# INTRODUCTION

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The great quantity of salts (especially chlorides and sulphates) in initial and concentrated sea water as well as its elevated temperature and flow create favorable conditions for intensive corrosion of carbon steels and corrosion of austenite stainless steels used in the equipment and pipelines of desalting plants. Besides, the rigidity of the above conditions makes it extremely difficult to achieve good anticorrosion effect by the sole use of traditional paint and varnish polymer coatings. These conditions require special coatings with stepped up protective properties stable in hot sea water.

Two of the most aggressive corrosion environments for steel structures are elevated temperatures and exposure in the marine tidal and splash zone areas. There are now cold applied tape based products available, which protect steel pipe or pilings, exposed in these environments. These two distinct coatings are cold-applied systems and may be used as coatings on original projects or as rehabilitation coatings. The elevated temperature coating is a three layer system comprised of a high temperature liquid adhesive (primer) and a tape made from a heat resistant multiple alloy polymers with a high temperature resistant adhesive. Operating underground and submerged steel pipelines at elevated temperatures greatly increases the severity of conditions leading to corrosion and the breakdown of coating materials. Thus, as pipeline

operating temperatures increase, the problems associated with corrosion mitigation and the selection of pipeline coating materials becomes many times more critical. The laws of physical chemistry and thermodynamics explain why this occurs: the rates of all chemical reactions and physical phenomena, such as the oxidation reaction of steel and coating materials, the absorption and permeation of water and gases increase rapidly as temperatures go up. Superimposed on the natural deleterious effects of higher operating temperatures are the effects brought on by the imposition of cathodic protection on the coated buried or submerged pipelines. Nunn characterized these as being "the worst case scenario" for the performance of pipeline coatings [1]. He describes some of the aspects of Mobil Pipeline Company's elevated temperature testing programs for high temperature pipeline coatings. Most international operators of elevated temperature pipelines, spend large mounts of time and money on the research, testing and evaluation of pipeline coating materials intended for high temperature usage.

## 1-1. THE USE OF POLYPROPYLENE IN PIPELINE COATINGS

Despite the fact that the pipeline coating represents only about 5% of the total cost, the choice of the most effective coating is a key point to guarantee the life of the installed pipelines.

Since the eighties, polypropylene copolymer coatings have been used for the protection of the external surface of on-shore and off-shore pipelines. Polypropylene is one of the most suitable coatings when high mechanical properties (impact resistance, penetration resistance, etc.) and/or heat resistance are required. Polypropylene has also been used in ordinary pipelines giving advantages compared with the standard coatings, e.g. fusion bonded epoxy resin, coal tar enamel and polyethylene. New applications for polypropylene copolymers such as pipeline coatings have recently been developed; these include an insulating coating obtained with foamed polypropylene and an internal coating obtained by spraying a polypropylene adhesive powder.

Since 1957, when polypropylene was introduced onto the market, it has shown a marked, steady growth due to its versatility, high mechanical properties, relatively low cost; all these advantages have increased its penetration into many market sectors like automotive components (bumper, dashboard, etc.), packaging, fumitories, appliances, fibers and consumer products. Today with a worldwide production of 12 million ton/year it is still considered a relatively 'young' material. The commercial success of polypropylene is based on two key factors:

- its excellent intrinsic properties

- the versatility of the new advanced processes to produce grades tailored to meet the market requirements

Furthermore, from its production as a raw material to the time it becomes waste, polypropylene is environment friendly. Being inherently pure, it is non-toxic and non-tainting, making it especially suitable for food contact. The production plant produces material without the emission of any liquid or gaseous effluents and with very low energy consumption. Polypropylene waste can easily be incinerated without the formation of residual ash and noxious fumes of any sort, at the same time producing a high degree of thermal energy. Polypropylene can also be recovered and recycled into second life products. Since the eighties polypropylene copolymers have been introduced into the anticorrosion coating market, mainly in pipelines where other coating systems had shown some weakness, like, for example, in pipelines operating at high temperature.

## 1-1-1. Three Layer Polypropylene Coating

The coating is composed of a thin layer of epoxy resin, an intermediate layer of modified polypropylene copolymer and a polypropylene outer layer [2, 3]. The inner surface of the epoxy resin layer interacts with the oxides of the metal and the outer surface with the polar groups grafted onto the polypropylene backbone of the intermediate layer. The

intermediate layer and the outer layer are completely compatible; this provides good adhesion between the layers and high resistance to cathodic disbondment.

Different layouts can also be used, for example, heating the steel with flames, using a liquid epoxy, applying the polypropylene adhesive in powder form, using a cross head extrusion instead of lateral extrusion etc.

It is worthwhile remembering that polypropylene can be processed with standard polyolefin extruders and that, in comparison with medium or high density polyethylene, a high production rate can be achieved.

External three layer polypropylene coating technology combines the advantage of epoxy resin (i.e. good adhesion, high cathodic disbonding protection and excellent interfacial properties) with the outstanding physical-mechanical properties, high chemical resistance, low water permeability and wide service temperature range of polypropylene.

In the past, bituminous materials were widely used as external pipeline coatings. These protective materials are easy to apply, but they soften at high temperatures and become brittle at low temperatures; moreover they are susceptible to damage during handling and transport.

Nowadays, thanks to their remarkable properties, polyethylene and epoxy resins play a more important role guaranteeing better corrosion protection [4]. Both of these materials present

some weaknesses which may reduce their application range. Epoxy primers are essentially stiff, brittle materials which absorb water especially at high temperature. For these reasons it is preferable to employ epoxy coated pipes in dry environments and, in all cases, they must be carefully handled.

Polyethylene withstands a maximum temperature of 70 °C; this may cause defects on the coating during storage, handling and installation especially in hot areas; moreover polyethylene indentation resistance and impact resistance is not so high, especially as temperature increases [5].

Comparative evaluation of four materials used in anticorrosion coatings, analyzing the coating resistance during storage, transport and laying operations, the coating capability to protect the steel against corrosion and the coating resistance with the time [6-9].

With the three layer polypropylene system [10, 11] such a strong adhesion is achieved between coating and steel that generally strip necking occurs up to 100 °C. By choosing suitable polypropylene copolymers it is possible to obtain high impact resistance both at high and low temperatures. The polypropylene coating does not require any rock-shields due to the very high indentation resistance even at 100 °C; for the same reason problems that occur when pipes are stored in piles in hot areas are strongly reduced. Using a suitable thermal

stabilizer package the polypropylene coating can withstand high continuous operating temperatures. Accelerated tests were performed at 150 °C in an oven with forced air in order to predict the life span of this high thermal stabilized coating; according to the Arrhenius Equation. In the case where the pipeline operates at ordinary temperatures only a standard stabilizer package is required to guarantee over 30 years of operating life.

UV stabilization is necessary because the coated pipes are stored outside before laying the pipeline; in any case, if high continuous service temperatures are expected, it is advisable to reduce the direct sun exposure time (we suggest it should not exceed 6 months) and/or to give a coat of paint or to use other kinds of UV shielding.

The polypropylene coating provides very low water absorption thus increasing the reliability of the coating over time, especially in the case of sea lines. Polypropylene coatings provide outstanding mechanical properties and for this reason they are usually not damaged during shipping, storage, handling and installation. In any case procedures are available for practical, efficient restoration of the coating area which has been damaged [12, 13].

If the metal is not exposed or the exposed area is very small polypropylene hot melt stick can easily be used. For major

damage two different technologies can be used according to the pipeline operating temperature:

(i) Primer, polypropylene tape with butyl-based adhesive and a polypropylene sheet for pipelines operating at room temperature;

(ii) Epoxy primer and extruded adhesive polypropylene or co extruded sheet of adhesive polypropylene / polypropylene top coat applied using an induction heating system for pipelines operating at temperatures up to 120 $^\circ$C.

The welded joints made during installation must be protected on site using practical, efficient methods, which guarantee both adequate and long-term protection. Different procedures may be applied depending on the pipeline operating temperature range [14]. For standard temperature operating pipelines polypropylene based tapes can be used. In the case of pipelines operating at high temperatures the induction heating system must be used together with epoxy primer and polypropylene adhesive powder or co extruded items of adhesive polypropylene / polypropylene top coat [15].

