 Gloss (D 523 – 89)

The degree of gloss a coated film may be directly measured using a gloss meter. There are various models available, some of which are designed for laboratory use and some of which are portable. Gloss meter contain a light source set at a specific incident *angle to the coated sample; a photo-electric cell, which is a set at the same angle as the angle of incidence, measures the reflected light. The amount of reflected light, which depends on the surfaces specular reflectance is displayed on a meter as a percentage of the incident light. The geometry of angle are used according to the gloss level involved and the reasons for measurement as follows :*

1- *The 60° geometry is normal for general use.*
2- *The 20° geometry is advantages for comparing specimen 60° gloss higher than 70°. It gives a sensitive measure for high gloss paints.*
3- *The 85° geometry is useful only for comparing specimens have 60° gloss value lower than 10.*

2.5.4 Adhesion (D 3359 – 95)

Adhesion, is a very important property of a paint system, and some useful empirical information can be obtained by the cross hatch test. If a coating is to fulfill function of protecting or decorating a substrate, it must adhere to it for expected service life. These test methods cover procedures for assessing the adhesion of coating films to substrates by applying and removing pressure-sensitive tape (25 mm wide semi- transparent tape) over cuts in the film. In this test method a lattice with six cuts in each direction is made in the film to the substrate (space the cuts 1 mm), pressure-sensitive tape is applied over the lattice and then removed, and adhesion of the film is assessed from the amount of the coating removed. The adhesion is reported as follow:

Table (2.2): *The adhesion scale*

Classification	***Percent Area Removed***
5B	*0% None*
4B	*Less than 5%*
3B	*5-15%*
2B	*15-35%*
1B	*36-65%*
0B	*Greater than 65%*

2.5.5 Impact (D 2794 – 93)

This method covers a procedure for evaluating the effect of such deformation. The organic coatings under test are applied to suitable thin metal panels. After the coatings have cured, a standard weight is dropped a distance so as to strike an indenter that deforms the coating and the substrate. The indentation can be either an intrusion or an extrusion. By gradually increasing the distance of the weight drops, the point at which failure usually occurs can be determined. Films generally fail by cracking, which is made more visible by the use of a magnifier, by the application of a copper sulfate solution on steel, or by the use of a pinehole detector.

2.6. Testing of corrosion resistance properties

three different techniques have been employed for studying corrosion and corrosion inhibition of the samples of painted steel.

2.6.1 Gravimetric techniques

Gravimetric measurements were carried out in glass bottle contain 100ml of the corrosive solution of (0.1M) NaCl. Rectangular *steel specimens with a surface area of 0.2 cm^2 were used. The sheet samples were hanged in the corrosive medium. At the end of each test the specimens were carefully washed by distilled water and acetone, dried and then weighted.*

The corrosion rate (W) was calculated in (mpy) unit according to the following equation [88] *:*

$$W=1.437*mg/At$$

Where; mg is the weight loss in milligrams, A is the surface area of the used specimens in dm^2, and t is the time of immersion in days.

Accordingly; the values of surface coverage (θ'') were calculated using the following equation[89]*:*

$$\theta''=1-(W/W^o)$$

Where W and W^o are the corrosion rates (mpy) of steel specimen in presence and absence of the additive, respectively.

The present inhibition efficiency (IE%) was determined using the following equation[90] *:*

$$IE\%=[1-(w/w^o)]*100$$

2.6.2 Physical tests

Rinse specimens after scratching them in a solution of (0.1M) NaCl for about 21days using a gentle stream of air; make the following tests for measuring the corrosion resistance according to ASTM standard for corrosion:

2.6.2.1 Determination the degree of blistering of paints (D 714-87)

This method employs photographic reference standard to evaluate the degree of blistering Figure (2.8, 2.9, 2.10, 2.11) that *may developed when paint systems are subjected to conditions which will cause blistering. While primarily intended for use on metal and other nonporous surface, this method may be used to evaluate blisters on porous surface, such as wood, if the size of blisters falls within the scope of these reference standards.*

A quantitative physical description of blistering would include the following characteristic determined by actual count:

2.6.2.1.1 Size :

Reference standards had been selected have been selected for four steps as to size on a numerical scale from 10 to 0, in which No. 10 represents no blistering. Blistering standard No. 8 represents the smallest size blister easily seen by the unaided eye. Blistering standards Nos. 6,4and 2 represents progressively large sizes.

***2.6.2.1.2 Frequency** :*

Reference standards had been selected for four steps in frequency at each step in size, designated as follows:

Dense, D
Medium dense, MD
Medium, MFew, F

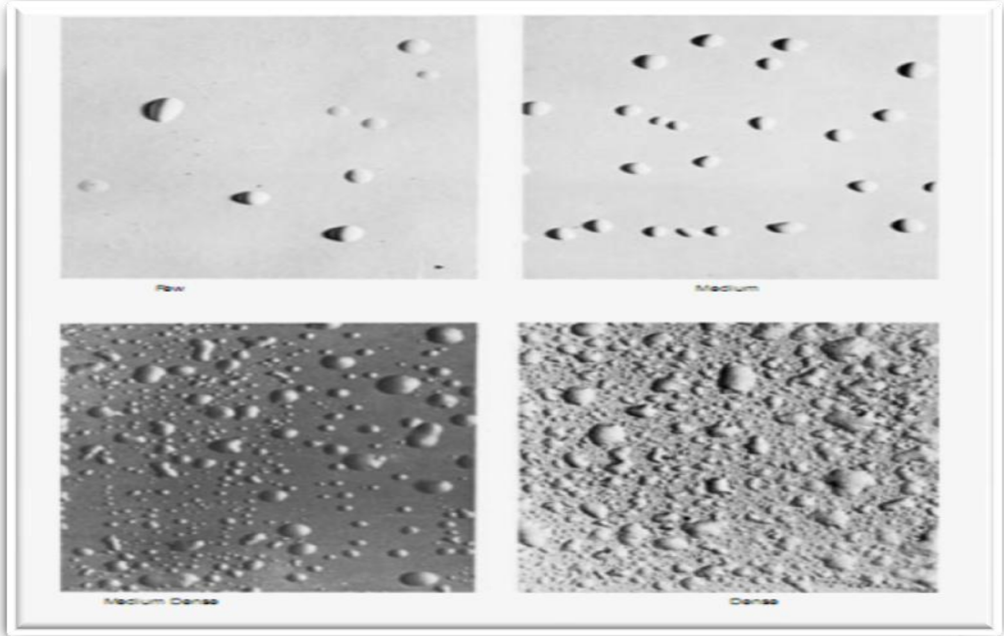


__Figure (2.8):__ Blister size no (2)

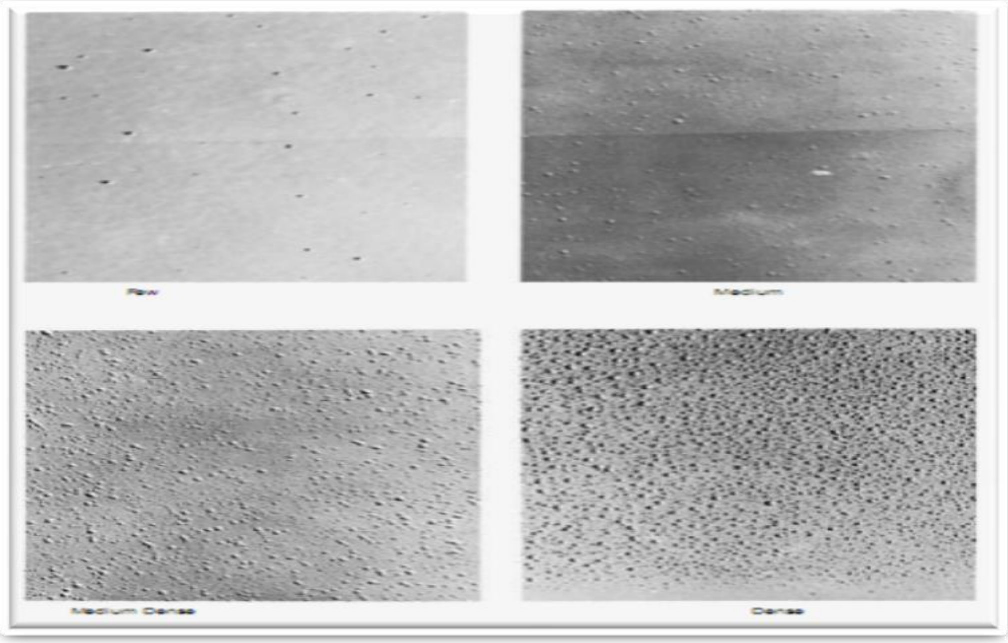


__Figure (2.9):__ Blister size no (4)

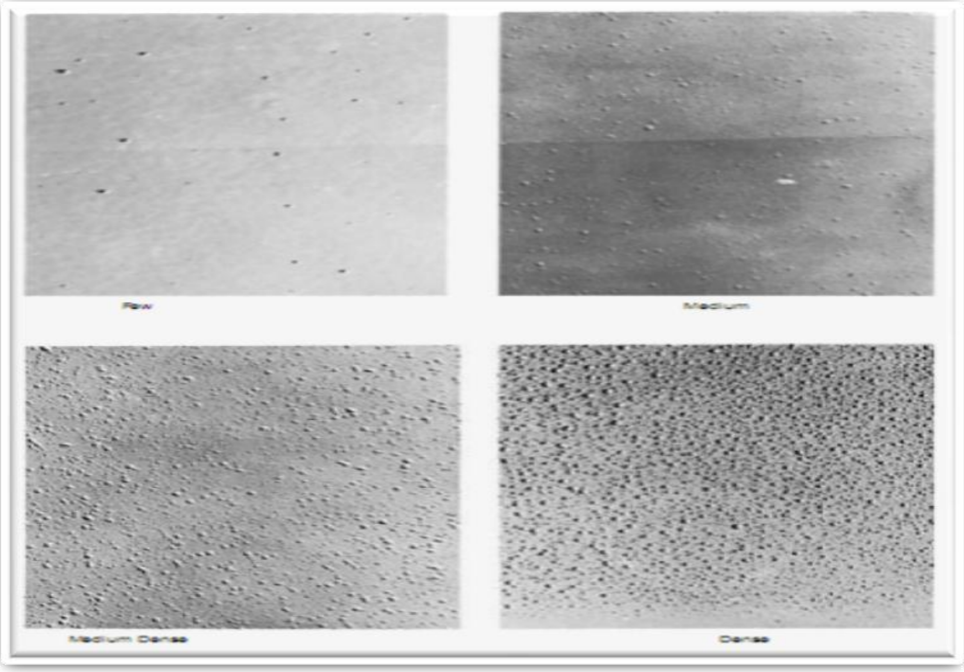


Figure (2.10): *Blister size no (6)*

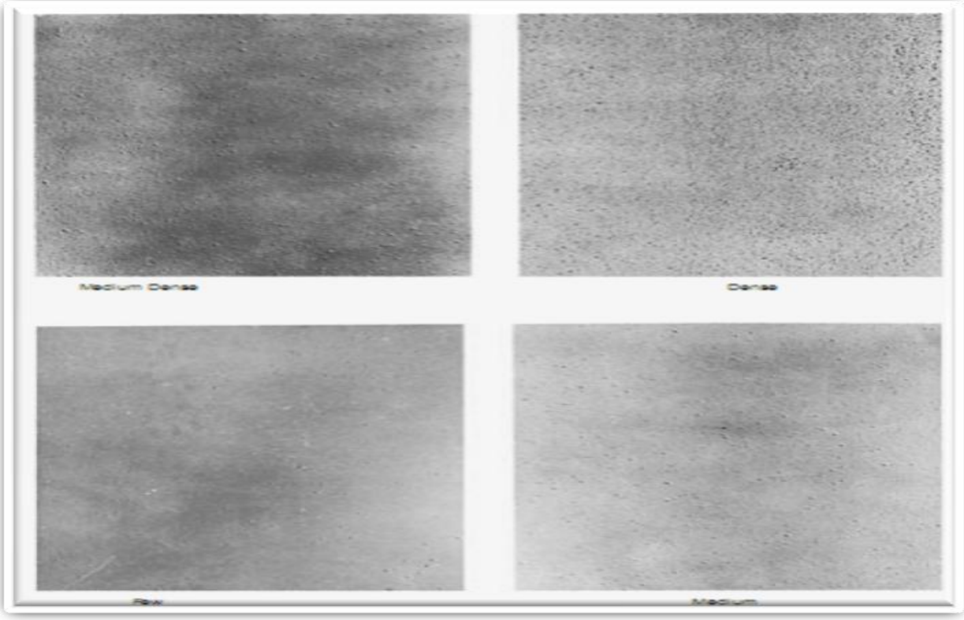


Figure (2.11): *Blister size no (8)*

2.6.2.2 Determination the degree of rusting on painted steel surface (D 610-95)

The color photographic reference standards available for use with this method are representative of degree of rusting on painted steel (or iron) surface.

