CHAPTER - 1

INTRODUCTION INCLUDING LITERATURE REVIEW
1.1 Introductory

Paints have been used for decorative propose for many centuries. The cavemen were probably the first to use the paint to record their legacy. The used the paints as the means of communication and decoration. Paint making and paint application were mint to be and art rather than science. But after industrial revaluation the whole scenario has been changed which lead sciences to emphasis more on better understanding of composition, constitution, application and testing of paints to meet the new requirement arose due to evaluation. This in turn slowly transferred the art obtain paint making into science which lead to discoveries of new materials and new ways of application of paints, to meet the stringent requirements of protection coupled with decoration in certain instance under divers services condition.

Major constituents of paint generally are pigments, binders and solvents with smaller quantity of additives. A dispersion of pigment in the binder constituent the paint film, the property of which depend on the nature of binder to large extend, but nature and quantity of pigments also effect the property of paint film.

Pigments generally gives aesthetic appearance it indicate color and opacity to paint film and some pigments also provides protection to much or less extent, to cured film from UV radiation and penetration of liquid and this can be attributed to their chemical composition and structure of pigments.

Binders in form of thermo sets resin or thermoplast polymers are the polymeric materials. Which form continues and adherent film which applied over a substrate and so often termed as film formers. They also bind pigments in the film. The performance properties of the paint film thus largely depend on the number of binder so more emphasis will be given on binders in this chapter.

Solvents are volatile compounds which leave the film by evaporation and so do not affect the performance properties of dry paint film. They are in corporate in paints to provide ease of processing during paint manufacturing and ease application.

Additives are included in a paint system for many different regions. Thought they are present in relatively small quantities, they can significantly influence properties of the liquid paint and/or the drive paint film. They are used either to overcome some defects or to provide certain properties and to improve overall performance for coating system. To reach the high
quality requirements up today, additive play a major role in formulation and functioning paint system. The produced thesis work is in contents of modification of alkyd resin. Hence, more trace about the review on resin has been given.

1.2 Resins (i.e. binders) for coating industries

A wide range of binders are commercial available for coating industries now a days but earlier chemist had to depend on natural product like, natural resin oil until the attempts were to modified the natural resin to produce synthetic natural products and lead to availability of synthetic polymers used in recent age. Very first synthetic plastic suitable for coating material and which is still in use today was Phenolic resin, developed by Leo Backeland in earlier 1900s [1]. After this, there came the new resin called alkyl in 1923 which is used till date. After the industrial revolution, extensive research in the field of polymer chemistry resulted in the availability of numbers of different resins for suitable for surface coating.

Resin is the continuous phase in a paint film and is largely responsible for the protective and the general mechanical properties of the film. A large numbers of resins with different chemical composition, solubility, nature of film formation, application characteristics and performance properties of their films are available for surface coating industries. It is generally found that the performance properties of a coating systems are best at higher molecular weight of resin, but it will be difficult to process high molecular weight during paint manufacturing or even at the time of paint application whereas at low molecular weight polymer will facilitate of processing during manufacturing of a coating system but at the loss of performance properties. To achieve optimum balance between ease of processing and performance properties to distinct methods are used to arrive at final films.

In the first approach film formation takes place solely due to evaporation of solvents from the film and no chemical reaction any sort is involve in the film formation. The resin used is of sufficiently high molecular weight to provide better performance properties but the dry paint film remain sensitive to parent solvent. Such type of resin is known as non-convertible resins.

In the second method initially a low molecular weight per polymer is used to provide ease of processing and application which is then converted to a high molecular weight polymer to provide better performance property through chemical reaction known as curing reaction involves the use of either simple chemicals called curing agent or another resin with some special functional group. Such resins are referred as convertible resins.
The most commonly used convertible resin in surface coating industry is briefly discussed below.

1.2.1 Alkyd Resins

Alkyd resins [2-4] form the largest group of the synthetic resins available to the paint industries and consumption is greater than that of any other resin for wide variety of application due to their low cost and versatility [5,6]. Alkyds are formed by polycondensation of a dibasic acid and a fatty acid and in a strict manner alkyds can be defined as oil modified polyester resin [7]. Most commonly used dibasic acid in alkyd synthesis is Phthalic anhydride while glycerols, Pentaerythritol, trimethylol propane, glycols etc. are used as fatty acid determines the dyeing characteristics of the alkyd resin. Saturated fatty acid yields non-dyeing or plasticizing resin while drying properties are conferred by unsaturated acids. Alkyds are compatible with most of the resins used in paint industries like rosin, epoxy, Phenolic resin, amino resin, polyurethanes etc. so it can be easily modified to achieve specific properties [8].