## 1-1-2. Thermal Insulating Coating

When hot fluids have to be transported in pipelines, and only a minimal temperature drop is allowed, in order to avoid flow difficulties, phase separation, etc., the applied coating must be

thermally insulating as well as effective against corrosion [16-19]. A four layer coating structure has been developed; it consists of an epoxy resin, a polypropylene copolymer adhesive, a thick layer of foamed polypropylene with 100% closed cells, and an outer sheath of solid polypropylene copolymer. This polypropylene foamed system can be an effective alternative to other solutions where for example polyurethane foam is used [20-22].

In the case of polyurethane the so called 'pipe in pipe' system has to be used because of the low resistance to hydrostatic pressure; moreover, because of the hydrophilic nature of the polyurethane foam, special precautions have to be provided to avoid any contact with water.

A further requirement of this application is that the coating must withstand the deformations occurring during the laying operation, for example with a reel-barge where the pipeline is bent onto the reel (typical diameter 16 m) and straightened off for laying. Moreover, for pipelines placed on the seabed in a region in which there is fishing activity, a very high resistance against impact of trawl boards is required.

The main advantages of this new thermal insulating and corrosion protective coating based on polypropylene technology are:

- possibility to produce the corrosion protection, the thermal insulating coating and the mechanical protection in a continuous extrusion process

- good product processability that ensures high production rate

- low water absorption and high compression strength (both also at high temperatures) that guarantee a constant thermal insulation

- absence of chemical interaction with the sea water and high thermal stability that provide long coating life

- high flexibility that allows the laying with a reel-barge

## 1-1-3. Polypropylene Powder

Adhesive polypropylene grades in powder form have been developed for anticorrosion coating application. These powders can be applied using both fluidised bed and electrostatic spray technology. Actually polypropylene powder has been used to protect different metal items against corrosion. In the pipeline field the following applications can be highlighted:

- as an adhesive in the small diameter pipe coating for repairs and field joint protection in polypropylene coated pipelines

- for an internal pipe coating

The polypropylene powder is food grade, that means it complies with the legislations, recommendations or communications regarding the items in contact with foodstuffs of the following countries: Belgium, Denmark, France, Germany, Greece, Italy, Ireland, Luxembourg, Portugal, Netherlands, United Kingdom, Spain and USA; moreover it is accepted to be used for water applications by KIWA (Secretariat of the Sub-Commit- tee on Toxicity of the Dutch Committee on Health Aspects of Chemicals and Materials for Water Supply).

Accelerated tests have been carried out in order to evaluate the features of the internal pipe coating where some holes are present and contact with corrosive water is forecasted. Different coating thicknesses (200-480 μm) and different defect shapes (straight line, cross, star) have been evaluated in the laboratory. The steel plates have been polarised as anode at + 120 mV as regards spontaneous voltage, using distilled water slightly acidified with sulfuric acid as the electrolyte; it is steadily saturated with oxygen by the bubbling of air. The test period was 75 days which corresponds to more than two years at standard operating conditions and the disbonding length is in the 0.8-2.1 mm range with lower values in the case of the higher coating thickness and in the case of defects with a straight line shape.

## 1-1-4. Weighted Coating

Offshore pipelines of large diameter usually have negative buoyancy. In order to maintain the sea line on the seabed a thick layer of concrete is applied onto the anticorrosion coating [23, 24]. An alternative solution is to apply an anticorrosion coating of suitable thickness using filled polypropylene. Therefore using one-step continuous technology it is possible to apply onto a pipe of any size a weighted coating against corrosion; moreover the coating can withstand a bending operation (no slotting is required) [25], has high impact resistance and very low water absorption.


## 1-2. USING THE DIRECT CURRENT VOLTAGE GRADIENT TECHNOLOGY DURING CONSTRUCTION OF NEW PIPELINES

External coatings on buried pipelines offer the first line of defense against corrosion with cathodic protection systems in place to protect bare metal at coating defects. Holiday detection before pipe lying does not guarantee pipelines are without coating defects after pipe laying. The coating is more than likely to be damaged during pipe construction. The DC voltage gradient "DCVG method to locate coating defects on underground pipelines was initially used for rehabilitation of older pipelines. This technique is now increasingly gaining popularity as a good quality control tool when used on newly

laid pipelines to detect coating damage most of which could be attributed to construction work.

The direct current voltage gradient "DCVG" method of delineating coating defects [26, 27] is primarily used for rehabilitation of older underground pipelines. The technique is however rapidly gaining popularity worldwide as a good quality control tool for newly laid pipelines. It is well known that coatings are used as a primary means of external corrosion control on buried pipelines with cathodic protection "CP" systems in place for protecting minor defects on coatings. Only a certain number of coatings defects can be tolerated on new pipelines. Large defects on coatings can also pose problems for the CP system. Whilst the original coating is usually applied and tested to high quality standards this will in no way guarantee that newly laid pipelines will be free of coating defects. Damage to pipeline coatings may occur during pipe laying and backfilling. Field joint welding does take place and as a result of this weld joints are often coated using manual systems which are sensitive to the standard of workmanship. In worst case scenarios weld joints could be found to have been left uncoated. The DCVG technique allows the determination of all coating defects that occurred during construction of new pipelines. Defects can then be prioritized and decisions taken for excavations in order to carry out repairs. Preliminary survey results on different

coating systems for new pipelines to date indicate that refurbishment criteria are coating specific.

## 1-2-1. The DCVG Technique

When cathodic protection current flows through the soil to a coating defect on a pipeline a voltage gradient is established in the ground due to the resistive nature of the soil. From Ohm's law, this voltage gradient will be higher in high resistivity soils. The DCVG techniques utilizes a sensitive millivoltmeter to measure the voltage difference between two copper/copper sulphate half cells "probes" placed in the soil voltage gradient region. The voltage gradient is normally larger and more concentrated the greater the current flowing and the closer observations are made to a defect. When the half cells are spaced 0.5 m or so apart in this voltage gradient one half cell will adopt a more positive potential than the other allowing the direction of current flow to be established. To ease interpretation and to separate what is being monitored from the other DC sources the DC signal is switched ON and OFF using an interrupter connected to a transformer rectifier unit. The signal is asymmetrically switched with a cycle of 1:2 s OFF and 0:2 s ON. To survey a pipeline the operator walks directly above or just to the side of the pipe placing the probe tips on the ground one in front of the other. As the operator gets closer to a defect the needle of the millivoltmeter will deflect in a

direction towards the defect. The needle deflection will get stronger the nearer the defect. When the defect is passed the needle will deflect in the opposite direction. By retracing steps the meter can be nulled i.e. no deflection of the needle in any direction. In this position the defect should be on a line mid-way between the probe tips. By turning at right angles to the pipe and repeating the same procedure a point is found where the two lines cross. This point should be directly above the coating defect. It is thus not necessary to be directly over the pipeline since the technique allows the operator to always be located above the pipeline.

The DCVG technique at present does not give the exact physical size of a coating defect under stray current conditions. The technique does however enable comparison of located defects with other defects found in the same area. The % IR is used to reflect size: importance of a defect. It is important to realize that when excavating one does not look for direct correlation between % IR and physical defect size. For example if one takes two defects with the same %IR one near a river bed "low resistivity area" and one in a high resistivity dry area it is quite conceivable that there will be a difference in actual physical size. The % IR criteria is influenced by many parameters such as soil resistivity, depth of pipe pH, gases in the soil, soil compaction, consumption of cathodic protection current, physical size and shape.

## 1-2-2. Determining which Defects Require Repair

In order to ensure effective maintenance of pipelines, only those defects that really need it should be repaired. This is done in such a manner as to bring back into balance the relationship between the size, number and distribution of coating faults, and the effectiveness of CP at all individual coating faults. The DCVG technique allows this to be achieved. To prioritize defects for repair purposes, the following are considered important:

- Defect location-defects near houses, under city streets, railway lines etc. are of high priority when it comes to choosing those that should be repaired.

- Defect size/importance (% IR assessment)-DCVG surveys carried out on older pipelines have yielded the following guidelines for prioritizing defects during repairs. The situation is significantly different on new pipelines. The majority of defects have %IR less than 5. The approach to repair defects based on the % IR assessment can be different for different coatings but generally defects on new pipelines with %IR greater than 5 have been recommended for repairs.