The color photographic reference standards and the associated rust-grade scale cover only rusting not accompanied by blistering and evidenced by visible rust.

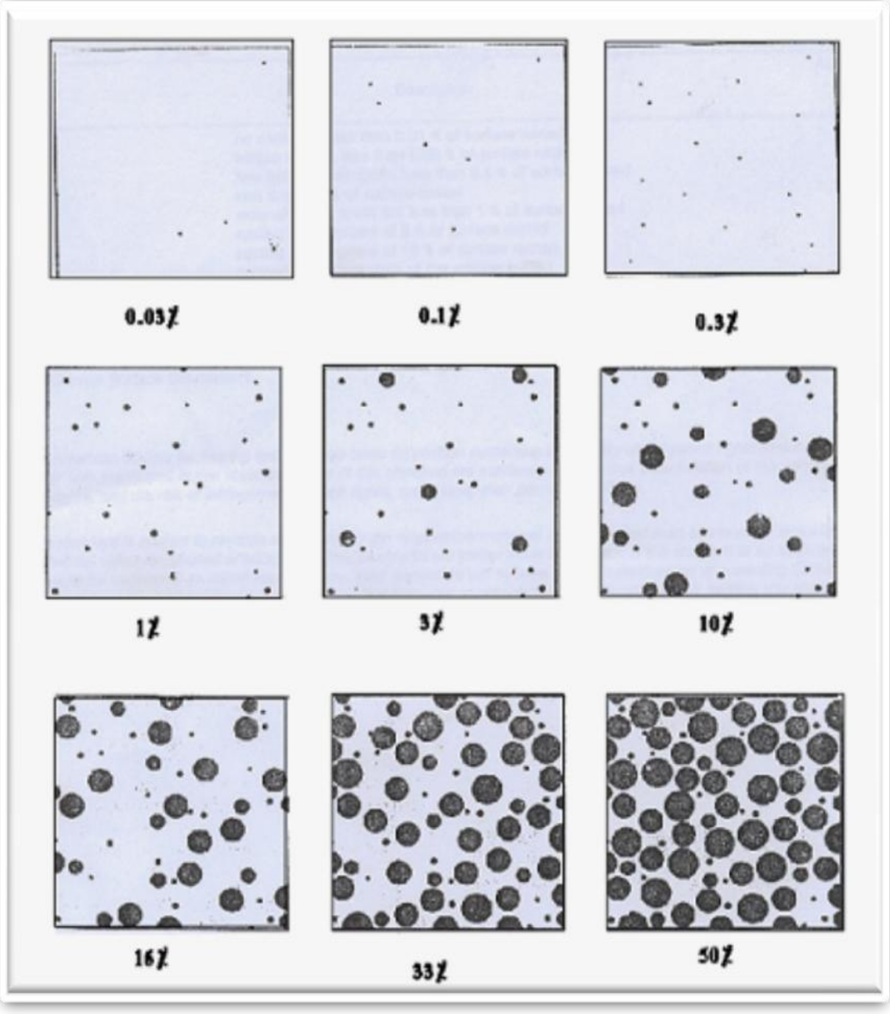


Figure (2.12): *Examples of area percentage*

2.6.2.3 Determination of painted or coated specimens subjected to corrosive environments (scribe failure) (D 1654-92)

This method covers the treatment of previously painted or coated specimens for accelerated and atmospheric exposure tests and their subsequent evaluation in respect to corrosion, blistering associated with corrosion, loss of adhesion at scribe mark, or other film failure.

Painted or coated specimens subjected to a corrosive environment are evaluated by recording the average (mean) maximum and minimum creep age from the scribe mark.

Table (2.3): *Rating of Failure Scribe*

Representive mean creepage from scribe		
Millimetres	***Inches Approximate***	***Rating Number***
Zero	*0*	*10*
Over 0 to 0.5	*0 to 1/64*	*9*
Over 0.5 to 1.0	*1/64 to 1/32*	*8*
Over 1.0 to 2.0	*1/32 to 1/16*	*7*
Over 2.0 to 3.0	*1/16 to 1/8*	*6*
Over 3.0 to 5.0	*1/8 to 3/16*	*5*
Over 5.0 to 7.0	*3/16 to 1/4*	*4*
Over 7.0 to 10.0	*1/4 to 3/8*	*3*
Over 10.0 to 13.0	*3/8 to 1/2*	*2*
Over 13.0 to 16.0	*1/2 to 5/8*	*1*
Over 16.0 to more	*5/8 to more*	*0*

2.6.3 Electrochemical methods

Each specimens was cut in rectangle shape for usage as a working electrode. Specimen was fixed to Pyrex glass after scratching by means of aralldit, while the electrical contact was made through thick copper wire soldered to the electrical end, not exposed to the solutions.

2.6.3.1 Potentiostatic polarization technique (Tafel polarization)

At the start of each experiments, the working electrode was stand for 10 minutes in the test solution to attain its steady state potential. The polarization scan rate was 10mv/sec.

The anodic and cathodic Tafel lines are extrapolated to the corrosion potential (E_{corr}) and the intercept of the two Tafel plots is the corrosion current density. The percentage inhibition efficiency (IE%) and surface coverage (θ'') were calculated according to following equation [91,92]*:*

$$IE\% = [1 - (i_{corr}/i^{o}_{corr})] * 100$$

$$\theta'' = 1 - (i_{corr}/i^{o}_{corr})$$

Where i_{corr} and i^{o}_{corr} are the corrosion rates in terms of current density of steel specimen in the presence and absence of the polyaniline nanocomposite.

2.6.3.2 Potentiodynamic anodic polarization technique (Pitting potential)

At the start of each experiment, the working electrode was stand for 10 minutes in the test solution to attain its steady state *potential. The polarization scan rate was 1mv/sec. The pitting potential was determined at pitting initiation.*

Sodium chloride solution of (0.1M) concentration was used as a corrosive medium for studying the pitting corrosion on each specimen.

2.7. measuring the electrical properties

The samples used in the measurement were in the form of pellets in the form of circular disk specimens of …..mm diameter and ……mm thickness, pressed using a pressure of …… Ton at room temperature. The surfaces of each pellet were carefully polished and then coated with silver paint (BDH). Before conducting the experiment the surfaces were checked for good contact. The sample was located between two cell electrodes and then was inserted into non – inductive furnace, used for heating the samples with constant rate. The temperature of the sample connected to thermometer with junction in contact with the sample. The accuracy of measuring temperature is $\pm 1^{o}C$.

The real part, ε, of the dielectric constant, was calculated using the relations:

$$\varepsilon = L\ Cs / A\ \varepsilon_o, \text{-------------------------------} \Leftarrow (1).$$

Where L is the thickness in m, A is the area in m^2, *Cs is the capacity in F, and* $\varepsilon_o = 8.85 \times 10^{-12}\ C^2/Nm^2$.

The conductivity constant, was calculated using the relations:

$$1/\rho=\varepsilon_0\ \acute{\varepsilon}\ \sigma \text{-------------------------------} \Leftarrow (2).$$

Where;

$$\acute{\varepsilon}= C\ L/\varepsilon_0 A \text{-------------------------------} \Leftarrow (3).$$

$$\sigma = 2\ \pi\ f\ L\ C\ \tan(\sigma'/A) \text{-------------------------------} \Leftarrow (4).$$

Where C is capacitance, f is the frequency, σ' *is the dielectric loss*

Result and Discussion

3.1. Synthesis of PANI and PANI- Zn_3 $(PO_4)_2.4H_2O$ nanocomposite.

Single route 'in-situ' deposition polymerization method was employed to synthesis ***PANI*** *and* ***PANI- Zn_3 $(PO_4)_2.4H_2O$*** *nanocomposite.*

Initially, during the polymerization of ***PANI*** *and* ***PANI- Zn_3 $(PO_4)_2.4H_2O$*** *nano composite in water was colorless. Nonetheless, 10–20 minutes after the addition of the initiator APS solution into the aqueous solution, the milky color of the solution turned blue and later green and turned dark green at the end of the polymerization, indicating the formation of protonated emeraldine form* ***PANI****.*

3.2. Elemental analysis

The obtained results for the study of the presence of elements in the nanocomposite are analyzed by ***EDAX*** *were presented in Figuer (3.1). It shows the presence of* ***C, N, O, Cl, Zn*** *as beside as* ***P****.* ***Zn*** *and* ***P*** *which refer to both polymer and* ***$Zn_3(PO_4)_2.4H_2O$*** *are present in the* ***PANI-Zn3(PO4)2.4H2O*** *nano composites.*

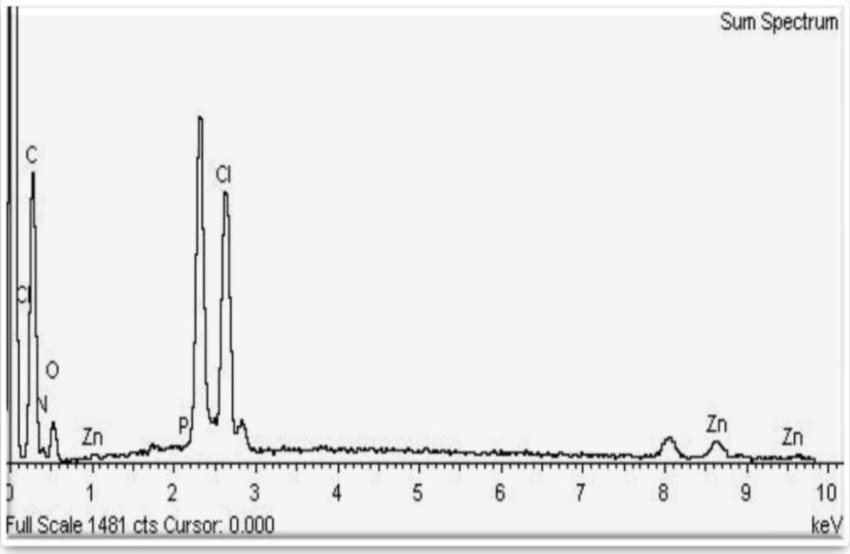


Figure (3.1): *EDAX of PANI- Zn3(PO4)2.4H2O nanocomposite*

3.3. Vibrational Spectroscopic Characterization of PANI and its Composite (FTIR)

*FT-IR analysis of the **PANI** and **PANI-$Zn_3(PO_4)_2.4H_2O$** nanocomposites prepared using 18 wt% of **$Zn_3(PO_4)_2.4H_2O$** were performed.*

*The spectra is presented and compared in Figure (3.2). The characteristic peaks of PANI Figure (3.2a) were at 3436 and 3220 $cm^{-1}$is due to the asymmetric and symmetric stretching modes of NH^{2+} group; respectively[93], and peaks at 1470 cm^{-1}1 and 1657 $cm^{-1}$is due to the stretching of the C-N bonds of benzenic and quinonic rings, respectively, and are present due to the conducting state of **PANI**[94,95]. When they appear in equal intensities, PANI is in the emeraldine base form[96]; peak at 1563 cm^{-1} is due to quinoid (N=Q=N) ring stretching mode; peaks at 1292cm^{-1} and 1240 cm^{-1} is* *due to deprotonation of the aromatic amines of the polymer; the band characteristic of the conducting polymer due to the delocalization of electrical changes was observed as a sharp and strong band at around 1106 cm^{-1}. The* ***PANI-*** **$Zn_3(PO_4)_2.4H_2O$** *nanocomposites shows at transmission curve Figure (3.2b) similar peaks to that of* ***PANI****, and some shifts were observed at lower wave length .*

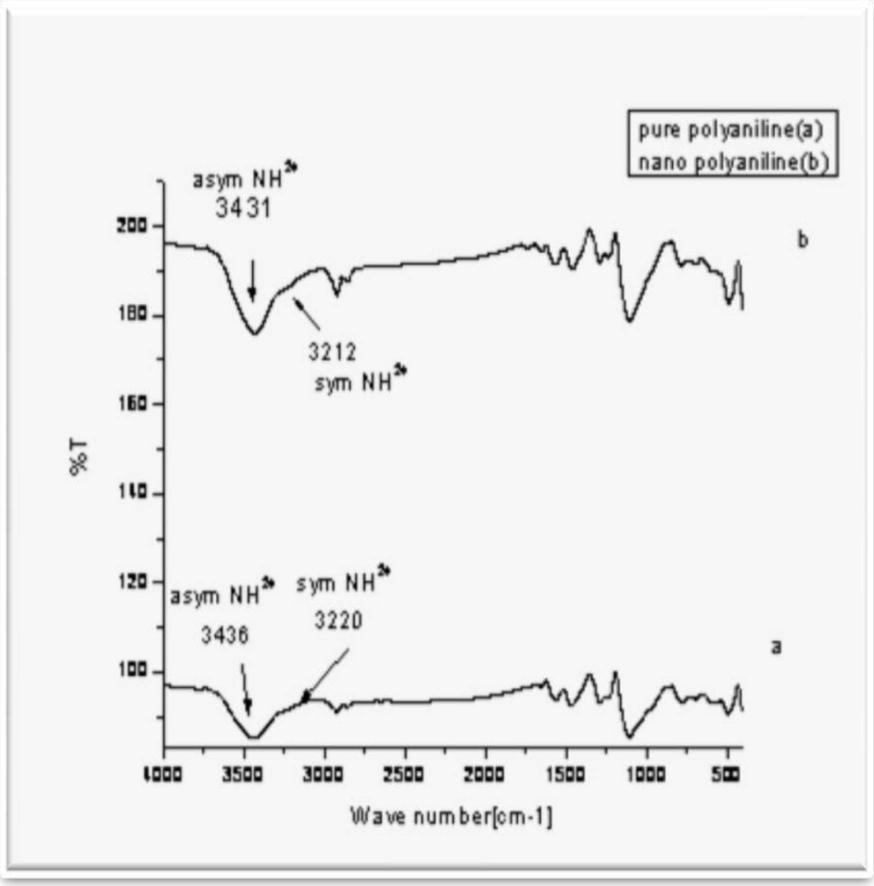


Figure (3.2): *FTIR of pure polyaniline, nano polyaniline*

3.4.Determination of molecular weight by gel permeation chromatography (GPC)

The obtained results of molecular weights of the prepared PANI were determined and it were as presented in Table [3.1], the average molecular weight (M_w) the number average molecular weight ($M_{n,)}$ and the polydispersities (p_{in}¯) showed slightly an increase in case of polyaniline zinc phosphate nano composite than that prepared for polyaniline .