![Idealized alkyd structure based on glycerol](image)

where
- \( \text{aryl ring} \) : phthalic residue
- \( \text{polymer chain} \) : glycerol residue
- \( \text{fatty acid residue} \) : Fatty acid residue

Idealized alkyd structure based on glycerol
Alkyd is the ‘work horse’ of coating industries which find applications in printing inks, decorative as well as industrial coating and water soluble and electro deposition systems.

1.2.2 Phenolic Resins

The formation of resinous materials by the reaction of phenol and formaldehyde has been known for many years [9, 10]. Phenolic resin finds application in protective coatings [11, 12]. The reaction of phenol and formaldehyde alone is slow but in presence of acid different products: Novolac and Resoles.

Novolac:

Resoles are produced when molar ratio of formaldehyde to phenol is greater than one and acid catalyst is used. Since they are insoluble in oils and hydrocarbon solvents, they are not used in surface coating industries but widely used in plastic industries as a thermoplastic material. Resoles are produced when the molar ratio of formaldehyde to phenol is greater than one and
alkali catalyst like sodium hydroxide or lime is used. Resoles are thermo-setting and soluble in oils so they are used widely in varnish making but if they are further heated, they react to produce insoluble and infusible products and result in little application in surface coating industries.

It is found that resoles react with rosin to give products which could be esterified with polyhydric alcohols and the resulting resins are soluble in oils and these resins are known as rosin modified Phenolic which finds extensive application in decorative undercoats, primers, marine paints and in certain types of printings inks.

1.2.3 Polyester Resins

\[
\begin{align*}
\text{diacid} & \quad \text{(n+1) diol} \\
\text{HO} & \quad \text{HO} \\
R-C & \quad R'-OH \\
\text{OH} & \quad \text{nH}_2\text{O}
\end{align*}
\]

Polyester

The product obtained from the condensation polymerization of a polyhydric alcohol and polyfunctional acid is known as polyester resin [13] and widely used in surface coating industries. The most commonly used polyfunctional acids are maleic anhydride, Phthalic anhydride, Adipic acid, sebasic acid etc. whereas ethylene glycol, propylene glycol, diethylene glycols are used as polyhydric alcohols. Depending upon the raw material used, Polyester can be either saturated polyester or unsaturated polyester. Both find extensive use in surface coatings [14-18]. Unsaturated polyester is cured by many different ways but the basic reaction of curing is free radical initiated addition reaction. Free radical initiation can be achieved either at elevated temperature by use of an electron beam or UV beam or certain metal ions as a catalyst by decomposition of peroxides. Unsaturated polyesters are generally dissolved in reactive solvent such as styrene to produce final resin and then curing is carried out. Saturated polyesters are such
formulated so that they produce high hydroxyl contents as they are mainly used in production of polyurethanes. They also react with some amino resins.

1.2.4 Epoxy Resins

Epoxy resins [19] are the products of condensation of epichlorohydrin and diphenylol propane derivative is 2, 2’-bis (4-hydroxyphenyl) propane also known as its trivial name Bisphenol-A. They are formed by condensing the reactants in presence of alkali and resulting product is known as diglycidyl ether of bisphenol-A (DGEBA).

$$\text{Bisphenol-A} + \text{Epichlorohydrin} \rightarrow \text{Diglycidyl ether of bisphenol-A (DGEBA)}$$

Where, $$R = \text{H}_2\text{C}=\text{CH}-\text{C}=\text{Cl}$$

Epoxy resins contain hydroxyl and epoxy groups. They can be cured by cold curing or stoving with a wide range of materials which includes amino and Phenolic resin, amines, anhydrides, polyamides and isocynates etc.

The resulting films of epoxy resins are very abrasion resistant, resistant to chemical attack and show a high degree of adhesion to metal and other surfaces and thus widely used in industrial maintenance field [20, 21].

1.2.5 Amino Resins

These [22] are derived by reaction between formaldehyde and either urea or melamine to produce urea formaldehyde or melamine-formaldehyde respectively. They are not used on their
own as a coating material as they give very brittle films but widely used in combination with
alkyd resins mainly and also with other resins in co-cure systems.