- Corrosion status of defects-the most dangerous defects are those with anodic/anodic behaviour. Once found, these defects must be repaired and investigations carried out as to the occurrence of such status. Since DCVG

readings are instantaneous, REVG (remote earth voltage gradient) recordings are carried out at these defects to confirm anodic /anodic behaviour. These defects are used as reference points in adjusting the CP system to achieve protection at all other anodic/anodic defects.

• Stray current activity-defects in areas of high stray current activity should be carefully studied. Identification of those defects discharging stray currents is important and can be easily determined using the DCVG technique.

## 1-3. THE USE OF PAINTS AS ORGANIC COATINGS

The mechanism by which an organic coating protects a metallic material from the environment is a complex process that is not well understood. Many properties of polymers (processability, electrical properties, chemical, thermal, mechanical and environmental stability) affect their suitability and reliability as protective organic coatings [28]. Among these properties, the nature of the water/coating interactions are important in determining the change in polymer properties during use as well as the permeability of the paint to aggressive ions, since water provides the medium in which ions can diffuse through the coating to reach the metallic substrate. It is currently accepted that the adsorption and transport of charged (ions) and uncharged (water, oxygen)

species affect the corrosion behaviour of a polymer/metal system.

A survey of the literature reveals that the protection offered by an organic coating can be ascribed to one of the following mechanisms: (i) depression of the anodic and/or cathodic reaction; (ii) introduction of a high electrical resistance into the circuit of the corrosion cell; and (iii) as a barrier to aggressive species (oxygen, water and ions) [29-32].

Many papers have addressed the physical nature of organic coatings as a barrier to aggressive permeates [33-40]. The concept of a paint film as an impermeable membrane has been largely discredited by permeability data for water and oxygen [33]. In many systems, the water permeability was found to be high enough to sustain the corrosion rate of the bare substrate, indicating that in these cases the rate-determining step in the corrosion process is not related to the rate of water and/or oxygen transport to the metallic interface [33]. Less well documented is the effect of coating composition on the protection of the metallic substrate [41, 42]

Paints can be divided into three groups according to their drying or curing mechanism,e.g. oxidative drying, physical drying and chemically cured paints.

## 1-3-1. Oxidative Drying Paints

The drying of these paints involves a chemical reaction of paints with atmospheric oxygen. Again the solvents need to evaporate after application, but the final drying is a result of a reaction between the binder and the oxygen in the air. The oxidative drying paints are based on one component. When these paints have dried the original solvent will not dissolve them. However stronger solvents can cause problems such as lifting of the oxidative drying paint. The drying process of oxidatively drying paints will proceed at a slower rate at lower temperatures. Some of these paints may be applied down to +5 $^\circ$C or may be down 0 $^\circ$C.
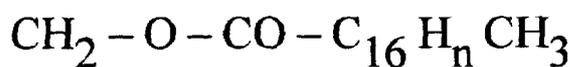
## a- Oils and fatty acids

Vegetable oils and their derived fatty acids still play an important role in surface coatings today because of their availability as a renewable resource, their variety and their versatility. Oils are mixed glycerol esters of long chain (generally $C_{18}$) monocarboxylic acids known as fatty acid as represented below.

$$CH_2 - O - CO - C_{16} H_n CH_3$$
$$|$$
$$CH - O - CO - C_{16} H_n CH_3$$
$$|$$
$$CH_2 - O - CO - C_{16} H_n CH_3$$
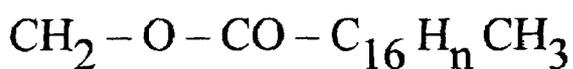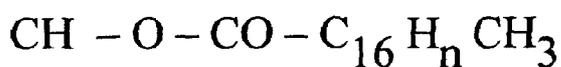
n may be 32,30,28 or 26

Unrefined oils also contain free fatty acids.

oils are classified as drying, semi – drying , or non – drying and this is related to the behavior of the unmodified oil, depending on whether it is, on its own, able to oxidize and crosslink to dry film . This behavior is directly related to the concentration of the various fatty acids contained in the structure. Fatty acids may be saturated (no double bonds), mono – unsaturated (one double bond) or polysaturated (two or more double bonds). Polysaturated fatty acids may be conjugated or non-conjugated. High conjugation is reflected in higher drying ability.

Drying oil may be heated at temperature of 240 °C to produce stand oils, where the viscosity increase is due principally to dimerization reactions through double bonds of unsaturated fatty acid moieties [43].So called boiled oils were once prepared by heating metal oxides in oil until fatty acids released during bodying solubilized by the oxides as soap. Now boiled oil may be prepared more conveniently by blending commercial driers with stand oil [44]. Hydrogenated castor oil (HCO) has some application in alkyd resins for stoving application and can be used in dispersants and surfactants [45]. Oils and fatty acids containing unsatuaration can be reacted with maleic anhydride . Where conjugated double bonds are present a Diels – Alder reaction is possible

and proceeds exothermically [46].The drying oil fatty acids under heat treatment have found several applications in coatings. The most exploited reaction of these unsaturated groups is autoxidative cross – linking, accelerated by the presences of heavy metal drier and also with the aid of heat in stoving compositions [47]. The theoretical of autoxidative dry have been well reviewed [48], and the mechanisms recently further investigated [49, 50].

It is accepted that the first steps in autoxidative drying are free radical in nature and involve hydroperoxide formation. It is unclear whether added metal drier effect hydroperoxide formation. It is however, well established that further decomposition and cross linkining reactions of hydroperoxide are accelerated by the presences of metallic driers [51].

The actual cross linking reaction following radical formation are complex, and as well as the desired high molecular weight compounds, scission products with aldehyde prominent [52, 53]. Are also produced, giving characteristic drying smells. Yellowing is also a feature [54].

## b- Alkyd resins

The alkyd resin was one of the first applications of synthetic polymers in surface coatings technology; Alkyd resins are the reaction products of polybasic acid, polyhydric alcohol and monobasic fatty acid or oil. It may be considered a successful

chemical combination of oil or oil derived fatty acids into a polyester polymer structure, thus enhance the mechanical properties, drying speed, and durability of these oleoresinous vehicles formed over and above those of oil themselves. These resins today comprise about the half of all resins used in the surface coating industry. In spite of large number of other synthetic resins being available for use in paint formulations. The alkyd resins surpassed all of them in versatility, and low-cost, combining a broad spectrum of performance properties. More than one polyhydric alcohol or polybasic acid may be used in the same alkyd resin to obtain special properties. Therefore it will be seen that the term "alkyd resins" include a very wide variety of resinous products. The important group of such resins is the oil modified glyceryl phthalate resins; they are the reaction products of the trihydric alcohol (glycerol), and the dibasic acids (phthalic acid) modified with either drying or non drying oils.

## c- Modified alkyd

The term " modified alkyd " is used to describe products obtained by chemical modification during alkyd preparation and that incorporate chemical agents of type other than those include in the definition. Alkyd may be modified with natural resin, phenolic resin, polyamide resin, vinyl resin and also melamine- formaldehyde resin to improve its physical,

chemical and mechanical properties. Shukla et.al [55]. Prepared non-phthalic alkyd from rosin –maleic adduct and maleopimaric acid. Maleopimaric acid based alkyd possess better alkali, manufactured alkyd resin with good drying properties, useful as binder for a good hardness primers, by reacting vegetable oil, polyols, and carboxylic acid, polyesterifing the product with phthalic anhydride in presence of rosin acids and maleic anhydride. Alkyd resins modified with phenolic compounds have been described and showed better solvent and alkali resistance [56]. Recently, solvent – type coatings based on alkyd / polyesteramide resins have been described [57-61]. These types of resins combine the useful properties of alkyd and polyamide resins. In alkyd resins when no fatty acids are used, or when they are completely replaced by other type of acid, the product can be considered as "oil-free alkyd"