Table (3.1): gel permeation chromatography (GPC)results

samples	***average molecular weight(M_w)***	***number average (M_n)***	***Polydispersities (p_{in}¯) M_w/M_n***
polyaniline	***6048***	***4477***	***1.3508***
Polyaniline nanocomposite	***10745***	***7843***	***1.3689***

From the table (3.1) it can be detected that, the average molecular weight increased from 6048 for PANI alone to 10745 for the prepared PANI in presence of Zinc phosphate nanoparticles; also the number average increased from 4477 to 7843 also the polydispersities from 1.3508 to 1.3689. These results mean the presence of Zinc phosphate nanoparticles keep on polymer hemoginite where the polydispersities are fairly equal.

3.5. Thermogravimetry Analysis (TGA)

TGA is widely used to study the thermal stability and all physical process involving the weight changes with the temperature, such as to measure the diffusion characteristic and the moisture uptake of a sample. In addition, it is also employed to investigate the thermal degradation, phase transition and crystallization of polymers.

The thermogravimetric profiles of **PANI** *and* **PANI-$Zn_3(PO_4)_2.4H_2O$** *nanocomposites (Figure 3.3) with a high variation degradation temperature. In case of pure polyaniline the first stage 7% weight loss at temperature up to 84.9°C is associated with the loss of water molecules from the polymer matrix* [93,95, 96,97]*. The second stage that commences after 84.9°C until 207.4°C, the weight loss (about 14 %) is due to the removal of the acid dopant bound to the polyaniline chain and low-molecular-weight oligomers. A slow and somewhat gradual weight loss profile observed starting at 207.4 °C onwards, represents degradation of the skeletal polyaniline chain structure after the dopant has been removed* [93, 95,96, 98]*. Above 502°C, the results obtained are associated with the residues only.*

In the other hand; the first stage of polyaniline nanocomposite 13% weight loss at temperature up to 107.9 is associated with the loss of water molecules from the polymer matrix. The second stage that commences after 107.9°C until 216.7 °C, the weight loss (about 10%) is due to the removal of the acid dopant bound to the polyaniline chain and low-molecular-weight oligomers. A slow and somewhat gradual weight loss profile observed starting at 216.7°C onwards, represents degradation of the skeletal *polyaniline chain structure after the dopant has been removed. Above 550.25°C, the results obtained are associated with the residues only.*

Table(3.2):*TGA of PANI and its composite*

Temperature range (ºC) (Weight loss, %)			
samples	***1st step***	***2nd step***	***3rd step***
PANI	***50-84.9***	***84.9-207.4***	***207.4***
PANI nanocomposite	***50-107.9***	***107.9-216.7***	***216.7***

From the TGA results obtained; it can be observed the presence of Zinc phosphate nanoparticles increase the stability of the prepared polyaniline nanocomposite; where the stages of degradations were shifted to higher temperatures values. The first stage which represent loss of water molecules occurred up to 107.9ºC instead of 84.9ºC. Also the second stage which due to removal of the acid dopant was shifted. The third stage which represents degradation of the skeletal PANI chain after

the dopant has been removed was shifted from 216.7ºC to 550.25ºC.

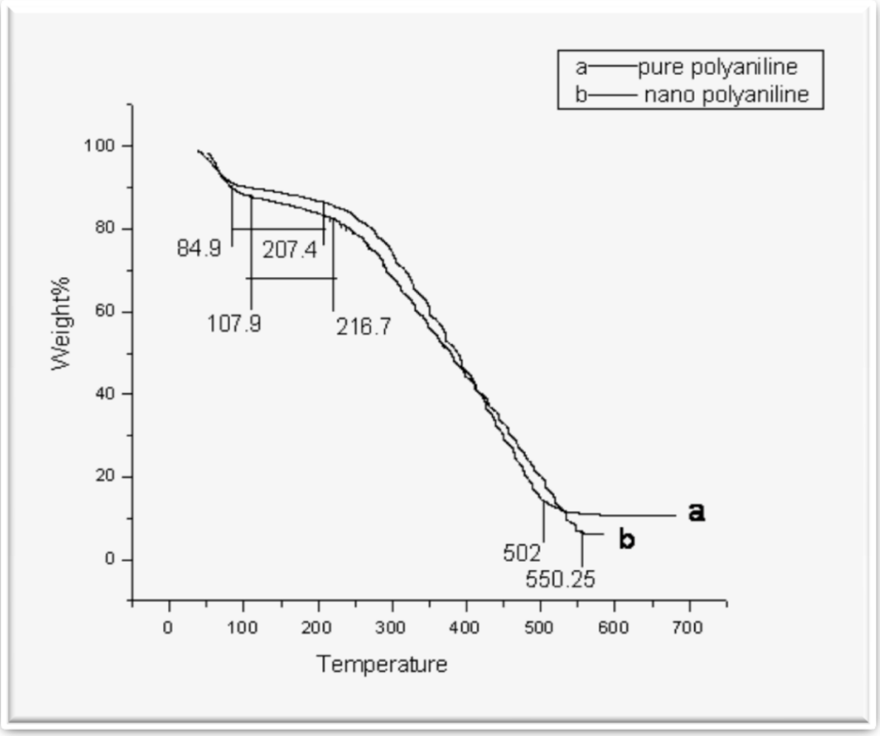


Figure (3.3):*TGA curves of PANI and its composite*

3.6. X-Ray Diffraction (XRD)

Many materials, especially polymers, have a substantial volume fraction without crystalline order. Though these regions are often termed amorphous, they frequently have specific local order. Structural information and crystallinity of the doped ***PANI*** *can be obtained by X- ray studies. The X-ray diffraction analysis is a powerful tool to determine the structure and crystallization of polymer matrices. The effect of* $Zn_3(PO_4)_2.4H_2O$ *addition in the* ***PANI*** *and its composite were analyzed through the same XRD technique. The respective diffraction patterns of pure* ***PANI*** *and its composite,* $Zn_3(PO_4)_2.4H_2O$ *are shown in Figure (3.5,3.6).*

Just like the regular rigid polymers that own lots of benzene rings, the XRD pattern of PANI obtained is very similar to previous reports [99, 100] *where the orientation of the polymer has been taken on the basis of a pseudo orthorhombic cell* [100]*. As reported in most literature, most of the forms of* ***PANI*** *essentially amorphous and show the presence of broad high-angle asymmetric scattering peaks stretching from 2θ between 15 – 25. The main peaks of the synthesized* ***PANI*** *Figure (3.4a) itself seems to comprise at least three broad separate peaks indicate an* **amorphous** *shape:*

Table (3.3): *Position of pure PANI peaks*

Position 2Theta(2Θ)	***15.5700***	***20.3700***	***25.87***
d-spacing (Aº)	***5.69141***	***4.35984***	***3.56123***

The main peaks of ***PANI nanocomposite*** *Figure (3.4b) comprise at least thirteen broad separate peaks indicate a sharp peak determine a* **semi crystalline** *shape:*

Table (3.4): *Position of PANI nanocompsite peaks*

Position 2Theta(2Ө)	***d-spacing (A°)***
14.5900	***6.07142***
19.5900	***4.53163***
21.1300	***4.20471***
24.9871	***3.56371***
27.3300	***3.25238***
29.6674	***3.01131***
30.9600	***2.91326***
31.4853	***2.84146***
37.3491	***2.40773***
40.2100	***2.24278***
42.1477	***2.14405***
45.8925	***1.97580***
49.8900	***1.82796***

From table (3.3,3.4) we can see the effect of presence of nano Zinc Phosphate on the XRD where the main peak of pure PANI 2Ө=25.87 had been shifted to 2Ө=27.33

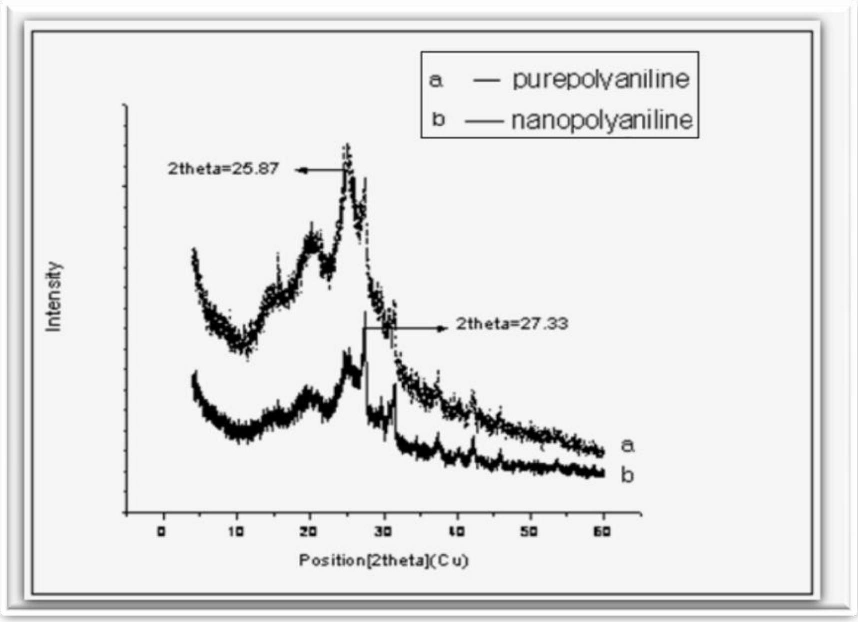


Figure (3.4): *XRD of PANI and its composite*

The peaks of nano zinc phosphate tetrahydrate particles exhibit an ***Orthorhombic Pyramidal*** *shape where a≠b≠c & α=β=γ=90º as shown in figure (3.5).*