**Urea Formaldehyde**:

![Urea Formaldehyde structure](image)

**Melamine Formaldehyde**:

![Melamine Formaldehyde structure](image)

Amino resins used in surface coating industries are generally modified with butanol. The
modification of amino resins with butanol provides solubility in normal coating solvents and
better compatibility with order resins in co-cure systems. Melamine formaldehyde shows better
properties than urea-formaldehyde in terms of color retention and exterior durability.

Amino alkyd systems are widely used in stoving finishes of all types. Amino resins are
also used with many other resins like saturated polyester, epoxies, acrylics etc.

**1.2.6 Polyurethane Resins**

The basis of formation of these polymers [23] is reaction of a diisocyanate with
compounds containing an active hydrogen atom to produce urethane linkages. There are many
compounds that contain active hydrogen like water, alcohol, amines hydroxyl group etc. Thus a
polyurethane film may contain ester, ether, amide, urea or other groups. The hydroxyl
component may be polymeric polyols like polyesters, polyether etc. Diisocyanates generally
used are toluene diisocyanates (TDI), isophorone diisocyanate (IPDI), hexamethylene
diisocyanate (HMDI) etc. Polyurethanes can be either single pack or two pack system.
Polyurethane coating facilities low temperature curing. They provide wide range of flexibility and hardness. They also process good adhesion [24] and exhibit excellent weather resistance [25]. Other film properties are good resistance to moisture [26], Chemical attack [24, 27] and many solvents [24].

The main aim of research in surface coating resin modify the existing resins to meet the new requirements for high performance or some specialized and applications with keeping the point of cost effectiveness in mind.

Today the use of renewable and non-conventional raw materials for preparation of resins is one of the important areas which can be explored by the researchers. Oils from both the origins, vegetables and animals, are such raw materials which are widely used to modify variety of resins to achieve desirable properties. Among the various oil-modified resins, alkyd resins are widely used in surface coating industries [28] and as the present work in context to modification of alkyd resin, the discussion about alkyd resins is given as follow.

1.3 Alkyd Resins
Alkyds are essentially short-branched polyesters formed by poly condensation of a dibasic acid and a polyhydric alcohol in the presence of the glycerides oil or oil derived fatty acids. The presence of the oil facilitates good pigment wetting properties and, when unsaturated, allows coherent films to be formed on cure but properties like hardness, durability color and gloss retention are adversely affected [29].

Alkyds are relatively inexpensive in terms of raw materials and manufacturing costs. Alkyd resins are easy to pigment and are compatible with most substance used in surface coating industries and have they can be easily modified for special application.

Other polymers may offer better properties in some specific area of application but alkyds have widest range of acceptable properties in terms of surface coating along with cost and versatility.

1.3.1 Raw Materials for Alkyd Resins

1.3.1.1 Dibasic Acids

![Phthalic anhydride](image1)

![Isophthalic acid](image2)

![Terephthalic acid](image3)

![Trimellitic acid](image4)

The main dibasic acids most commonly used is Phthalic anhydride when improved film hardness and chemical resistance are required, isothalic acid and terphthalic acid are also employed in alkyd resin manufacture. Phthalic anhydride is widely used as it does not suffer from major solubility problem and reacts at low temperature as compare to other anhydrides. Trimellitic anhydride has been increasable used in water soluble or water dispersible alkyds.

1.3.1.2 Polyhydric Alcohols
The most widely used polyhydric alcohols are glycerol and Pentaerythritol but in some specific areas of application trimethylol propane and sorbitol are also employed.

Glycerol contain to primary and one secondary hydroxyl group and it can be used in alkyds of all fatty acids contain or oil lengths were as Pentaerythritol contains four primary hydroxyl groups and thus from relatively complex resin with better performance properties like fast drying greater hardness, better gloss etc. The higher functionality of Pentaerythritol limits its used in short and medium oil types of alkyds as it gel rapidly but widely used for long and medium long oil alkyds.

1.3.1.3 Oils/ Oils derived fatty acids.

The oils used in paint industries are derived mainly form vegetable and to a much Sesser extent animals sources. They are testers of glycerol and fatty acid, non-volatile and unstable at higher temperature. These oils very in properties according to nature of fatty acids combined with glycerol it indicated they may be saturated or unsaturated. In the case of unsaturated oil, oil possess important properties of setting slowly to a solid and adherent film when spread on surface and expose to the air. This process is known as drying and oils can be classified into following groups based on their drying properties.