## d- Alkyd blends

The term "alkyd blend "is used for the physical mixture formed by "cold cutting" as alkyd solution (mixing with another resin or polymer solution at moderate temperature). For example, an alkyd solution cold cut with the cellulose nitrate will be considered as alkyd / cellulose nitrate blend [62]. The properties of alkyd resins depend on the nature and amount of the modifying oil incorporated. Therefore they are

conveniently classified according to the type of oil present which they contain into: drying oil resin, semidrying oil resin, and non-drying oil resin. Alkyd resins are also conveniently classified in terms of their oil length, i.e., and the amount of oil, which they contain. Thus, the resins which contain less than 45 % oil are generally termed short oil-length resins, the resins which contain 45%-55% oil are considered to be medium oil-length resins, the resins which contain 56%-70% oil are considered to be long oil-length while those with more than 70% are very long oil-length resins. The short oil length resins generally results in the need for aromatic solvent, giving higher viscosity resins at lower solids. If formulated with drying or semidrying oils. In case of the medium or long oil length, the alkyd can air-dry oxidatively at room temperature. Otherwise it will not do so, and to form hard films it must be stoved with crosslinking resin. Medium and short oil alkyds give hard films with good gloss retention and chemical resistance; they are less flexible than long alkyds and normally dried by stoving [63]. Rapid drying, elasticity, mar-proofness and durability distinguish the alkyd as a group. Their principal weakness resides in the ease with which the ester groups, which form so large a part of the molecules, are hydrolysed, particularly under alkaline conditions. Even in this respect it is possible to produce alkyds with greatly improved resistance to hydrolysis by using of acid containing stirically hindered

carboxyl groups, such as "Versatic acids", one of the chemically produced monobasic acids. It is a mixture of heavily branched aliphatic acids with 9 to 11 carbon atoms and with most (>93%) of carboxylic groups attached to a quaternary carbon atom [64].

Polyester finishes are very hard, tough, resistant to solvent and resistant to moderately hot objects. This is extremely useful property for furniture finishes, clear or pigmented. Their adhesion to most surfaces is poor and the films are not flexible in the ordinary sense, unless soft sufficient flexibility to withstand to the expansion and contraction of the substrate as the humidity varies is obtained by spacing out the cross-links. This can be done by decreasing the proportion of unsaturated acid in the polyester resin, or by using long chain, flexible saturated acids or alcohols. The mechanical standing and polishing properties of the finish will suffer if cross-linking is excessively reduced. Unlike epoxy finishes, polyesters undergo appreciable volume shrinkage on hardening. This can cause loss of adhesion, pulling away from edges and other defects, upon out door exposure; the varnish (wax type) has good gloss retention, but tends to fail by cracking, especially on expanding and contracting substrate [65].

Njoku et al [66]. Prepared an alkyd resin from rubber seed oil, the alkyd then evaluated as varnish for many uses. Viscosity measurements of these types of alkyds were carried out in

different solvent at oil contents of 20,30,40,50, and 60%. The study showed that, the di-methyl formamide was better solvent for these alkyds than the other solvent examined [67].

Another air drying alkyd composition was prepared from sunflower fatty acid, pentaerythritol, phthalic anhydride, trimellic anhydride, trimethylol propane trimethacrylate, the prepared alkyd compositions gave dry film thickness of 100-125 μm suitable for manual applications [68]·

Short and medium alkyd resins were modified using per formulated toluene isocyanate. The modified resins were incorporated in a set of paint formulation, where the corrosion protection efficiencies were enhanced by the improvement in the hydrophobicity of these alkyds [69]. Medium oil alkyd resin was synthesized by sorbitol and pentaerythritol instead of glycerol, the synthetic process and condition were investigated. The modified alkyd varnish shows excellent properties with regard to drying time, adhesion, impact, strength and water resistance [70].

The alkyd resin was prepared from synthetic or vegetable oil acid and their manufacture for water resistant coating was discussed by Istartescu et al [71]. This alkyd resin containing 1-15% excess – OH group at high molecular weight, 5-25% excess –OH group at medium molecular weight and 15-40%

excess-OH group at low molecular weight exhibit good ability to wet pigment and for weather resistant paint.

Recently new paint formulations based on modified alkyd were discussed in a China patents [72]. The modified alkyd resin consisting of vegetable oils 30-60% polyhydric alcohol's 5-15 % polybasic acid 10-35 % Dacron , 10-45% and diluent 20-65%. A resin lacquer prepared from soya oil, pentaerythritol, phthalic anhydride and Dacron was mixed with pigments, talc, a diluents and drying agent were milled and filtered to form title paint.

Alkyd of high viscosity can be emulsified by the inversion technique using simple hydrophilic non-ionic and anionic surfactant, fined dispersed, stable emulsions were obtained by adding water to the alkyd / emulsifier mixture at constant temperature. The influence of type and concentration of the surfactant on the inversion properties and droplets size were studied [73].The stability of linseed oil varnish and alkyd resin in water emulsions stabilized by non-ionic and surfactant has been studied. In the case of alkyd resin, the best emulsifiers were to be non-ionic surfactant, such as ethylene and propylene oxides in addition to (nonyl) phenol oxyethylene fatty alcohol. The stability can be improved by xylene and butanol addition as well as by increasing the resin concentration to 50% by weight [74].

## 1-3-2. Physical Drying Paints

The drying process of this type of paint consists exclusively of the evaporation of solvents / diluents and thinners. Most of the solvent are very volatile is making the drying process quick. Typical for the physical drying paints is that the dry coat will redissolve in the original solvent. When applying the second coat the first coat will soften and to some extend dissolve and the two coats will be mixed. Physical drying paints can be applied at low temperatures, below zero. The Substrate should of course be dry and free from ice. At lower temperatures the evaporation of the solvents will proceed at slower rate. A common physical drying paints are vinyl's, chlorinated rubber, acrylics, bitumen's and coal tar

### *a- Acrylic polymers*

Acrylic polymers are widely used for their excellent properties of clarity, strength, chemical and weather resistance. The term acrylic has came to represent those polymers containing acrylate and methacrylate esters in their structure along with certain other vinyl unsaturated compounds. Both thermoplastic and thermosetting systems are possible, the later formulated to include monomers possessing additional functional groups that can further react to give crosslinks following the formation of initial polymer structure; various references in the literature

fully discuss the formulation and use of acrylic polymer in coatings [75, 76].

## b- Thermoplastic acrylic resins

Thermoplastic acrylic resins have found application particularly for automotive topcoats both for factory application, and currently still refinishing. Molecular weight and molecular weight distribution need carefully specification and control for lacquers, too high a molecular weight gives low spraying solids; low molecular weight degrades film strength, mechanical properties and durability. It has been found that the optimum molecular weight is in the region of 80 000 gm / mole.

## c- Thermosetting acrylic resins

Thermosetting acrylic resins were formulated to overcome the defects of thermoplastic compositions, advantages from thermosetting resins occur in improved chemical and alkali resistance, higher application solids in cheaper solvents, and less softening at higher service temperature. Normal thermosetting acrylics may have molecular weight of 10 000 – 30 000 gm / mole [77].

## 1-3-3. Chemical Curing Paints

The drying of these paints involves a chemical reaction between the binder (Base) and a hardener (curing agent). Before use the base and the curing agent must be mixed and a chemical reaction takes place. The curing of the paint involving both the chemical reaction between the components and evaporation of the solvent starts immediately after mixing. When these paints have cure they form a network so dense that the original solvent will not dissolve them. The drying process of chemical curing paints will proceed at a slower rate at lower temperatures. Such as polyurethane's, polyesters and epoxy tar

### a. Polyester resins

Polyesters are generally condensation product of di- or polyhydric alcohols and di- or polybasic acids. The term is abroad, and includes saturated polyester, polyester fiber – forming, polyester modified by fatty acids and drying oil (alkyd) and unsaturated polyester [78 -83].

In the surface coating industry the name "polyester" is rarely applied to oil modified alkyds and is reserved for types containing no oil or fatty acid modification. These polyester are two kinds, saturated and unsaturated.

Unsaturated polyester resins that contain reactive bonds in their polyester molecules and which are subsequently

polymerized to crosslinked structures. They are based on maleic acid or anhydride saturated crosslinked polyester in which polyesterfication and cross-linking occur in the same step (alkyd resin). Polyallylester is special type of unsaturated polyester. It was made by batch process which allow on easy change over from one formulation to mother [84]

Most unsaturated polyesters are not suitable as coatings because atmospheric oxygen inhibits the cross – linking reaction. To circumvent this difficulty, a number of photochemical methods have been developed to cure unsaturated polyester coating. Among them is the incorporation into the polymer of photosensitive groups [85, 86] Saturated polyesters, is derived from saturated aromatic dicarboxylic acids and mixtures of polyhydric alcohols having an average hydroxyl functionality greater than two. These polyesters are produced with free hydroxyl groups.