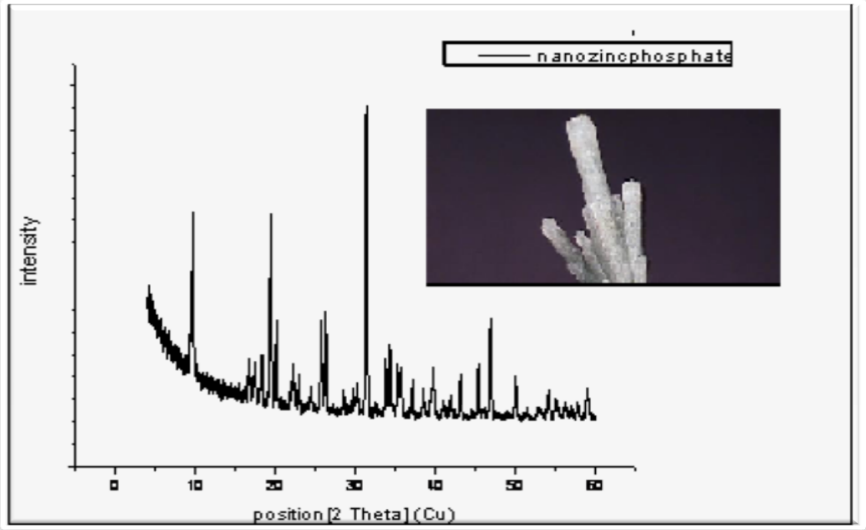


Figure (3.5): *XRD of nano Zinc Phosphate tetrahydrate*

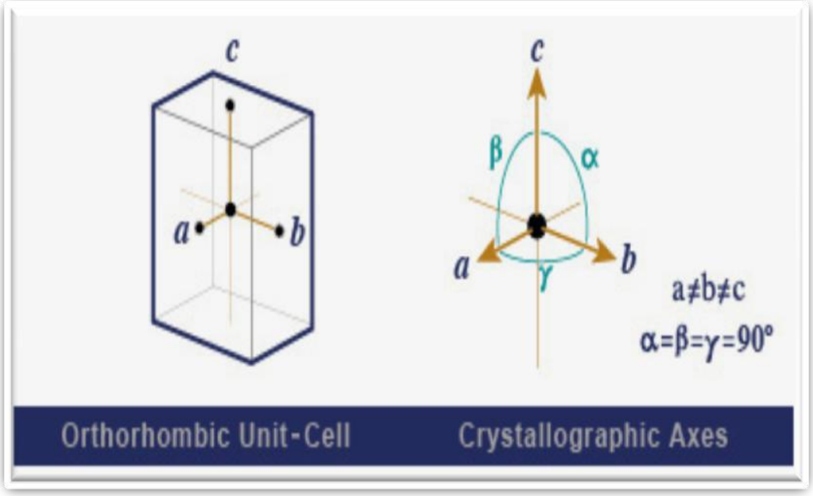


Figure (3.6): *Orthorhombic unit cell & crystallographic axes*

3.7. Morphology and size of nano Zinc Phosphate tetrahydrate and PANI/ Zn_3 $(PO_4)_2.4H_2O$ Nanocomposite

Using ***TEM*** *we can compare the morphology and size of the prepared* Zn_3 $(PO_4)_2.4H_2O$ *and* **PANI-** Zn_3 $(PO_4)_2.4H_2O$ *nanocomposites loaded by 18wt. % of* Zn_3 $(PO_4)_2.4H_2O$*.* Zn_3 $(PO_4)_2.4H_2O$ *nano particles represented in Figure (3.7) are in* **spherical and some tube** *in shape; XRD determine that the tube shape is an* **Orthorhombic Pyramidal** *shape with very small size (nano range); its average diameter was about* ***(10nm)****, and there were aggregates due to their large surface area and the interaction between the particles. The* **PANI-** Zn_3 $(PO_4)_2.4H_2O$ *nanocomposites photograph Figure (3.8) was found tube in shape; or in an* **Orthorhombic Pyramidal** *shape with very small size nanometer diameter; its average diameter about* ***(57nm)****, and they are aggregates may be due to their large surface area formed and increasing the interaction between the particles. From the TEM we can understand that the polymerization of polyaniline* *takes placed on the surface of nano Zinc Phosphate tetrahydrate particles to be obtained this shape.*

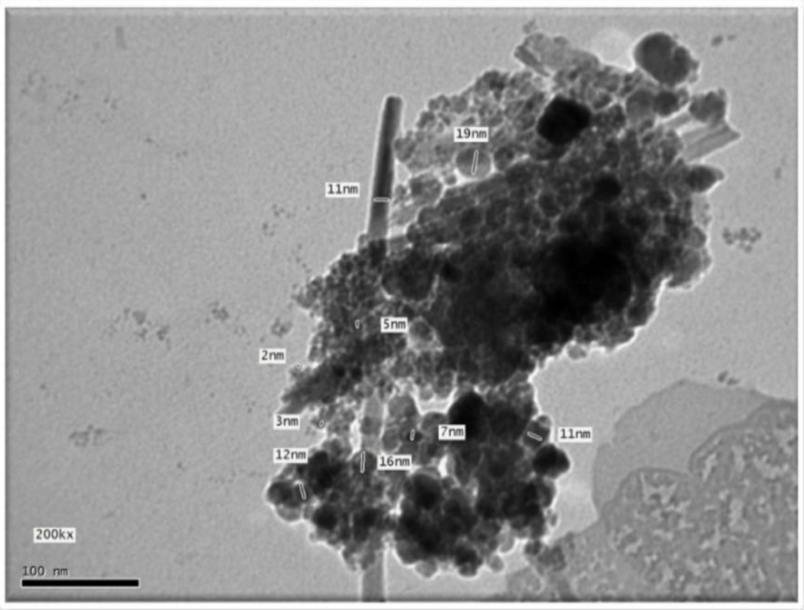


Figure (3.7): *TEM of* $Zn_3(PO_4)_2.4H_2O$

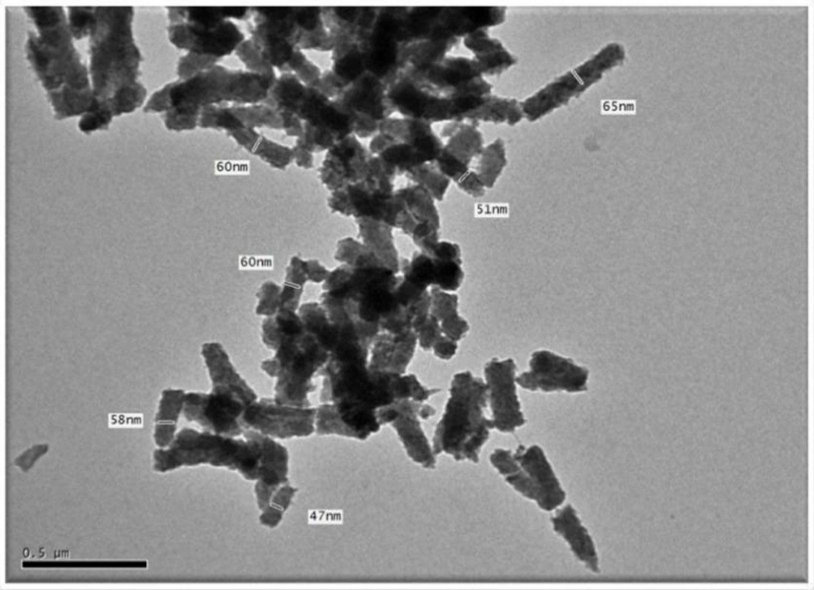


***Figure (3.8)**: TEM of PANI-* $Zn_3(PO4)_2.4H_2O$ *nano composites*

3.8. Testing of Painted film measurements

The physical properties of painted film panels were studied to evaluate of the presence of PANI/Zinc phosphate nanocomposite. The obtained results are shown in table (3.5):

1. *All painted films have a suitable drying time.*
2. *Painted films containing PANI- $Zn_3(PO_4)_2.4H_2O$ nano composites have better gloss than the blank one.*

Table (3.5): *The measurements of painted film*

Tests	***Amounts of PANI/Zinc phosphate nanocomposite***				
	0.0gm	***0.1gm***	***0.2gm***	***0.3gm***	***0.5gm***
Fineness	*4.5H*	*4.5H*	*4.5H*	*4.5H*	*4.5H*
Drying time (hr.)	*4*	*4*	*4*	*4*	*4*
Gloss at 60^0c	*19.5*	*35*	*36*	*26.4*	*27*
Adhesion	*GT0*	*GT0*	*GT0*	*GT0*	*GT0*
Impact at 100Kg.Cm	*OK*	*OK*	*OK*	*OK*	*OK*
Bending	*OK*	*OK*	*OK*	*OK*	*OK*
Film thickness	*50M*	*50M*	*50M*	*50M*	*50M*

9. Corrosion resistance Measurements

9.1 Gravimetric Measurements

A variety of methods are used for the determination of corrosion rate of the painted panels such as weight loss, thermometry, chemical analysis, and electrochemical investigations.

Steel, when exposed to an industrial atmosphere, reacts to form rust as a reaction product, of approximate composition, Fe_2O_3-H_2O*. This compound is loosely adherent and does not form a protective barrier that isolate the metal from the environment.*

The inhibition corrosion for steel is very important due to use it in packaging application. In the present part of this study, the effect of some compounds as inhibitor on the corrosion rate of steel is studied by the weight loss technique. Finally, the mode if inhibitive action of the tested compound is proposed on the basis of the known inhibitive theories.

The corrosion rates (mpy) obtained from the weight loss measurements of steel painted with epoxy unmodified and modified with polyaniline nanocomposite of different ratios in 0.1M NaCl are given in Table (3.6).

Table (3.6): *Rate of corrosion (mpy) obtained from weight loss measurements at different amounts of polyaniline nanocomposite in 0.1M NaCl at different time of immersion at 298K*

Amount of PANI nanocomp-osite	**14 days**			**35 days**		
	W (mpy)	**θ''**	**IE%**	**W (mpy)**	**θ''**	**IE%**
0	$6.3*10^{-6}$	--------	-------	0.8813	--------	------
0.1	0	1	100	0.2512	0.7149	71
0.2	0	1	100	0.0240	0.9728	97
0.3	0	1	100	0.0288	0.9673	96
0.5	$5.7*10^{-6}$	0.0952	9	0.2646	0.6998	69

The table (3.6) shows that all the different ratio from the PANI – Zinc phosphate nanocomposite can reduce the corrosion rate of the steel.

Inspection of the tables reveals that, the corrosion rates of steel painted with epoxy only increased with increasing the time of immersion with high rate.

Also the corrosion rates of steel painted with epoxy resin modified with polyaniline nanocomposite slightly increased with increasing the time of immersion and the lowest rate due to the role of ***PANI*** *in corrosion protection is by the virtue of its redox behavior.* ***PANI*** *is expected to capture the ions liberated during the corrosion* *reaction of steel in the presence of NaCl, water and oxygen get doped and liberate the dopant ions which form a passivating layer even when there is initiation of the corrosion process at the substrate and this may be due to the increase in electrical conductivity of PANI nanocomposite, which in turn increase the electrical conductivity of epoxy primer as shown in figure (3.9, 3.10). Thus, it acts as a self healing coating with improved corrosion resistance. Since the release of the ions by* ***PANI*** *would be facilitated if it is in the form of thin layer on nano-* **$Zn3(PO4)2.4H2O$** *support, its corrosion prevention will become more effective than if it is in the form of solid particle. Also the presence of nano Zinc phosphate in the paint formula has very important role in the protection of steel due to its mechanism of the phosphatisation of the iron surface and the formation of compounds with hydroxyl groups of the binder agent. Also; it can inhibit the cathodic de-adhesion process at the interface as shown in Figure(3.11).*

The rate of corrosion (mpy) was determined according to “Gravimetric technique” *in page 57, also we can determined* θ'' ***value*** *and IE%.*