- Dryings oils E.g. Linseed oil, Tung oil etc.
- Semi drying oil E.g. Soyabean oil, tobacco seeks oil etc.
- Nondrying oils E.g. Caster oils etc.

Drying oils of linseed type consist of glycerol of fatty acids containing two or three isolated double bond whereas in case tung oil it consist of conjugated unsaturated fatty acid which result in greater reactivity and drying properties than linseed oil. Semi drying oils consist of acids with only one or two double bonds. Nondrying oils contain glycosides from saturated fatty acids which have no drying properties or may contain small amount of acid with one double bond.

Fatty acids are large group of compounds consisting of long hydrocarbon chain of above 16 carbon atoms and upwards, attached to a carboxyl group and they are present in oil in varying amounts as glycosides. These fatty acids are either saturated or unsaturated and in letter case they can be conjugated or non-conjugated. Thus fatty acids are one which governs the drying properties of oils and in terms of alkyls. This is discussing in detail letter in this chapters. Fatty acids can be separated from oils by hydrolysis of glycerides/oils.

1.3.2 Manufacture of Alkyds Resins

Alkyds are essentially short-branched polyester chains formed by the polycondensation of dibasic acid and a polyhydric alcohol in the presence of glycerides oil or oil derived acids. Glycerides oils are not readily reactable with other raw materials used in alkyds resin manufacture as they are tri-glycerides and due to stearic hindrance do not react easily. To overcome this problem of reactivity following techniques are employed.

Alcoholysis of oil

This is a technique in which oil is pre-reacted with a polyol to convert tri-glycerides oil into reactive monoglyceride which can easily take part in polycondensation reaction. During alcoholysis of oil ester interchange takes place between oil and polyol.
Alcoholysis is generally carried out at temperatures of 240 °C-260 °C in presence of basic catalysts like litharge, lead acetate, lithium hydroxide etc. The presence of basis catalysis greatly speeds up the ester interchange between oil and polyol. Alcoholysis is normally carried out under inert atmosphere to prevent ingress of air which can lead to discoloration of product. The progress of alcoholysis reaction is monitored by measuring the tolerance of reaction mixture to alcohol. Initially the tolerance of oil-polyol mixture to alcohol is low but as the reaction proceeds and ester interchange between oil and polyol takes place resulting in monoglyceride formation, tolerance of reaction mixture increases. This technique is also known as monoglyceride (MG) process.

**Acidolysis of oil**

In this technique oil is first reacted with acid. This technique is normally used only where there are problems of reactivity or solubility of dibasic acids encountered. Acidolysis requires temperature above 260 °C and even presence of catalyst does not affect the reaction rate much and process take much longer time. Thus

There is more risk of discoloration and polymerization of oil associated with acidolysis of oil.
**Fatty Acids Process**

As the name itself indicates, this process uses the fatty acids derived from oils. Fatty acids separated from oil are used and not as such oil is used. Since fatty acids contain carboxylic group, they easily react with polyol and so there is no need to carry out alcoholysis or acidolysis of oil. Thus fatty acid, polyol and dibasic acid are together charged directly and polycondensation is carried out to produce alkyd resin. Fatty acids are expensive as compare to oils but they facilitate shorter process time and better products. To make it cost effective generally a mixture of fatty acids and oil is frequently used.

**Polycondensation**

\[
\begin{align*}
\text{R-OH} + \text{HOOR} & \rightarrow \text{R-OOR} + \text{H}_2\text{O} \\
\end{align*}
\]

During polycondensation reaction in alkyd resin manufacturing a series of simple etherification reactions takes place in which a hydroxyl group reacts with a carboxyl group to form an ester link with removal of a molecular of water as a byproduct.

Commercially two techniques are employed in alkyd resin manufacture.

**Fusion Process**

In this process, the reactants (after alcoholysis, if oil is used) are charged into the reactor together at temperature of between 180 °C and 260 °C. An inert gas is purged in the reactor to prevent ingress of air and to facilitate removal of water of the reaction which is essential for progress of polycondensation reaction. Since in this process higher temperature is encountered, there is a considerable loss of volatile reactants for which allowance has to be made to have necessary degree of process control. This process is generally used for longer oil length formulation where loss of volatile reactions will not have much serious effect on process control parameters.