Catalysts are frequently used to increase reaction rate in polyester preparation, although the choice of catalyst needs care since color may be adversely affected. Tin catalyst is particular useful [87].

Polyesteramide resins (PESA) combine the properties of both polyester and polyamide resins. Preparation and evaluation of some polyesteramides in the field of surface coating were reported by Gast [88-90] and Naser et al [91].

Theoretically, oils or oil fatty acids are reacting with diethanolamine (DEA) for the formation of diethanolamine derivatives of the corresponding fatty acids, according to the following series of equations:

$$
\begin{array}{ccccc}
CH_2-O-COR & CH_2-CH_2-OH & & CH_2-CH_2-OH & CH_2-OH \\
| & | & & | & | \\
CH-O-COR + & 3\ NH & \xrightarrow{\hspace{2cm}} & 3\ RCO-N & + \quad CH-OH \\
| & | & & | & | \\
CH_2-O-COR & CH_2-CH_2-OH & & CH_2-CH_2-OH & CH_2-OH \\
\\
[OIL] & [\ DEA] & & [HEFA] & Glycerol
\end{array}
$$

**Or**

$$
\begin{array}{ccc}
& CH_2-CH_2-OH & \qquad CH_2-CH_2-OH \\
& | & \qquad | \\
R-COOH + & NH \xrightarrow{\hspace{2cm}} & \quad RCO-N \qquad\qquad + H_2O \\
& | & \qquad | \\
& CH_2-CH_2-OH & \qquad CH_2-CH_2-OH
\end{array}
$$

Fatty acid    [DEA]                   [HEFA]

The aminolysis of oils is generally catalyzed by basis. The hydroxy ethylamide derivatives of linseed and soya been oils were prepared by heating one mole of oil, three moles of DEA and 0.07 mole of sodium methoxide as a catalyst. The reaction temperature was 115 $^{o}C$ and the reaction was completed in about 35 minutes. The course of the reaction was followed by

thin layer chromotographic technique. After completion of this reaction, the hydroxy ethyl amide derivatives were extracted from the librated glycerol by ether, which followed by successive washing of the ether layer with 15 percent sodium chloride solution then drying over anhydrous sodium sulphate. The time of formation of such amide derivatives depends upon temperature, catalyst concentration and type of unsaturated fatty acid. Different catalysts were used and it was found that lead monoxide and zinc oxide had highly reactivity. Sodium methoxide, Sodium hydroxide and lithium hydroxide were moderately reactive. Calcium hydroxide and barium hydroxide were weakly reactive [92].

A method used for aminolysis of oil involves using of ammonia and catalyst at relatively high temperature and pressure. This method is different from that used for the preparation of different fatty acid amide [93-96]. Preparation of diethanolamine derivatives of oil fatty acids in solvent medium and the use of it in field of the preparation of various types of polyesteramide resins have been studied [97].

Parameters affecting the formation of diethanolamine derivatives of stearic acid were also studied, these parameters include the effect of reaction temperature and catalyst concentration and it was found that the most effective catalysts are lithium hyroxide and sodium hydroxide.

The prepared diethanolamine derivatives of fatty acid were considered as the dihydric alcohols followed by condensation with polybasic acids or anhydride in a manner similar to those adopted in the alkyd formation. Both primary amine and hydroxyl group are found in ethanolamine ($H_2N$-$CH_2$-$CH_2$-OH) and these may be reacted to form resins with both ester and amide linkages. Although the amide linkage has greater resistance to alkali, it is usually quite dark in color [98].

The polyesteramide resin prepared from adipic acid, ethylene glycol, hexamethylenediamine, terephthalic acid copolymer were useful as a glazing paint for electric wires [99].

Excess of linseed or soya bean diethanolamide was used over the dibasic acids or anhydride to produce polyesteramide terminating in the hydoxyl groups. Which then reacted with di-isocyanates under the influence of amine catalyst to form urethane / polyesteramide. Films from various polymers had a wide range of drying rate, hardness and chemical resistance properties depending on the chemical linkages (ester, amide, urethane), which they contain, and on the curing conditions employed [100]. Applications of polyesteramide were indicated, with particular attention to its uses as flame retarding additives in plastic formulations [101].

The functional polyesteramides were prepared by reacting hydroxyl and amine dimers in a three –necked flask equipped with a stirrer. Temperature was increased slowly to about 100

°C where di-carboxylic acid or anhydride was added. The temperature was then raised to about 170-180 °C and the reaction was continued under stirring and in a stream of oxygen free dry nitrogen until water evolution was ceased. The progress of the reaction was followed by checking periodically the acid value of the reaction mixture.

The reaction conditions and properties of saturated and unsaturated polyesteramide polyol obtained were reported. The incorporation of the polyesteramide polyol resins as interfacial agents had been found to significantly improve the mechanical properties of the jute fiber composite. It had been also found that increasing the hydroxyl value of that polyol results in a better bonding of the composite up to a certain optimum limit, the hydroxyl value beyond which the molecular weight of the interfacial agents as well as its bonding decrease. Use of polyesteramide polyol resin of optimum hydroxyl value and molecular weight also significantly improves the water resistance capacities of jute – epoxy composites [102].

Polyesteramide resins containing pentachlorophenol residue in their structure were prepared by replacing a part of phthalic anhydride by itaconic acid derivatives of pentachlorophenol. Inclusion of such residue, lead to substantial antimicrobial growth control [103].Various polyesteramide resins were prepared in which a stiochimetric amount of hydroxy ethyl

fatty acid amides were replaced by nicotinic and isonicotinic derivatives of diethanolamine and triethanolamine. Such as resin compositions showed to have antimicrobial growth effect and corrosion inhibition [104].

## b- Amino resins

Amino or nitrogen resins are the condensation products of certain compounds with two or more amine groups, particularly urea [CO (NH$_2$)$_2$] and melamine, with formaldehyde [HCHO]. These condensation products are generally alkylated and may also be partly polymerized. The family of acrylamide-derived thermosetting acrylic resins bears considerable. The major amino resin types are those derived from melamine (MF) and urea (UF), with benzoguanamine also used, Resins based on glycoluril [105] Find some use for cure of powder coatings [106]

## c- Phenol formaldehyde resins

These thermosetting resins are credited with being the first commercialized wholly synthetic polymer or plastic. The basic raw materials are formaldehyde [HCHO] and phenol [C$_6$H$_5$OH], although almost any reactive phenol or aldehyde can be used. The phenols used commercially are phenol, cresols [CH$_3$C$_6$H$_4$OH], xylenols [(CH$_3$)$_2$C$_6$H$_3$OH], p-t-butylphenol [C$_4$H$_9$C$_6$H$_4$OH], p-phenylphenol [C$_6$H$_5$C$_6$H$_4$OH],

bisphenols [(C$_6$H$_4$OH)$_2$], and resorcinol [C$_6$H$_4$(OH)$_2$]. The aldehydes used are formaldehyde and furfural [C$_4$H$_3$OCHO].

In the early years of coating industry, only naturally occurring resins were available to enhance the properties of natural oils. Early in this century, the availability of the hard oil - soluble phenolic formaldehyde (PF) resin allowed amore scientific approach to varnish making. The development of heat – reactive , soluble phenolic resins in turn enabled the development of baking finishes with excellent solvent and corrosion resistance; these resins still find application a lone or in blends with alkyd or epoxy resins for can coatings, and tank and drum linings [107].