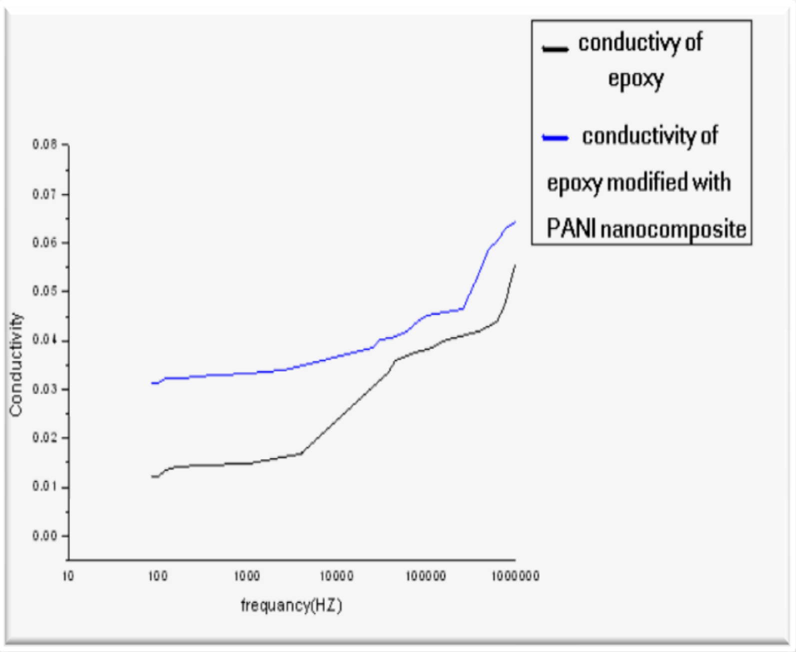


Figure (3.9): *Relation between frequency & conductivity*

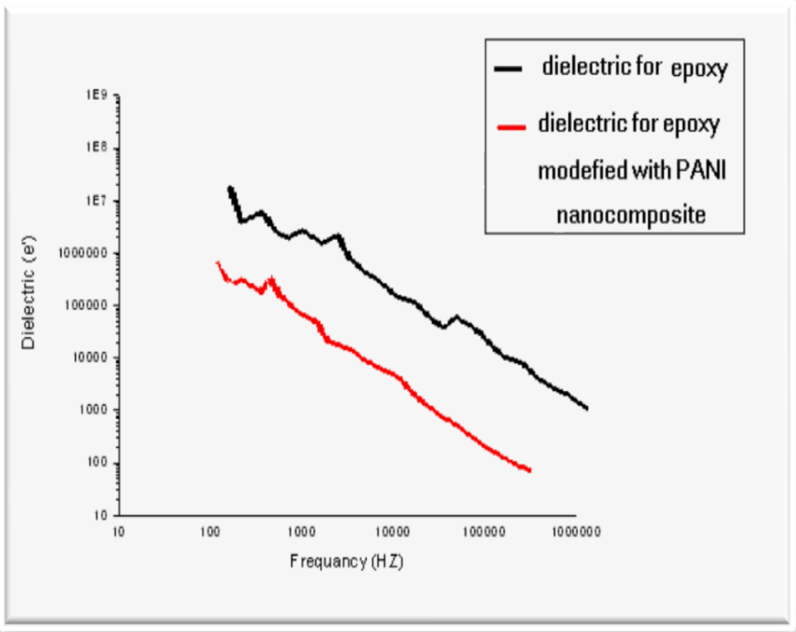


Figure (3.10): *Relation between frequency & dielectric*

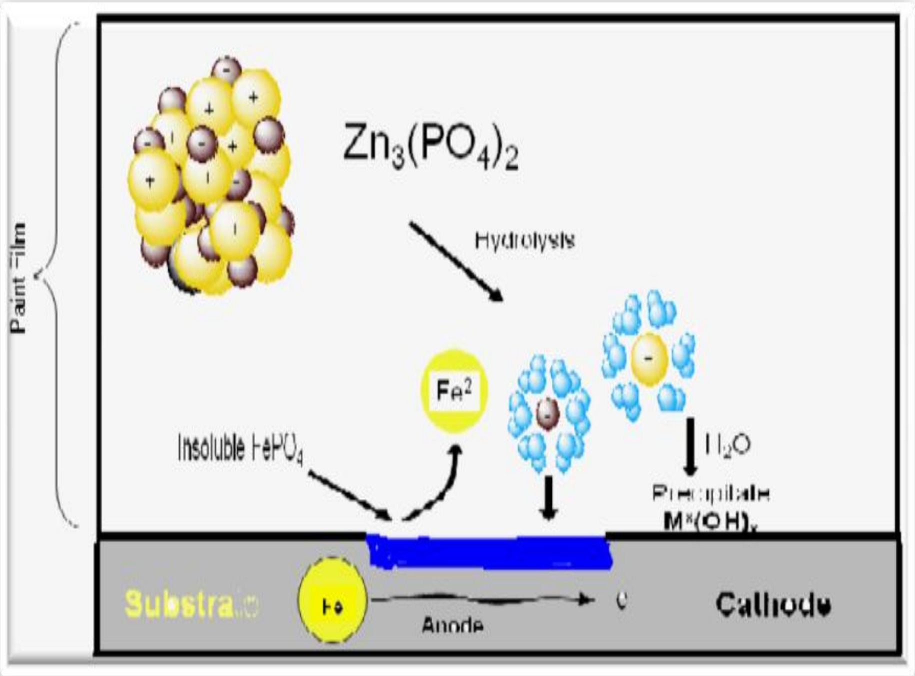


Figure (3.11): *phosphatisation of the iron surface by zinc phosphate*

Although at high amounts of polyaniline nanocomposite it had a lower corrosion inhibition after 14 days as it gives 9% corrosion inhibition but by the time its inhibition efficiency increased (69%) and this is may be due to irregular diffusion of the particles in painted film due to the crowd between them.

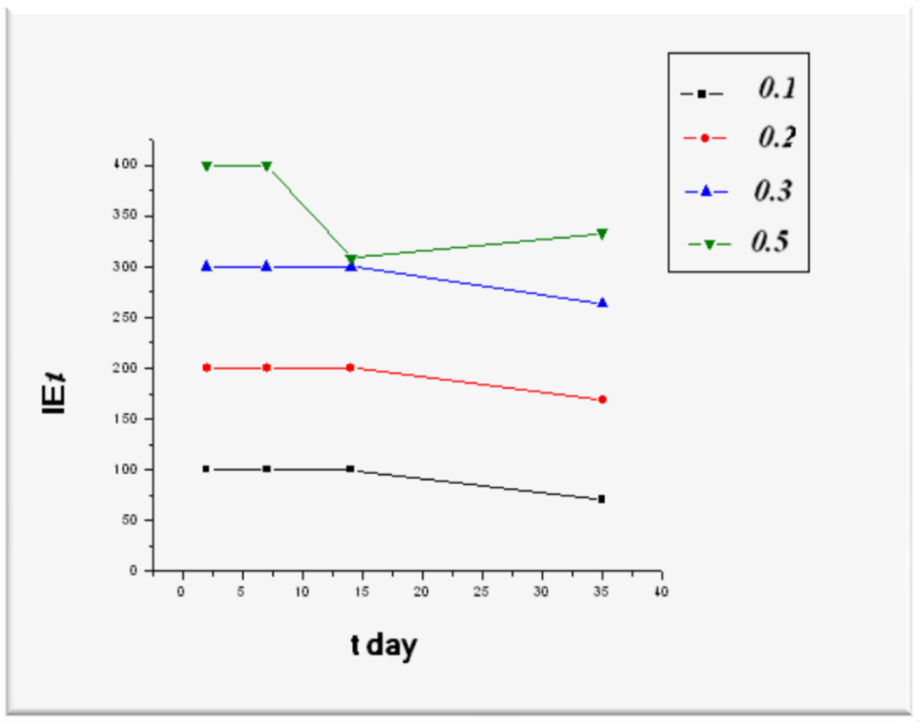


Figure (3.12) : *The effect of time of immersion in days on the inhibition efficiency of different amounts of polyaniline nanocomposite on steel in 0.1M NaCl.*

Figure (3.12) represents the change in inhibition efficiency with time for corrosion resistance of painted film of steel at different amounts of PANI Zinc phosphate nanocomposite in the paint formulations.

Inspection of this figure reveals that, the inhibition efficiency of polyaniline nanocomposite was slightly decreased as the time of immersion increased. Initially, inhibition efficiency reached its maximum values due to the formation of more protective layers, and then decreased with increasing the immersion time. At low inhibitor amounts (0.1gm), the decreasing of inhibition efficiency was due to *the presence of uncovered area on the metal surface, but at high inhibitor amounts (0.5gm) , the decreasing due to the irregular diffusion of the particles in painted film due to the crowd between the particles.*

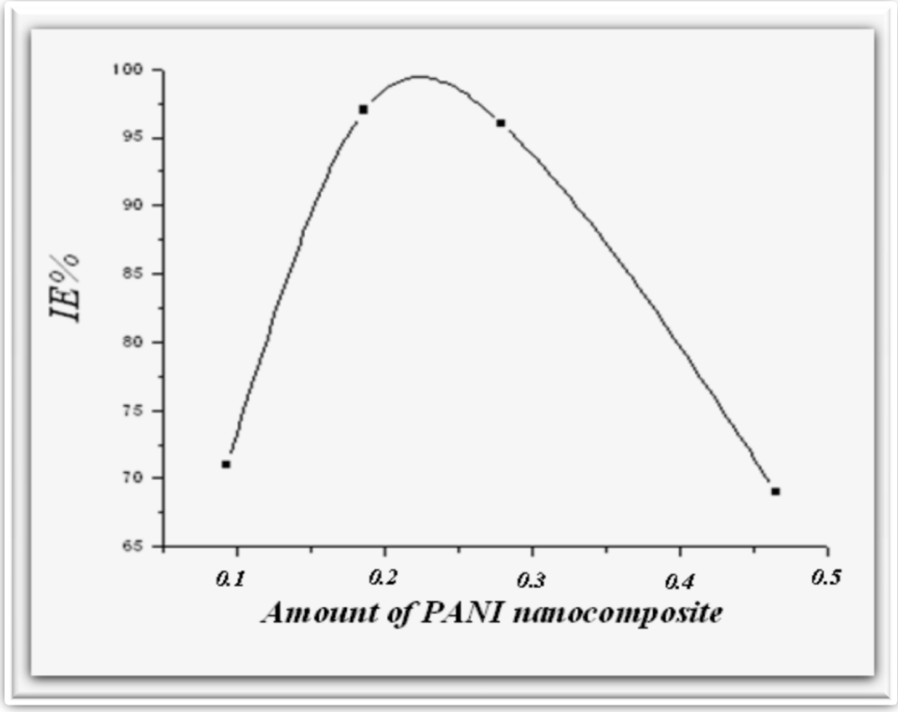


Figure (3.13): *The effect of amounts of polyaniline nanocomposite on their inhibition efficiency on steel panels in 0.1 M NaCl after 35 days of immersion at 298K.*

Figure (3.13) represents the change in the inhibition efficiency on steel panels with increasing the amounts of PANI nanocomposite.

As shown in this figure it can be seen that, for polyaniline nanocomposite the inhibition efficiency increases with increasing its amounts up to a certain limit value at which more increasing of amounts led to a slight decreased of the inhibition efficiency.

The order of increasing of inhibition efficiency was as the following according the amounts of PANI/Zinc phosphate nanocomposite in the painted formula as the following:

Blank<0.5<0.1<0.3<0.2

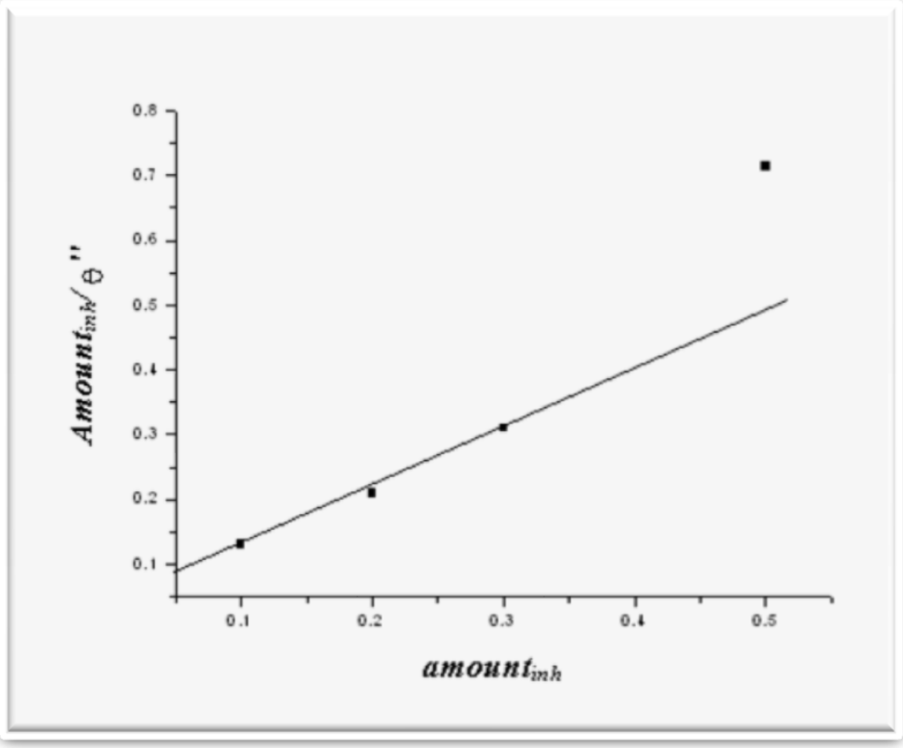


Figure (3.14): *The plot of Langmuir adsorption isotherm for the different amounts of polyaniline in 0.1M NaCl after 35days of immersion.*

The basic assumption of Langmuir adsorption isotherm holds the adsorption of molecules independently with a characteristic local standard free energy. Langmuir adsorption isotherm could be written in the following form [101,102]*;*

$$Amount_{inh}/\Theta'' = amount_{inh} + (1/K_{ads})$$

$$K_{ads} = 1/55.5(e^{-\Delta G_{ads}/RT})$$

Where amount$_{inh}$ is the inhibitor amount and K_{ads} is the adsorption equilibrium constant, and ΔG_{ads} is the change of the free energy of adsorption.

Table (3.7): *Adsorption parameters of Langmuir equation for polyaniline nanocomposite*

Organic additive	**Log K_{ads}**	**ΔG_{ads}, KJ/mol**
Polyaniline nanocomposite	**3.474**	**-24.05**

9.2 Physical measurements

Photographic recording of steel painted films immersed in a solution of (0.1M) NaCl for 21days using a gentle stream of bubbles is shown in Figure (3.15,3.16). The obtained results are given in Table (3.8).