**Solvent Process**

This process is widely used in alkyd resins manufacture as it has many advantages over fusion process. In this process reactants are heated together at temperature between 200°C-240°C with a solvent (most commonly used solvent is Xylene) which helps in many ways during the
process. The solvent and water of reaction form an azeotropic mixture which is distillated off from the reactor; condensed and passed into a separator where water is removed as waste and solvent is recycled to reactor. This will also result in short process time without encountering higher temperature. The blanket of solvent vapor prevents ingress of air thus enabling low color products with minimum use of an inert gas. Since solvent is being recycled to the reactor most of the volatile reactants lost from the reactor are returned with solvent to reactor, thus providing much better control over process control parameters. Solvent process offers a uniform resin composition with a narrow molecular weight distribution and higher molecular weight resins with a corresponding improvement in drying and film performance properties.

Polycondensation is monitored by measuring residual acid and hydroxyl value at regular interval of time till the required molecular weight at specified residual acid and hydroxyl value has been achieved. When this point is reached, the alkyd is cooled down to 180 °C to prevent further reaction and diluted with solvent to the required solids or nonvolatile content.

1.3.3 Classification of Alkyd Resins
The nature and the amount of oils/fatty acids determine the characteristics of an alkyd resin and thus alkyds are classified in terms of oil length and oil type.

1.3.3.1 Oil Length
This is the amount of oil/fatty acid present as percentage of the nonvolatile content. Although it does little to describe the complex polymer system, it is universally used throughout surface coating industry and is a convenient method of classification for alkyds. On the basis of oil length, Alkyds can be classified as:

1) Long oil alkyd -Oil content greater than 55% W/W.
2) Medium oil alkyd- Oil content 45-55% W/W.
3) Short oil alkyd-Oil content less than 45% W/W.

1.3.3.2 Oil Type
Depending upon nature of oil i.e. either saturated or unsaturated, alkyds can be further classified as:

a) Oxidizing Alkyds
Oxidizing alkyds contain drying or semi-drying (unsaturated) oils or fatty acids and film formation takes place by oxidation. The oil length in such alkyds is usually in excess of 45% W/W.
b) Non-oxidizing Alkyds

A non-oxidizing alkyd contains non-drying (saturated) oils or fatty acids and is not able to form film by oxidation. They form film by reacting with other polymers and this is known as curing. Non-oxidizing alkyds generally have oil lengths below 45%.

From above classification, it is not necessary that all oxidizing alkyds are used in air-drying systems and all non-oxidizing alkyds are cured. The characteristics of an alkyd resin and mainly the film properties are related to the oil type and oil length. The longer oil length, the more the alkyd reflects properties of oil and shorter the oil length, the more properties of polyester chains predominates. When selecting an alkyd for a particular application, it is necessary to specify both oil length and oil type to achieve balance between properties derived from polyester chain and those derived from oils.

1.3.3.3 Area of Application

On the basis of area of application, alkyds can be further classified as:-

I) Air Drying Alkyds

The unsaturation in the fatty acid chains is unaffected during alkyd resin manufacture and so the mechanism of film formation in such alkyds is same as that of oils. The molecular weight of alkyds is higher than that of oil so less cross-link are required to form a film resulting in rapid drying as compare to corresponding oil.

Semi-drying oils discolor less on drying than the highly conjugated drying oils. Keeping the above point in mind, resin formulator can employ semi-drying oils in alkyds to have rapid drying capability with better color. Oil lengths of 50-60% are generally used for such alkyds but it must be remembered that though higher oil length provide improved drying rates, they also adversely affect color and gloss retention as well as durability of film.

II) Force Drying Alkyds

Alkyds based on unsaturated fatty acids and oils can be cured rapidly at temperatures in the range of 10-160 °C because increased temperature greatly accelerates the oxidation of fatty acids. Moreover, in this case C-C bond type cross links are formed and the resulting films are more chemically resistant and durable than in case of air-drying systems where C-O-O-C bond type cross links are formed.
Rapid curing means that short oil lengths can be used and providing more polyester components to have improved durability, gloss retention and color. Oil lengths of 40-50% are normally employed for this type of resins.

III) Plasticizing alkyds

Since alkyds have better compatibility with resins like nitrocellulose, amino resins etc. they are used as a plasticizer with such resins to provide increased flexibility, adhesion and gloss. Plasticizing alkyds are not intended to make films on their own so they are generally formulated on non-drying oils or fatty acids like castor oil and fatty acids derived from castor oil or coconut oil and coconut oil derived fatty acids. The later being less used as it is more expensive.