### d- Polyurethane resins

Polyurethanes have the widest range of polymer applications throughout the world: fibers, elastomers, foams, skins, adhesives, coatings, etc. [108] the basis of formation these polymer is reaction of an isocyanate group (-NCO) with compounds containing an active hydrogen atom. The latter attaches itself to the nitrogen atom of the –NCO group. A number of materials contain active hydrogen atoms, and the reaction of an isocyanate group with some of these can be represented as follows.

$$- \ N = C = O + - OH \rightarrow \ -NH - CO -$$

Urethane unit

Polyurethanes are two – pack materials, i.e. the material containing the active hydrogen and isocyanate are packed in separate containers and mixed together immediately before use. The isocyanates are either aromatic or aliphatic. Aromatic isocyanates dry faster than aliphatic but when used extremely they chalk and yellow rapidly. Aliphatic isocyanates possess superior retention and ultraviolet resistance so that they are recommended for exterior finishing coats. Because of the toxicity of isocynates and the danger of inhaling droplets while spraying, producers have in the past striven to develop systems avoiding the use of isocyanate, but with similar properties. For these, the isocyanate component could be replaced by a crosslinker such as a melamine / formaldehyde resin masked isocyanate polyurethane curing systems [109] Polyurethane may be difficult to formulate because of "pot life" difficulties, where conflict occurs between the need to accelerate curing but retard bulk solidification to protect the application equipment. A development has been to accelerate curing of this system after application, by exposure to an atmosphere containing volatile amine catalyst (vapour phase curing) [110,111]

## e- Epoxy resins

Epoxy resin is defined as a molecule containing more than one epoxide groups. The epoxide group also termed as, oxirane or ethoxyline group, is shown below,

$$R-CH-CH_2$$

Epoxies consist of two components that react with each other forming a hard, inert material. Part A consists of an epoxy resin and Part B is the epoxy curing agent, sometimes called hardener.

The general procedure for the synthesis of epoxy resins are based on polycondensation of bisphenol A and epichlorohydrin under normal or higher pressure in the presence of NaOH as a catalyst.Epoxy resins were first offered commercially in 1946 [112]·These resins are thermosetting polymers and have been used in many industrial applications, such as surface coating, adhesives, structural composites, printed circuit boards and insulating materials for electronic devices, etc., [113,114]. Because of their good heat and chemical resistance, and superior mechanical and electrical properties, in addition to their excellent processibilities. However, cured polymers from epoxy resins are relatively brittle with poor crack resistance. Therefore, there have been many studies on improving fracture toughness of epoxy

polymers. The most widely known method is to incorporate a rubber material into an epoxy polymer matrix. [115,116].

These resins have excellent electrical properties, low shrinkage, good adhesion to many metals and resistance to moisture, thermal and mechanical shock.

Viscosity, epoxide equivalent weight and molecular weight are the important properties of epoxy resins.There are two main categories of epoxy resins, namely the glycidyl epoxy, and non-glycidyl epoxy resins. The glycidyl epoxies are further classified as glycidyl-ether, glycidyl-ester and glycidyl-amine. The non-glycidyl epoxies are either aliphatic or cycloaliphatic epoxy resins. Glycidyl epoxies are prepared via a condensation reaction of appropriate dihydroxy compound, dibasic acid or a diamine and epichlorohydrin. While, non-glycidyl epoxies are formed by peroxidation of olefinic double bond.Glycidyl-ether epoxies such as, diglycidyl ether of bisphenol-A (DGEBA) and novolac epoxy resins are most commonly used epoxies.

## Diglycidyl Ether of Bisphenol-A (DGEBA):

Diglycidyl ether of bisphenol-A (DGEBA) is a typical commercial epoxy resin and is synthesized by reacting bisphenol-A with epichlorohydrin in presence of a basic catalyst.
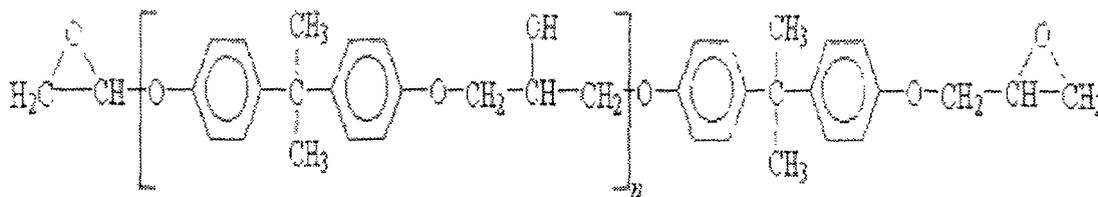
**Structure of DGEBA**

**Novolac Epoxy Resins:**

Novolac epoxy resins are glycidyl ethers of phenolic novolac resins. Phenols are reacted in excess, with formaldehyde in presence of acidic catalyst to produce phenolic novolac resin. Novolac epoxy resins are synthesised by reacting phenolic novolac resin with epichlorohydrin in presence of sodium hydroxide as a catalyst.
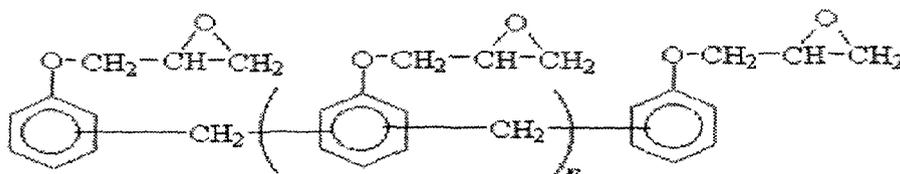


**Structure of novolac epoxy resin**

Novolac epoxy resins generally contain multiple epoxide groups. The number of epoxide groups per molecule depends upon the number of phenolic hydroxyl groups in the starting phenolic novolac resin, the extent to which they reacted and the degree of low molecular species being polymerised during synthesis. The multiple epoxide groups allow these resins to achieve high cross-link density resulting in excellent temperature, chemical and

solvent resistance. Novolac epoxy resins are widely used to formulate the moulding compounds for microelectronics packaging because of their superior performance at elevated temperature, excellent mouldability, and mechanical properties, superior electrical properties, and heat and humidity resistance

The curing process is a chemical reaction in which the epoxide groups in epoxy resin reacts with a curing agent (hardener) to form a highly crosslinked, three-dimensional network. In order to convert epoxy resins into a hard, infusible, and rigid material, it is necessary to cure the resin with hardener. Epoxy resins cure quickly and easily at practically any temperature from 5-150°C depending on the choice of curing agent [117].The curing agent selection plays the major role in determining many of the properties of the final cured epoxy. These properties include pot life, dry time, penetration and wetting ability. The commonly used curing agents for epoxies include amines [118], polyamides, phenolic resins, anhydrides, isocyanates and polymercaptans. The cure kinetics and the $T_g$ of cured system are dependent on the molecular structure of the hardener. The choice of resin and hardeners depends on the application, the process selected, and the properties desired. The amine and phenolic resin based curing agents, described below, are widely used for curing of epoxy resins.

Amines are the most commonly used curing agents for epoxy cure. Primary and secondary amines are highly reactive with epoxy. Tertiary amines are generally used as catalysts, commonly known as accelerators for cure reactions. Use of excessive amount of catalyst achieves faster curing, but usually at the expense of working life, and thermal stability. The catalytic activity of the catalysts affects the physical properties of the final cured polymer [119,120].

In general aliphatic amines are highly reactive, short pot life and highly volatile.

Examples:

- Diethylene triamine (DETA)  $H_2N\text{-}CH_2CH_2\text{-}NH\text{-}CH_2\text{-}CH_2NH_2$ .

- Aminoethyl piperazine (AEP)  $HN\underset{CH_2\text{-}CH_2}{\overset{CH_2\text{-}CH_2}{\diagdown}}N\text{-}CH_2\text{-}CH_2\text{-}NH_2$
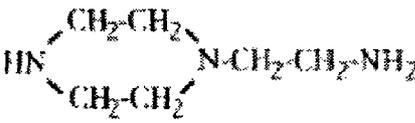
The curing behaviour of diglycidyl ether of bisphenol A (DGEBA) with aromatic diamines having aryl-ether, aryl – ether- carbonyl, or aryl – ether – sulfone linkages. The reactivity of the diamines depends on the structure. The presences of ether linkages in these diamines imparts flexibility to the network and influences the glass transition temperature $(T_g)$. Curing of DGEBA with rigid rod – like

diamines may yield a network having reduced flexibility and higher $T_g$ [121].