Panels are rated for rusting on a scale from 10to 0, with 10 being no rust or less than 0.01% of surface rusted and 0 refer to sever rusting.

Blistering was also graded on a scale from 10 to 0, with 10 no blistering and 0 for largest blisters; blister frequency is denoted by F, M, MD, D for few, med., med. dense and dense respectively.

Scribe failure rated from 10 to 0, 10 being 0 mm failure from scribe and 0 being 25mm or more failure from scribe.

Standard test methods	Blank 0.0gm	Specimen1 0.1gm	Specimen2 0.2gm	Specimens3 0.3gm	Specimens4 0.5gm
1-degree of blistering	MD; blister size No.2	F; blister size No.2	F; blister size No. 4	M; blister size No. 4	M; blister size No.2
2-rating of failure at scribe	7	9	10	10	8
3-degree of rusting	33%	0.3%	0.03%	0.1	1%

Table (3.8): Results of physical tests

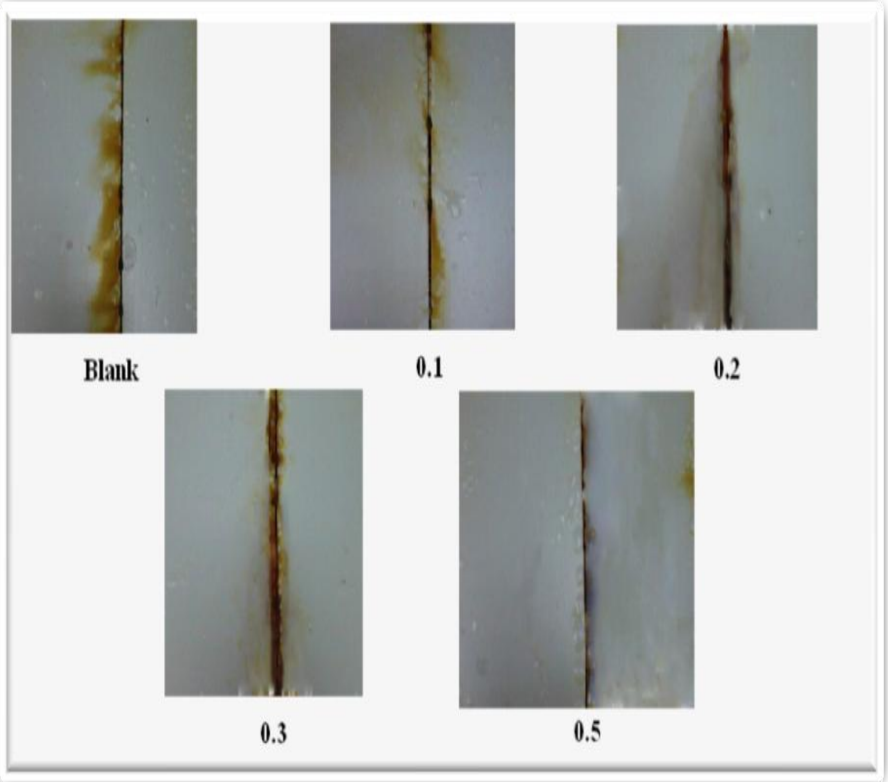


Figure (3.15): *painted films after corrosion test*

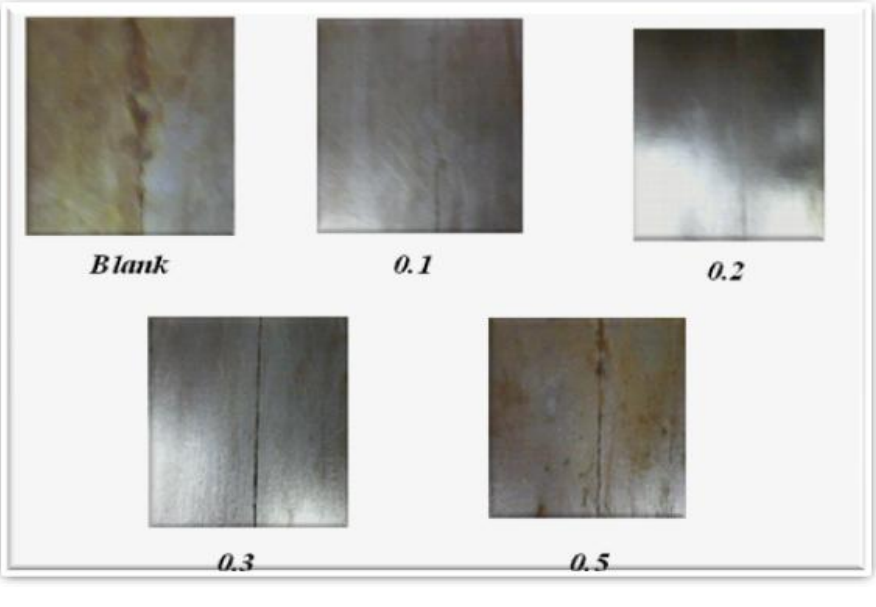


Figure (3.16): *panels after rusting test and paint removal*

*Table (3.8) and Figures (3.15,3.16) indicate that; The best ratio of adding **PANI- $Zn_3(PO_4)_2.4H_2O$** nano composites to the painted formula was 0.2gm ;whereas it show the best corrosion protection ,blistering resistance and no scribe failure, while the worst ratio was 0.5 due to an irregular diffusion of the particles in painted film and this may be due to the crowd between them.*

3.9.2.1 The surface morphology of the steels after corrosion

*By using **SEM** we compared between the morphology of steel without the modification with polyaniline (Blank) and the steel with 0.2gm polyaniline nanocomposite after immersion them in corrosive medium (NaCl 0.1M).*

The figures showed that the steel which painted without any polyaniline nanocomposite had a lower corrosion resistance Figure(3.17); in the other hand the steel which painted with epoxy resin modified with 0.2gm of polyaniline had a higher corrosion resistance and this is due to the healing effect of polyaniline where PANI is expected to capture the ions liberated during the corrosion reaction of steel in the presence of NaCl, water and oxygen get doped and liberate the dopant ions which form a passivating layer even when there is initiation of the corrosion process at the substrate Figure (3.18).

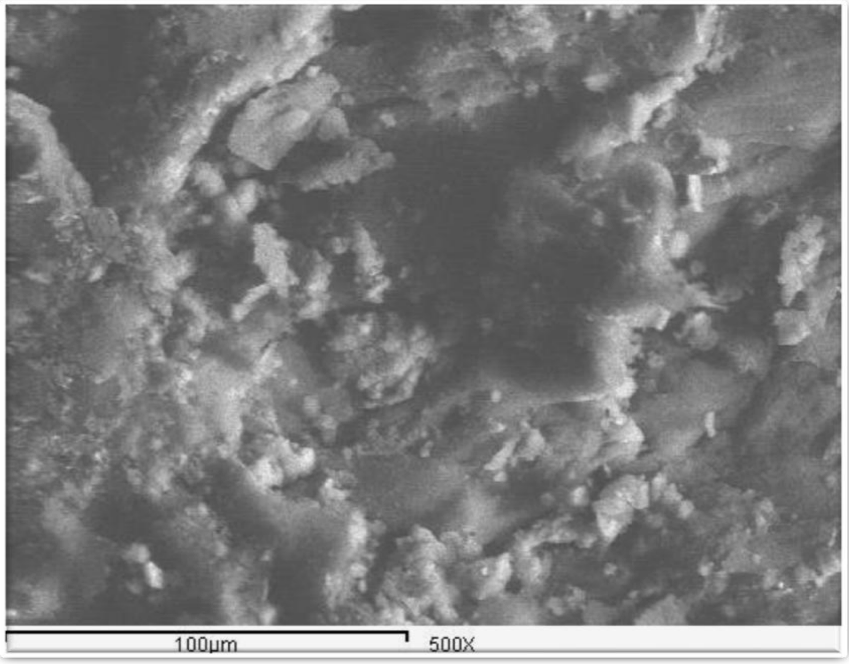
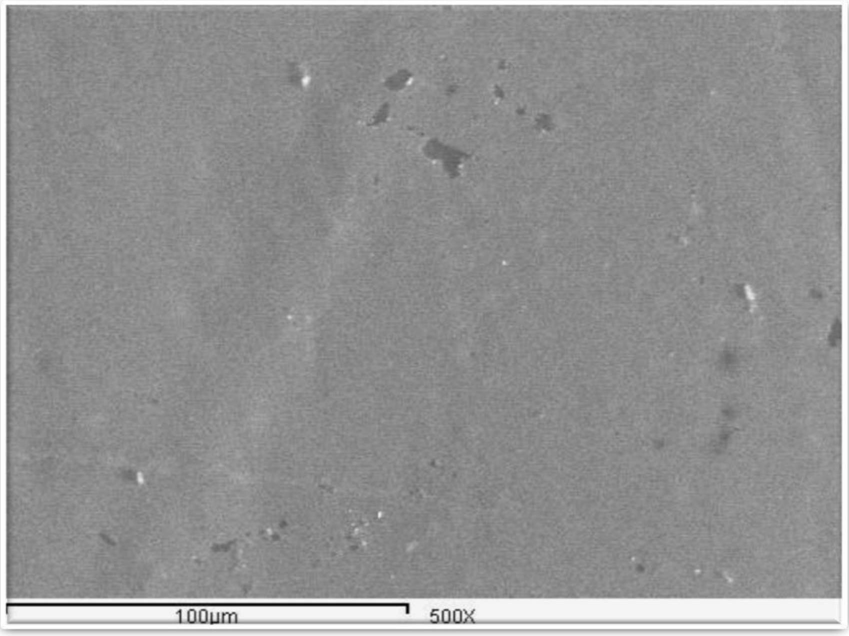


Figure (3.17): *SEM photograph of steel painted without any additives from polyaniline after corrosion*



Figure(3.18): *SEM photograph of painted steel containing (0.2g) polyaniline nanocomposite after corrosion*

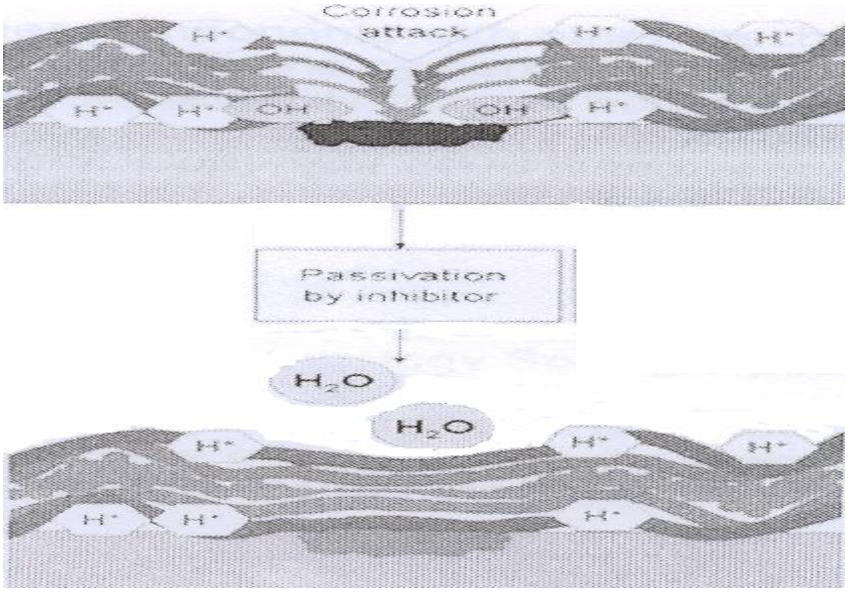


Figure (3.19): *Schematic mechanism of corrosion protection*

3.9.3 Electrochemical Measurements

3.9.3.1 Potentiostatic Measurements

Tafel extrapolations methods are used mainly to determine the corrosion rate. There are many advantages for electrochemical corrosion rate measurements. They permit rapid corrosion rate measurements, in that, they can be used for:

i) Monitoring the corrosion in various process streams.

ii) An accurate measurement of the very low corrosion rates which are difficult and tedious to perform with conventional weight loss or chemical analysis technique.

The corrosion rate is determined from the electrochemical technique as, the current density corresponding to the corrosion potential, which can be converted to a weight loss per specific time using Faraday`s law.

The effect of polyaniline nanocomposite, at different concentrations, on the corrosion of steel in 0.1M NaCl was studied using potentiostatic polarization technique as shown in figure (3.20). Inspection of these curves reveals that polyaniline nanocomposite suppresses both the cathodic and anodic reactions in the corrosive media. The electrochemical parameters obtained from the potentiostatic polarization measurements of steel painted with epoxy unmodified and modified with polyaniline nanocomposite with different ratios in 0.1M NaCl are given in table (3.9).