IV) Curing Alkyds

A co-cured surface coating system can be formulated on amino resin/alkyd resin combination. For such a system alkyd with shorter oil lengths having higher proportions of free hydroxyl groups is used. These free hydroxyl groups of alkyd react with reactive groups of amino or Phenolic resin during curing and film formation takes place. The amino resin /alkyd resin combination produces films with improved hardness, exterior durability, alkali resistance and cure time. The amino resin/alkyds resin combination provides low color products whereas the Phenolic resin/alkyds resin combination results in darker color products but they offer improved chemical resistance.

1.3.4 Modification of Alkyd Resins

No single polymer exhibits all desired properties of a surface coating system. The polymer has at least one property that is less than ideal. Commercial coatings are formulated in such a way to achieve balance between advantageous and disadvantages properties of a base polymer system.

Combination of different types of polymers is often used to obtain a coating with more desirable properties of individual polymers. It is very well known that alkyds have better compatibility with a wide range of reactive chemicals and polymeric materials such as amino resin, Phenolic resin, acrylics, vinyl etc. [29, 30] and they can be easily modified with such
materials to achieve desirable properties. The chemical modification of alkyds through fatty acid unsaturation or through functional has been extensively studied [31, 32].

1.3.4.1 Modification with Amino Resins

The amino resin/alkyd resin combination [33] results in films with improved hardness, exterior durability, alkali resistance, mechanical properties and solvent resistance [34]. The success of this modification lies in the compatibility of two resins. It has been reported that generally short oil alkyds with high proportions of hydroxyl group provide good compatibility with alkylated urea-formaldehyde of melamine formaldehyde [35]. To achieve rapid curing an acid catalyst is commonly employed in alkyd-amino system. Such modified system is widely used in industrial baking finishes, generally for top coats as they provide low color products.

1.3.4.2 Modification with Nitrocellulose

In this modification, alkyd mainly acts as a resinous plasticizer which imparts adhesion, flexibility and gloss to nitrocellulose. Alkyds generality based on coconut oil and castor oil with oil length of 55% are used for such system. However best compatibility is attained with short oil alkyds due to high degree of polarity obtained via ester and hydroxyl group. Castor oil based short oil alkyds are most commonly used as the hydroxyl groups in castor oil provide excellent compatibility, flexibility and adhesion at lower cost but where the cost is not prohibitive, coconut oil based alkyds are also used to achieve better desired properties. Such modified system is employed in automotive lacquers extensively and has also been recommended for traffic paints [36].

1.3.4.3 Modification with Chlorinated Rubber

Chlorinated rubber is compatible with alkyds of similar linearity and low polarity. Such modified system shows improved toughness, adhesion, durability, drying rate and excellent resistance to acid, alkali and water [37]. Such system is mainly used in concrete floor paints, swimming pool paints and road marking paints.

1.3.4.4 Modification with Phenolic Resins

Phenolic resins and in particular resole type, when combined with drying oil alkyds shows excellent gloss retention durability and better resistance to water and alkali [38]. Such systems are cured at elevated temperatures and products are darker in color so mainly used in undercoat applications and primers.
1.3.4.5 Modification with Silicone Resins
Silicone modified alkyds are produced by copolymerization alkyd with certain silicone intermediates i.e. low molecular weight siloxane to give polymers with highly improved durability and gloss retention and increased heat resistance [39]. They are also characterized by good drying properties and outstanding weather resistance.

1.3.4.6 Water-soluble Alkyds
One of the important and interesting modification of alkyd resin in recent years is water soluble alkyd in which water-soluble or water-reducible alkyd resin is produced which upon curing results in a water-resistant film. The resin for its modification is formulated in such a way that it contains a number of free hydroxyl and carboxyl groups in a well distributed manner throughout resin molecule which are neutralized by organic bases, generally tertiary bases are preferred. Curing takes place by stoving in which organic base is volatilized and cross linking occurs.

1.3.4.7 Modification through Unsaturation of Alkyds
Alkyds based on drying oil fatty acids are used for such modification in which alkyds are co-polymerized with vinyl or acrylic monomers like styrene, methyl methacrylate, n-butyl acrylate etc. The resulting polymers [40, 41] possess the desired application and wetting properties of alkyds along with strength, chemical and weather resistance of acrylic or vinyl resin.