In general aromatic amines are less reactive than aliphatic amines, require higher temperatures (150-160 °C) and longer reaction times than aliphatic amines and the most common types are solid at room temperature

Examples

- Meta-phenylenediamine (MPDA)
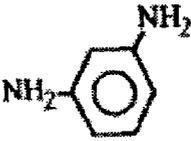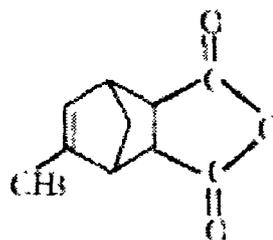
- Methylene dianilene (MDA)
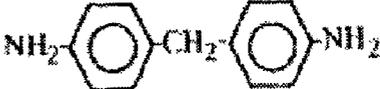
**Anhydride Curing Agents**

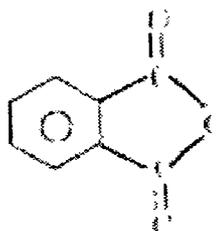**Cyclic anhydrides are typically used.**

- Less reactive than aromatic amines

- Cure reaction occurs in two steps

- High temperatures

- Long pot life

- Low exotherm

- Long cure cycle

Examples

- Nadic methyl anhydride (NMA)

- Phthalic anhydride (PA)

These types of curing agents are used in encapsulation processes when large residual stresses are very undesirable.

Epoxy resins when cured with phenolic hardener, gives excellent adhesion, strength, chemical and flame resistance. Phenolic novolac-cured epoxy systems are mainly used for encapsulation because of their low water absorption, excellent heat and electrical resistance. An accelerator is necessary for the complete cure to occur.

## 1-4. EPOXY COATING IN PETROLEUM FIELD

Epoxy is one of the most important coating materials used for steel protection in petroleum field. It can be used in external coating, internal lining and for offshore platform and production plants coatings.

## 1-4-1. Epoxy-Based Resins as External Coatings for Mild Steel

Epoxy resins are widely employed nowadays as organic coatings for the protection of metals against corrosion as a result of both the high mechanical resistance and the underwater durability of these resins. Because of their economical importance, these resins have been the subject of a number of studies aimed at the understanding the nature of the protection offered when used as anticorrosive coatings on metals [122-125]. The inhomogeneous structure of epoxy coatings as related to their protective action on a metallic substrate was first established by Mayne and coworkers [126], whereas the effect of ionic migration through the coating under an applied electric field and its consequence (cathodic delamination) for the corrosion of the metallic substrate has been addressed by Parks and Leidheiser [127]. Other investigators have examined the relationship between the transport properties of free films and the protective properties of applied films. Recently, emphasis has been placed on a laser technique in an advanced study of damaged coatings in order to evaluate the effect of the defect geometry on the corrosion and degradation processes in the coated metallic substrate [128-130]. Their resistance regarding the different corrosive agents depends on the type of resin as well as on the type and amount of hardener [131,132] and also on the curing

temperature. In general high chemical resistances are obtained from compositions of bisphenol-A type epoxy resins of higher molecular weight which are cured at a higher temperature. For many applications the need to cure at ambient temperature exists. For such purposes different polyamines, polyaminoamides, adduct amine hardeners and sometimes even polythiols are generally used as hardeners. The exception is the use of ionic hardeners. This type of hardener has an influence on the reactivity of the mixture and its viscosity and also has an impact on the physical and chemical properties of the product. In the area of epoxy resin solution coatings we use solid epoxy resins diluted with volatile solvents. A study regarding the size of the molecular weight of the epoxy resin and the type of polyamine on the chemical resistivity of coatings has already been published [133].

In general, for solventless and super-high-solid systems, low molecular liquid bis- phenol-A epoxy resins are used. They are sometimes diluted with reactive or non-reactive diluents to achieve sufficiently low viscosity [134,135]. Different demands are put on the diluents. The diluent should have a good miscibility with the resin and should also lower, as much as possible, the viscosity of the mixture. The diluent should also be colorless, odorless and physiologically compatible. When the coating is applied in layers the diluent should have a high evaporation rate. For a thin layer it is convenient to use a

diluent with a higher volatility. The diluent which remains in the coating should not have a negative impact on the mechanical or physical properties or on the chemical resistance of the materials [136,137].

In spite of the long historical use of solventless and super-high-solid coating systems, especially in the building industry and container coatings, there are limited comprehensive comparisons of the impact of individual factors on the chemical resistance of these materials.

*a- Model epoxy powder coatings and their adhesion to steel*

Fusion-bonded epoxy powder (FBEP) coatings, which mainly consist of epoxy resin and reinforcement fillers, have special significance for environmental and human health protection. They are received wide applications in flow-handling components such as pipelines, slurry pumps and hydraulic turbines due to their excellent chemical stability and good adhesion and compatibility with cathodic protection. They have almost no problems in single-phase corrosive fluid, but in liquid–solid two-phase flow, there exists a serious problem because slurry can weaken or even break the coating.

Development of more resistant powder coatings requires a better understanding of slurry erosion mechanism and of coatings response to the impinging stresses. Some researchers [138-142] have studied the influence of environmental factors

and reinforcement fillers on the erosion resistance of solvent-based organic coatings. But the effect of curing degree and fillers on the erosion resistance of FBEP coatings has been scarcely reported. The coatings against slurry erosion–corrosion should have both high flexibility and high hardness to withstand the interaction of chemical and mechanical attacks. The performance of FBEP coating is directly related to its curing degree. Generally, with increasing cross-linked density or with decreasing the length of elastically effective chain, the coating can be hardened, but the flexibility may be degraded and the internal stress and embrittlement was likely to be increased [143,144]Therefore, the relationship between the cross-linked density of coating and its erosion resistance is complicated. The previous study [145-147] found that the mechanism of FBEP coating was selective erosion and the material loss mainly comes from the resin matrix. If this is true, the more volume fraction and size of fillers would be beneficial to erosion resistance where good adhesion between resin matrix and fillers is not affected by the amount of fillers. Because of its obvious advantages in environmental issues, in many applications the use of powder coatings continues to grow strongly. Also epoxy resins are well known for their use in these types of coatings. They are used for heavy duty applications due to their excellent resistance against aggressive chemicals and corrosion. Their versatile chemistry allows

extensive modifications to tune their application and performance properties. With the emergence of powder coatings, epoxy resins were easily adapted to play a significant role there as well. Although epoxies based on aromatic phenols have shortcomings in the field of weatherability, their excellent anticorrosion performance will make sure that these resins will still remain an important building block of the future generations of functional powder coatings.

Because of the dramatic financial losses that potentially may result because of corrosion damage, investigations in the mechanisms of corrosion of steel have been numerous. Undeniably, this has resulted in large scientific progress. The general aspects of what factors make a good anticorrosion coating have been relatively well investigated [148]. However, despite progress, much of the detail that determines differences between similar formulations still remains obscure. This means that many of the semi-empirical discriminative test and comparison methods for coating performance, like the well known salt spray test, are still going to be with us for a considerable time to come. It is generally accepted that the unsurpassed corrosion protection available with epoxies results from a combination of factors. On one hand a crosslinked epoxy polymer matrix, containing many aromatic groups from the Bisphenol A structure, forms a rather good barrier to corrosion promoting compounds like water, oxygen and ions.

On the other hand, the presence of many secondary hydroxyl groups along the chain gives rise to a strong adhesion to metal. These hydroxyl groups are thought to bind strongly to the metal oxide surface by means of hydrogen bonds.

There is still scientific debate on the relative importance of the barrier versus adhesion properties in bringing about the protection [149-156]. It has been shown [148,151] that the barrier function to water and oxygen by itself cannot be considered sufficient in the prevention of corrosion, because the permeability of a coating for these compounds appears to be higher than the limit needed to initiate corrosion. More significance is now attributed to the ability of the polymer to prevent migration of ions through the coating and between the anodic and cathodic sites on the metal, thereby preventing the initiation of corrosion. In this respect, the strength and stability of the adhesion to the substrate may be a critical factor in the long term epoxy resin performance. However, there is an abundance of practical evidence that the mentioned good adhesion to metal is partly or totally lost when the epoxy coating is exposed to water or high humidity. Such exposure may quickly lead to coating detachment.