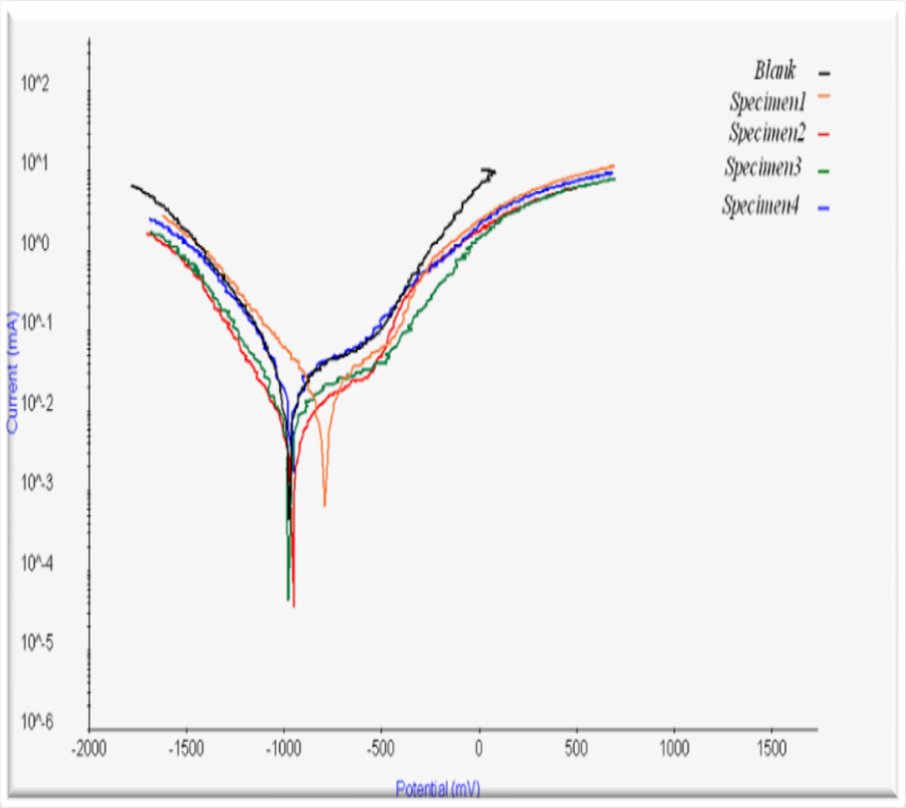


Figure (3.20): *Potentiostatic polarization curve of painted steel with epoxy unmodified and modified with polyaniline nanocomposite with different ratios 0.1M NaCl*

Table (3.9): *The electrochemical parameters obtained from the potentiostatic polarization measurements of steel*

Amount of PANI nano-composite	E_{corr} ***mV***	i_{corr} ***mA/cm***^{2}	***ϴ''***	***IE%***
0	***-976***	***0.016763***	***------***	***-----***
0.1	***-793***	***0.007892***	***0.5292***	***52***
0.2	***-958***	***0.002307***	***0.8623***	***86***
0.3	***-980***	***0.004844***	***0.7110***	***71***
0.5	***-958***	***0.013195***	***0.2128***	***21***

The table shows that all additives ratio can reduce the corrosion rate of the steel.

Figure (3.21) shows the relation between the inhibition efficiency and amounts of polyaniline nanocomposite in 0.1M NaCl at 298 K. the order of inhibition efficiency are:

Blank<0.5<0.1<0.3<0.2

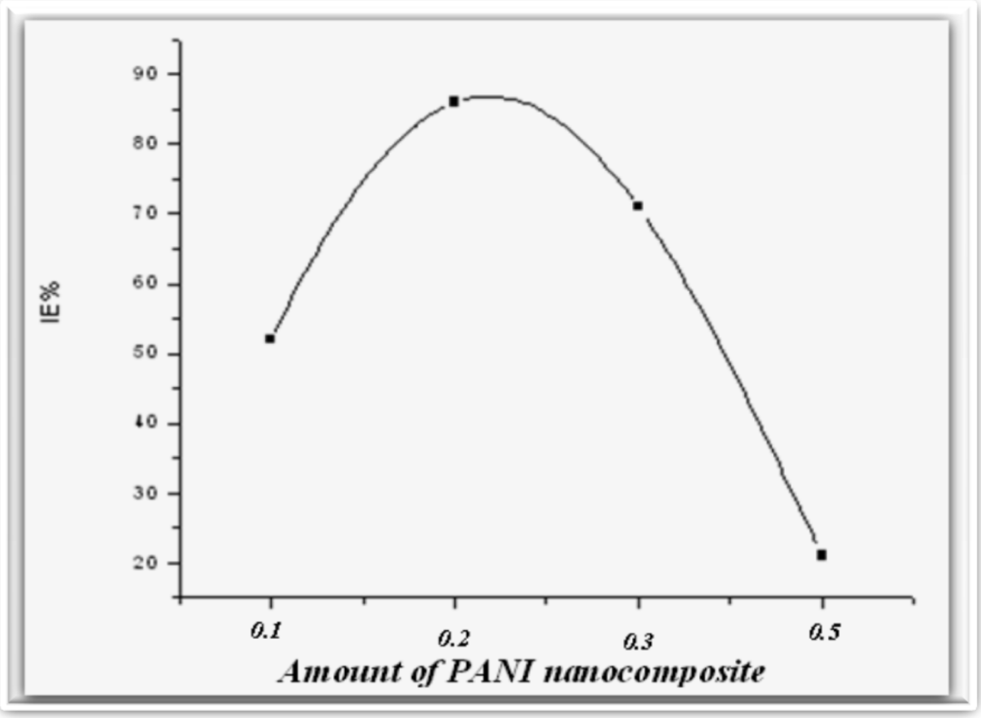


Figure (3.21): *Relation between the inhibition efficiency and amounts of polyaniline nanocomposite in 0.1M NaCl at 298K*

Figure (3.21) represents the change in the inhibition efficiency on steel with increasing the amounts of PANI nanocomposite.

At high amount of polyaniline nanocomposite it had a lower corrosion inhibition and this is may be due to irregular diffusion of the particles in painted film due to the crowd between them.

Adsorption of polyaniline nanocomposite on steel surface in 0.1M NaCl follows Langmuir adsorption isotherm as shown in figure (3.22).

Table (3.10) gives the adsorption parameters of polyaniline nanocomposite on the steel surface in 0.1 M NaCl obtained from Langmuir isotherm.

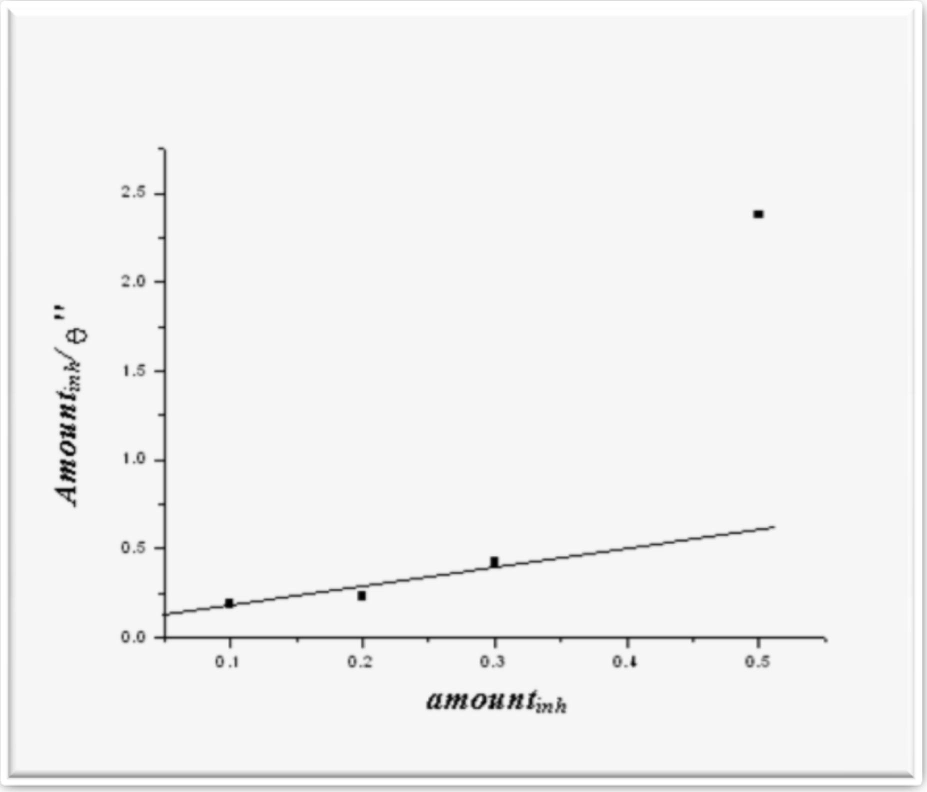


Figure (3.22): *The plot of Langmuir adsorption isotherm for the different amount of polyaniline in 0.1 M NaCl*

Table (3.10): *Adsorption parameters of polyaniline nanocomposite*

Organic additive	***Log K_{ads}***	***ΔG_{ads}, KJ/mol***
Polyaniline nanocomposite	***1.175***	***-10.95***

9.3.2 Potentiodynamic Anodic polarization Measurements

Pitting corrosion is a localized attack of the passivated metals. Local corrosion is a very damaging form of corrosion. Two basic requirements should be established by the corroding system to initiate the pitting corrosion; firstly, the metal must be passivated by an insulating film and the second is the presence of a specific anions such as; Cl^-, Br^-, I^-, $SO_4{}^{2-}$ *in the aggressive medium. Iron is passivated by a film of oxides*[103], *and therefore the presence of chloride ions in contact with the metal will initiate the pitting attack. The stability of the passive film formed on the steel alloy and its susceptibility to breakdown depend on the formation parameters namely; temperature applied potential, PH and solution composition. The compositions and the thickness of the formed film depend on the anodization potential*[104,105].

In the present part of the thesis, the effect of chloride ions on the pitting corrosion of steel is studied. Because of the general aggressiveness of sodium chloride, polyaniline nanocomposite is used to reduce the corrosion attack on the metallic materials.

Figure (3.23) shows the anodic potentiodynamic curves of steel samples in the potential range -2000 to 1500 mV at a scan rate of 1 mV/sec. Specimens [1 i.e. (0.1gm),2 i.e. (0.2gm),3 i.e. (0.3gm)] show no pitting whereas blank and specimen (4) show pitting which can be explained by three mechanisms; the initiation of the pitting attack could be due to the ability of chloride anions to penetrate the painting film, and attack the base metal surface with the assistance of the applied electric field across the painting film. In a second step, the pitting propagated involving the dissolution of the metal matrix and hydrolysis of the dissolved metal ions, which results in the high *degree of the acidity at the bottom of the corrosion cavity. The dissolution of the metal at the bottom of the corrosion cavity,*

$$M \rightarrow M^{+} + ne^{-}$$

is balanced by the cathodic reaction on the adjacent surface,

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH$$

The increased concentration of M^{+} *within the corrosion cavity results in the migration of chloride ions (*Cl^{-}*) to maintain neutrality. The formed metal chloride,* $M^{+}Cl^{-}$*, is hydrolyzed by water to the hydroxide form and the free acid,*

$$M^{+}Cl^{-} + H_2O \rightarrow MOH + HCl$$

The generation of the acid lowers the pH values at the bottom of the corrosion cavity, while the pH of the bulk solution remains natural [106] *. The corrosion rate inside the cavity remains higher than that of the bulk areas, and therefore bulk areas which act as cathode electrodes are partly or fully protected cathodes.*

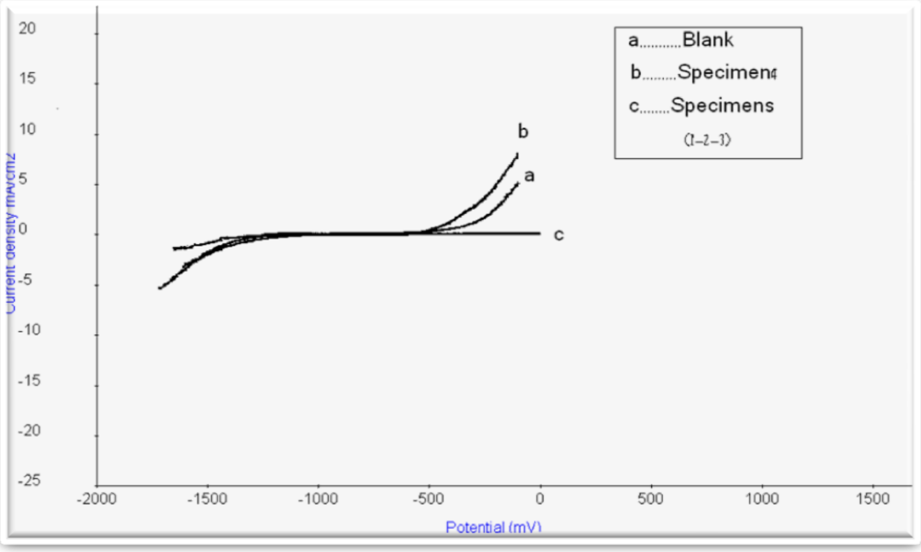


Figure (3.23): *Potentiodynamic anodic polarization curves of steel at different amount of PANI*

Figure (3.24) shows the pitting potential of steel as a function of log (PANI amount).

$$E_{pit} = a - b \log (PANI)$$

Where a and b are constants depend upon the type of additive used and amount.