Another way to prepare such systems is condensation of hydroxyl groups of alkyds with carboxylic acid groups of acrylic or vinyl copolymer. This way of modification is technically very attractive as it does not limit the use of unsaturation of alkyds. Saturated fatty acids containing alkyds with free hydroxyl groups can also be used for such modification and moreover the formation of acrylic or vinyl homopolymer is eliminated [42]. Acrylic or vinyl modified alkyds are widely used in fast drying finishes.

1.3.4.8 Modification through Functional Groups of Alkyds with Isocyanates
Alkyds resins are frequently modified by reaction with species containing isocyanates group to give resin with improved film hardness and durability. The hydroxyl groups of alkyds react with isocyanates compound (mainly diisocyanates) to give a high molecular weight three dimensional network obtained by joining the alkyd chains together with urethane linkages. The cured films exhibit faster drying rates and improved chemical and
abrasion resistance. Such systems find wide applications in wood finish and quick drying paints for high performance applications [43].

1.4 IPNs FROM CASTOR OIL BASED PU

Before the advent of 21st century, mankind will face the storage of coal and petroleum. These will definitely investigations in an alternate source. In plenty of sunlight, agriculture crops can be grown and harvested every year in the tropical country including India. Triglyceride oil is such as castor oil, lesquerella oil and vernonia oil that come from plants grown as renewable source. Such resources can be employed successfully in the IPN synthesis for important industrial application. Castor oil is a naturally occurring vegetable oil obtained from the tropical plants. It is a triglyceride of glycerol and ricinoleic acid.

\[ R \equiv -(\text{CH}_2)_7-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}-(\text{CH}_2)_5-\text{CH}_3 \]

Based on the special hydroxyl group functionality of castor oil has been used in the polyurethane formulation for its variable application in paints, varnishes, artificial leather etc. are known for very long time as well as castor oil based polyester from sebatic acid.

Knaub and Camberlin [44] reported a new reactive system based on castor oil, aliphatic diisocyanate and aromatic diamine. Such system would be interesting for CAST OR RIM (reaction injection modeling) and RRIM (reinforced RIM) processes. Frisch and his co-workers [45] have reported SIN based RIM system using elastomeric PU in combination with a plastic epoxy resin to produce a rapid reaction SIN. Depending on the composition, Frisch and his co-workers prepared IPN based RIM materials by curing at 100 °C for 5 min. followed by post curing 121 °C. RIM material in this way developed good phase separation, as indicated by TG. 3Tg peaks are observed via DSC. Two for the soft and hard segments of PU, and one for the epoxy. The invert shifting of TG indicates the extent of the actual phase mixing. The Frisch IPN, RIM system is an alternative to RRIM.

Manson and Sperling suggested RIM technology for making SINs from castor oil.
Sperling his co-workers [46] reported the novel reaction of hydroxyl as a special functionality in castor oil. These hydroxyl group were reacted with sebasic acid to form polyester while with 2,4-toluene diisocyanate for polyurethane formation using individually or mix polyester urethane and individually were interpenetrated with styrene and divinyl benzene polymerized to prepare IPN and SIN. They found the morphology of these IPNs depends on the method of synthesis. Modulus, temperature, stress, strains and impact resistant study on number of composition show IPN and SIN were tough plastic and reinforce elastomer depending on their composition.

Sperling and his co-workers [47] reported the polymerization and cross linking with sulphur or diisocyanate to form vulcanized urethane derivatives respectively. Both types were swollen with plastic froming monomer and polymerized in situation. IPN with wide range of composition were obtained and characterized using electron microscopic, mechanical properties and modulus temperature study. They saw that some of the IPN behave as reinforced highly extecible elastomeric at low poly styrene level and plastic at the high level of polystyrene and / or cross linking.

Recently, reports of IPN based on castor oil exhibited high strength and resistant to abrasion and hydrolysis have appeared.

The work of castor based IPN have been reported by our Indian scientist. It is concerned with the synthesis of IPN from castor oil based polyurethane and various vinyl monomers, methyl methacrylate, methyl acrylate, ethyl acrylate and n-butyl acrylate using ethylene glycol dimethacrylate as cross linker and benzoyl peroxide as an initiator.

1.5 Research Gap
As mentioned above the alkyd resins are widely used in surface coating industries due to following reasons:
1) Relatively inexpensive in terms of raw material and manufacturing costs.

2) Widest spectrum of acceptable properties in terms of surface coating usage on their own.

3) They can be easily modified for specialist applications as they are compatible with most substances used in surface coating including polymeric materials.