This phenomenon of wet-adhesion loss, which is also known for other binder systems, has been investigated by many coating scientists [150,154,155,157]. It can be attributed to the action of water that penetrates the coating down to the

polymer/ metal interface, or to compounds resulting from electrochemical decomposition of water at this interface. In both cases the bond between the hydroxyl (or other polar) groups from the resin and the metal oxide layer on the substrate is destabilized.

## b- Coal tar epoxy

A structure in constant contact with water whether it is a ship, a pier, or an offshore oil platform is subject to corrosion [158]. The battle against this scourge of the underwater industry continues with the development of new coating and outer jacket technology.

Prior to the 1950's, corrosion problems in this difficult marine exposure conditions were mitigated somewhat by conventional paints and coatings that were available at that time which included chlorinated rubber, bitumen's and coal tar mastics as well as ordinary metal primers and paint. In the early 60, other materials were available including zinc rich coatings, coal-tar epoxies, and there were developments in the so-called high performance coatings. Oil companies were required to stock as many as 200 items and suppliers in order to show progress in corrosion control regardless of their effectiveness. This requires a fresh look at and increased attention to coating material selection and coating performance evaluation for

condition of immersion water and desalination plants service as well as splash, and tidal zone in marine environment.

Coal tar epoxies are still among the most popular coatings. They are essentially a mix of coal tar and epoxy resins. Coal tar epoxies were at their peak of popularity in Europe in the 1960's through about 1990. After that, non-coal tar epoxies replaced coal tar epoxies due largely to health concerns over long term exposure and direct contact (by coating applicators) to the 'tar'. Where their use is permitted coal tar epoxies are suitable for protection from moisture, both in water immersion condition (such as barge hulls and pilings) and when buried underground pipelines and tanks. Moreover, a literature search made on the subject of coal tar epoxy coatings performance has indicated the occurrence of one major types of coal tar epoxy failure in Kuwait marine environment during the 80's [159].

## 1-4-2. Coating of the Internal Surface of Line Pipe.

Two – component epoxy polyamide can be used as internal coat for non - corrosive gas pipe lines. The cured epoxy coating should pass the following tests: specified dry film thickness, pin hole, adhesion, bend, stripping, water immersion, cure and salt spray test [160].

## 1-4-3. Coating For Offshore Platform and Production Plants

Two – component epoxy polyamide can be used for steel protection as a component of paint cycle [161]:

<u>Paint system no. 1</u>

The following paint system is suitable for the following areas:

1-coating for offshore platform

External surfaces of superstructure, areas above the splash zones up to 110 $^{O}C$

2-coating for production plant

Chimneys, furnaces and gas conveyors up to 110 $^{O}C$, steel support structures, ladders, pipe racks, containers, processing modules for gas-oil-and water treatment, refined product tanks, acid and alkaline solution tanks, external potable water tanks and external seawater-salt solution tanks up to 80 $^{O}c$

| PAINT SYSTEM | | |
|---|---|---|
| COAT | PRODUCT TYPE | NDFT ($\mu$m) |
| 1$^{st}$ | Inorganic zinc primer | 50-75 |
| 2$^{nd}$ | Epoxy primer | 40-60 |
| 3$^{rd}$ | Epoxy undercoat | 125-175 |
| 4$^{th}$ | Polyurethane top coat | 50 |
| Total minimum dry film thickness (DFT) | | 310 |

The alternative system:

| PAINT SYSTEM | | |
|---|---|---|
| COAT | PRODUCT TYPE | NDFT (μm) |
| 1st | Organic zinc primer | 50-75 |
| 2nd | Epoxy undercoat | 200 |
| 3rd | Polyurethane top coat | 50 |
| Total minimum dry film thickness (DFT) | | 310 |

Paint system no.2

The following paint system is suitable for the following areas:

1-coating for offshore platform

Galvanized steel panels, piping and fire fighting pipes.

2-coating for production plant

Galvanized chimneys, furnaces, steel support structures, ladder, pipe racks and gas conveyors.

| PAINT SYSTEM | | |
|---|---|---|
| COAT | PRODUCT TYPE | NDFT (μm) |
| 1st | Epoxy primer | 40-60 |
| 2nd | Epoxy undercoat | 125-175 |
| 3rd | Polyurethane top coat | 50 |
| Total minimum dry film thickness (DFT) | | 250 |

## Paint system no.3

The following paint system is suitable for the following areas:

1-coating for offshore platform

Internal surfaces of gas treatment units, internal sides of seawater and potable water tanks.

2-coating for production plant

Internal surfaces of salt solutions, seawater and potable water tanks

| PAINT SYSTEM | | |
|---|---|---|
| COAT | PRODUCT TYPE | NDFT ($\mu$m) |
| 1st | Epoxy primer | 75-125 |
| 2nd | Epoxy undercoat | 75-125 |
| 3rd | Epoxy top coat | 75-125 |
| Total minimum dry film thickness (DFT) | | 300 |

| PAINT SYSTEM | | |
|---|---|---|
| COAT | PRODUCT TYPE | NDFT ($\mu$m) |
| 1st | Epoxy phenolic | 75-125 |
| 2nd | Epoxy phenolic | 75-125 |
| 3rd | Epoxy phenolic | 75-125 |
| Total minimum dry film thickness (DFT) | | 270 |

## 1-4-4. Recycling Of Epoxy Resins

Wastes of thermosetting resins have caused many environmental problems because they were difficult to dispose arising from their network structures [162,163]Although many approaches to polymer wastes disposal have been already explored, landfill is still a main method of disposal [164,165]. Consequently, technologies of recycling of polymer urgently need to be developed and improved [166].

In recent years, the chemical recycling of polymer wastes has received a great deal of attention [167,168]·

Epoxy resins is of great importance for a number of diverse applications including coatings, adhesives, structural materials and electrical insulation, etc. due to its good processability during curing process for forming cross – linking [169-171].

We have been investigation the corrosion resistance of amine cured epoxy resins, finding that it had low resistance to acid solution, and was completely decomposed in high concentration acid and at high temperature [172,173].

The phenomena suggested the possibility of recycling of thermosetting resins by applying their decomposed products. Therefore, epoxy resin attracted interest as a candidate for chemical recycling.

The decomposition of typical bisphenol A type epoxy cured with amine in acid solution has been studied [174].

It was initially intended to apply a type for chemical recycling due to its poor corrosion resistance. However, it was found that the main chain of bisphenol A was easily broken, because of bisphenol A possessed quaternary carbon atom, which was susceptible to be attacked by acid to produce tertiary positive ion.

## 1-5. EPOXY CAN COATINGS

Metal cans used for food packaging have a thin plastic coating on the interior surface, which is essential to prevent corrosion of the can and migration of metal ions into food. Without this coating, food or beverages contained within metal cans could become tainted or spoiled. Protective coatings made using epoxy resins are widely used. Such coatings are inert and have been used safely for over 40 years.

In 1995, Brotons et al [175] reported that very small amounts of bisphenol A could migrate from can coatings into food during food processing. Consequently, later that same year a study was begun by The Society of the Plastics Industry, Inc., to quantify the migration of bisphenol A from can coatings [176]. In 1996 Sharpe et al [177,178], of the Center for Reproductive Biology in Edinburgh, Scotland, reported effects in rats given bisphenol A orally. In the January 1997 Nagel et al [179], at the University of Missouri, Columbia, reported

effects on the prostate glands of male mice whose mothers were fed bisphenol A. The results of a study on the migration of bisphenol A from food and beverage cans concluded that Human exposure to bisphenol A from can coatings is very small and possess no known health risk.Epoxy can coatings are approved for food contact use by the U.S. Food and Drug Administration, the European Union's Scientific Committee on Foods, the United Kingdom's Food Standards Agency, the Japan Ministry for Health and Welfare and other government agencies worldwide.No adverse health effects are expected following the proper application of the epoxy paint. However, during the curing process, the solvent in the paint will continue to evaporate (gas off) as the paint hardens over the next several days. The amount of solvent that evaporates decreases over time so that under "standard conditions," i.e. a temperature of 68 degrees F and a relative humidity of 50%, the workers should be able to safely enter the work area after 2 to 4 hours. This will depend on the amount of air "turn over," i.e., the ventilation of the area. For small confined spaces, one might wait a couple of days, whereas, in a large area like a garage or airplane hanger, one might return to the area after a couple of hours [180].