The results obtained show that the presence of the PANI nanocomposite inhibits the pitting corrosion where it shows no pitting corrosion for specimens [1 i.e. (0.1gm),2 i.e. (0.2gm),3 i.e.(0.3gm)] and a lower pitting corrosion than blank in case of specimen [4 i.e. (0.5gm)].

Accounting resistance to pitting attack in the order of ;

Blank<0.5

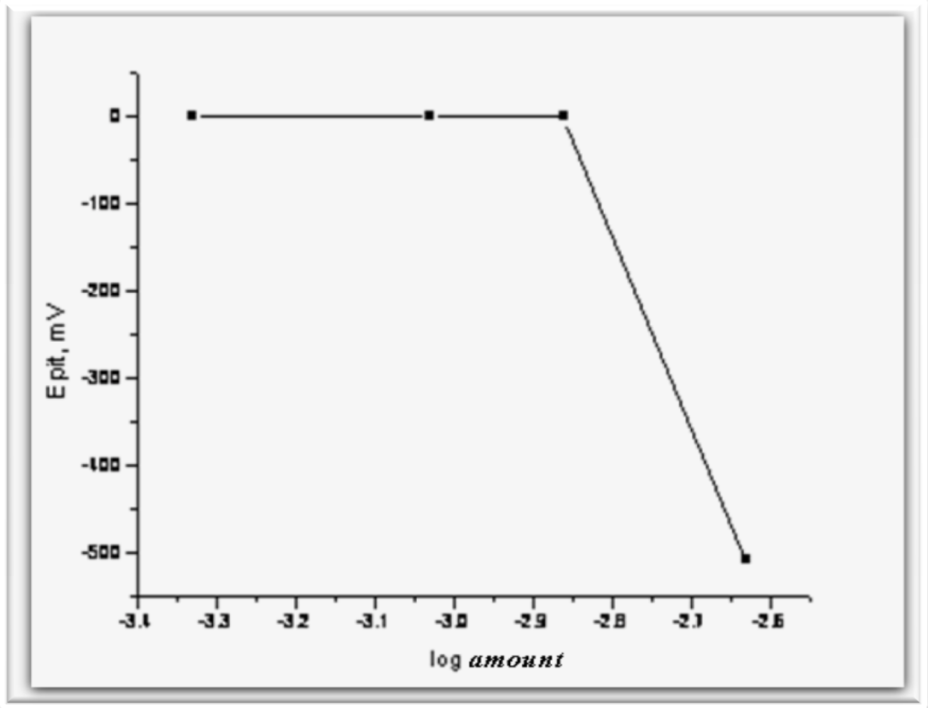


Figure (3.24): *Pitting potential as a function of amounts of PANI nanocomposite*

Conclusion

Nano-Zinc phosphate tetra hydrate with average size (10nm) was prepared via a novel method. PANI-Zinc phosphate nanocomposites were easily prepared by in situ polymerization with average size (57nm). Coating formulations prepared from PANI-$Zn_3(PO_4)_2.4H_2O$ *nanocomposite and epoxy resin exhibit excellent corrosion resistance in violent environments. Studies on the potentiostatic measurements (Tafel), weight loss and the physico-mechanical properties reflect that the formulation containing 0.2 g of PANI-*$Zn_3(PO_4)_2.4H_2O$ *nanocomposite is the best, while the potentiodynamic study showed that all formulations of PANI-*$Zn_3(PO_4)_2.4H_2O$ *nanocomposite containing epoxy resin showed a great ability to resist the pitting corrosion. The excellent improvement of performance of these coatings associated with the increase in the barrier to diffusion, prevention of charge transporting by the nano-size* $Zn_3(PO_4)_2.4H_2O$*, redox properties of polyaniline as well as very large surface area available for the liberation of dopant due to nano-size additive.*

Recommendation

Not long ago; the interconnect technology in electronics has been dominated by tin/lead based solders. However, as the environmental awareness increased, the toxicity of lead received universal attention and its overall adverse effect on human health is being closely monitored. Even small quantities of lead can lead to damage of brain, nervous system, liver and kidneys when ingested [107]*. Disposal of printed circuit boards (PCBs) containing leads to lead accumulation in water sources and can affect the biosphere.*

Hence, the pressure to eliminate or minimize the use of lead in electronic interconnections is growing. Therefore great efforts have been made to develop lead-free and environmentally sound interconnect bonding technology as an alternative to conventional Sn/Pb solders[108-117]*.*

From the study of conductivity of epoxy primer and epoxy modified with polyaniline zinc phosphate nanocomposite which shown in figure (3.9,3.10) we can say that, with more studying on epoxy modified with polyaniline zinc phosphate nanocomposite this formula can be used as ECAs in the future as its conductivity increased.

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Appendix

- ***Testing of corrosion resistance properties***

1) Gravimetric techniques

1.The corrosion rate (W) was calculated in (mpy) unit according to the following equation:

$$W=1.437*mg/At$$

Where; mg is the weight loss in milligrams, A is the surface area of the used specimens in dm^2, and t is the time of immersion in days.

2. The values of surface coverage (ϴ'') were calculated using the following equation

$$\Theta''=1-(W/W^o)$$

Where W and W^o are the corrosion rates (mpy) of steel specimen in presence and absence of the additive, respectively.

3. Inhibition efficiency (IE%) was determined using the following equation:

$$IE\%= [1-(w/w^o)]*100$$

2) Potentiostatic polarization technique (Tafel polarization)

The percentage inhibition efficiency (IE %) and surface coverage (ϴ'') were calculated according to following equation:

$$IE\%= [1-(i_{corr}/i^o_{corr})]*100$$

$$\Theta''=1-(i_{corr}/i^o_{corr})$$

Where i_{corr} and i^{o}_{corr} are the corrosion rates in terms of current density of steel specimen in the presence and absence of the polyaniline nanocomposite.

☒ ***Langmuir adsorption isotherm***

$$C_{inh}/\Theta'' = C_{inh} + (1/K_{ads})$$

$$K_{ads} = 1/55.5(e^{-\Delta Gads/RT})$$

Where C_{inh} is the inhibitor concentration and K_{ads} is the adsorption equilibrium constant, and ΔG_{ads} is the change of the free energy of adsorption.

3) Potentiodynamic Anodic polarization Measurements

$$E_{pit} = a - b \log (C_{inh})$$

Where and b are constants which depend upon the type of additive used and concentration.

Measuring the electrical properties

The dielectric constant was calculated using the relation:

$$\varepsilon = L\ Cs / A\ \varepsilon_o, \text{------------------------------} \Leftarrow (1).$$

Where L is the thickness in m, A is the area in m^2, Cs is the capacity in F, and $\varepsilon_o = 8.85 \times 10^{-12}\ C^2/Nm^2$.

The conductivity constant, was calculated using the relations:

$$1/\rho = \varepsilon_0\ \acute{\varepsilon}\ \sigma \text{------------------------------} \Leftarrow (2).$$

Where;

$$\acute{\varepsilon} = C\ L/\varepsilon_0 A \text{------------------------------} \Leftarrow (3).$$

$$\sigma = 2\pi f L\ C \tan(\sigma'/A) \text{------------------------------} \Leftarrow (4).$$

Where C is capacitance, f is the frequency, σ' is the dielectric loss

الملخص العربي

منذ أمد بعيد وعلم التعبئة يشكل عامل حيوي ورئيسي في الحياة الإنسانية لما له من دور في حفظ الأطعمة، ولكن في هذه الأيام لم يعد هذا العلم مقتصرا فقط على حفظ الأطعمة بعدما تعددت استخداماته والتي أصبح أهمها تيسير عمليات نقل الطعام والمنتجات الأخرى،

وانطلاقا من هنا ركزنا في دراستنا على أحد أنواع العبوات ألا وهي العبوات المعدنية لما تحيط لهذا النوع من مخاطر داهمة وأكثرها خطورة ما يسمى بخطر التآكل والذي يشكل تهديدا حقيقيا على الاقتصاد والحياة الإنسانية . ففي دراستنا اهتممنا باستخدام جزيئات البولي أنيلين متناهية الصغر كمادة مضافة إلى بطانة الإيبوكسي وذلك لما لهذه المادة من خصائص إلكترونية ودورها في المساهمة في تثبيط عملية التآكل للعبوات المعدنية . أولا قمنا بتحضير جزيئات الزنك فوسفات متناهية الصغر لما لها من دور في تحضير البولي أنلين متناهي الصغر؛ ولقد تأكدنا بعد ذلك من حصولنا على جزيئات البولي أنيلين باستخدام جهاز (IR) والمستخدم في الكشف عن المجموعات الوظيفية؛ كما استطعنا قياس الحجم الحبيبات للبولي أنيلين باستخدام جهاز (TEM) ؛ وأوضحت التحاليل الناتجة من جهاز (XRD) أن حبيبات البولي أنيلين متناهية الصغر شبه متبلورة؛ كما أثبتت تحاليل التحلل الحراري أن جزيئات البولي أنيلين متناهية الصغر تمتلك ثباتا حراريا عاليا

تم تحضير بعض تركيبات الدهان بإضافة البولي أنيلين للإيبوكسي بنسب مختلفة لاستعماله في طلاء الألواح المعدنية لاستخدامها في دراسة عملية التآكل تم ذلك كما يلي:

1- طريقة الفقد في الوزن

من النتائج التي تم الحصول عليها معدل التآكل أقل بصفة عامة مع زيادة الكميات المضاف من البولي أنيلين متناهي الصغر إلى حد معين بعدها يزيد معدل التآكل؛ حيث وجد أن أحسن نسبة مضافة كانت 0.2 جم؛ وأسوئه كان 0.5 جم.

2- الاختبارات الفيزيائية

أوضحت الدراسة الفيزيائية والمعتمدة على المواصفة القياسية الأمريكية أن العينات المضاف لها البولي أنيلين متناهي الصغر لها مقاومة تآكل أعلى من العينة الغير معدلة وذلك لما لجزيئات البولي أنيلين من سلوك في عملية الاختزال؛ فيعتقد أن البولي أنيلين يقوم بعملية قنص للأيونات المنبعثة أثناء عملية التآكل والناتجة من مهاجمتهم كلا من الماء والأكسجين للمعدن مما يساعد على تكوين طبقة خاملة كيميائيا تساعد في حفظ المعدن من الاستمرار في التآكل وهذه الخاصية التي يمتلكها البولي أنيلين توصف على أنها قدرة البولي أنيلين على الالتئام.

وقد تم دراسة شكل المعدن المطلي بالبادئ الإيبوكسي فقط وأخر مطلي بطبقة بطانة الإيبوكسي المعالج بالبولي أنيلين متناهي الصغر بنسبة 0.2 جم باستخدام (SEM)

حيث وجد أن بطانة الإيبوكسي المعدل له قدرة أكبر على مقاومة التآكل لما للبولي أنيلين من خاصية الالتئام.

3 – الطرق الكهروكيميائية

قد تم استخدام بعض الطرق الكهروكميائية مثل

أ – طريقة الاستقطاب البوتنشوستاتيكي

حيث أوضحت نتائج منحنيات الاستقطاب البوتنشوستاتيكي للكاثود و الأنود أن جزيئات البولي أنيلين متناهية الصغر تعمل كمثبطات للتآكل من النوع المزدوج حيث يؤدي وجودها إلى تشيط كلا من التفاعل الكاثودي و الأنودي ويرجع ذلك إلى خاصية الالتئام لهذه الجزيئات وبالتالي فهي تعمل على تكوين طبقة واقية من جزيئاتها على سطح المعدن لعزله عن وسط التآكل.

ب – طريقة الاستقطاب البوتنشوديناميكي

بدراسة جهد التآكل النقري للعينات في وجود كميات مختلفة من البولي أنيلين متناهي الصغر وجد أنه عند كميات معينة لا يوجد أي عملية نقر للعينة بينما مع زيادة الكميات تحدث انحراف في جهد التآكل النقري في الاتجاه السالب.

وقد جاءت نتائج دراسة ميكانيكية التنشيط في وجود كميات مختلفة من البولي أنيلين متناهي الصغر لتثبت أنها تتبع لانجمير أيزوثرم (منحنى تساوي حرارة الامتزاز) وقد تم الحصول على معدل التغير في المحتوى الحراري