Among the various alkyd resins used in surface coating industries commercially, DCO rosinated alkyd resin differs from other alkyds resins in its unique method of manufacturing in which often the raw castor oil is dehydrated ‘in situ’ in the presence of the polyol, phthalic anhydride and other reactants with phthalic anhydride also acting as a dehydration catalyst. However they form a special class since although they belong to the drying class and can if necessary be made by either of two standard methods using DCO or fatty acids, they are usually prepared quite different as describe earlier.

DCO alkyds have better color than linseed alkyds and do not discolor as much on staving or exposure to light. They are inferior to soyabean alkyds in this respect but on other hand their drying speed, water resistance and durability are superior. Long oil DCO alkyds have a tendency to gas check and dry with a slight residual tack. Short oil DCO alkyds if improperly made, may also gas check on staving but usually finishes are formulated to overcome this defect and industrial enamels produced from a mixture of a short oil DCO alkyds and a urea or melamine resin are used extensively.

Castor oil is used in various forms in the surface coating [48-49] and other industries [50-51].

Several modifications and its applications are given in the following chapters of the thesis. Epoxy resins are very well known and widely used in many industries due to their high chemical resistance, good adhesion, good physical properties such as toughness, flexibility and abrasion resistance etc. [52].

The modification of castor oil by reaction with epoxy resin has not been received attention academically or technically except few instances, one of repute [51] reported recently [53-54] interesting to study the use of castor-oil epoxy reaction products as a modifying agent for DCO resonated alkyd resin.

1.6 Objectives
The objectives of the produced research work are:

1. To develop castor oil-epoxy resin condensate product (COER)
2. To study the blending of Alkyd-COER-Caster-Oil based on polyurethane resin.

1.7 The Present Work

In the view of above objective, the research work was carried out in which the castor oil was reacted with various commercial DGEB epoxy resin to developed epoxy resin reaction product (COER) which were than blended with isocynated terminated polyurethane (ICOPU) resonated alkyd resin by admixing other resin or monomer. The coating behaviors of the resulting system were study and whole research work is bifurcate in to six chapter of the thesis.

The first chapter includes the introduction about the binders, various resin like ketonic resin from various Ketone, Phenolic resins, polyester resin, amino resin etc. this will comprise the research gaps, the objective of the proposed work and illustration of the present work.

Chapter 2 will comprised peered reviewed about the reaction of the castor oil with various isocynate terminated polyurethane (ICOPU) and various DGEB epoxy resin and the techniques used for the characterization of the prepared compound. The adopted experimental procedures will also be explained in this chapter.

The alkyd resins i.e. COER rosinated alkyd resin has been selected for the further study. The blending of alkyd resin, COERs-1 and ICOPU-1 at various proportion was carried out. Their performance properties on MS panels have been studying. All the details will be furnished in Chapter 3.

The alkyd resins i.e. COER rosinated alkyd resin has been selected for the further study. The blending of alkyd resin, COERs-2 and ICOPU-1 at various proportion was carried out. Their performance properties on MS panels have been studying. All the details will be presented in Chapter 4.

The alkyd resins i.e. COER rosinated alkyd resin has been selected for the further study. The blending of alkyd resin, COERs-1 and ICOPU-2 at various proportion was carried out. Their performance properties on MS panels have been studying. All the details will be shown in Chapter 5.

The alkyd resins i.e. COER rosinated alkyd resin has been selected for the further study. The blending of alkyd resin, COERs-2 and ICOPU-2 at various proportion was carried out. Their
performance properties on MS panels have been studying. All the details will be furnished in Chapter 6.

The whole work is scanned in scheme-1

\[ \text{Excess disocyanate (I-II)} \]
\[ \text{Castor Oil} \quad \text{Epoxy Resin (1-2)} \]
\[ \text{Isocyanated terminated poly urethens (ICOPU) (I-II)} \]
\[ \text{Castor Oil - Epoxy Resin Reaction Products (COERs)} \quad n = 1 \text{ to } 3 \]
\[ \text{Alkyd resin + (COERs) + ICOPU Blends} \]
\[ \text{Applied as steel panel} \]

Various Diisocyanates
1. Hexamethylene diisocyanate
2. Isophorane diisocyanate

Various Epoxy Resin
1. DGEBA
2. DGEBF

Evaluation of Film Properties

Scheme 1. Surface coating materials based on blending of commercial alkyd resin, COERs and ICOPU